# Mercury rule lets hazardous air pollutants off the hook

On March 15, the U.S. EPA issued the long-awaited and controversial rule establishing trading as the mechanism for reducing mercury emissions from coal-fired plants. Although the debate over the rule focused on how best to control mercury releases, critics say that an opportunity to also regulate several other hazardous air pollutants (HAPs), such as dioxins, arsenic, and lead, may have been lost.

The Clean Air Mercury Rule (CAMR) establishes the United States as the first nation in the world to address mercury from this pollution source. When combined with the new Clean Air Interstate Rule (CAIR), the provisions for power plants should ultimately cut mercury emissions by as much as 70% from 1999 levels, sometime after 2018, EPA officials say.

CAIR, which was announced on March 10, is designed to control $SO_2$ and $NO_x$ emissions. To do that, utilities most likely will install wet scrubbers and selective catalytic reduction systems, which capture mercury as a co-benefit, notes EPA. Indeed, these technologies might control several HAPs, says EPA's Jason Burnett, who declined to name which HAPs might be captured. "We have decided that after the implementation of CAIR and CAMR [any HAPs of potential concern] won't pose a hazard to human health," says Burnett, policy advisor to Jeffrey Holmstead, assistant administrator for air and radiation.

Environmentalists and many scientists have argued that mercury should be regulated under section 112 of the 1990 amendments to the Clean Air Act (CAA). This section requires that each plant install the maximum achievable control technology (MACT) and address the 189 HAPs listed in CAA found to pose a risk. That was also the view EPA finalized in the last days of the Clinton Administration. In 2000, EPA wrote that an evaluation showed that emissions of arsenic, chromium, and cadmium posed potential cancer risks.

COREL

**Not only is mercury coming out of the smokestack, but other pollutants, such as dioxins, arsenic, and lead, are also emitted.**

Under the Bush Administration, EPA now argues that these pollutants don't need to be controlled at each power plant. There is too much data uncertainty to regulate mercury emissions under section 112, the agency says. As for other non-mercury HAPs, these emissions don't rise to the level of cancer risk for humans, and therefore don't need regulation under the CAMR, says Burnett. However, "EPA does acknowledge that science continues to evolve and that we need to keep looking at a number of HAPs," Burnett adds.

Those at most risk live close to the power plants, where mercury hotspots occur, scientists and others say (*Environ. Sci. Technol.* **2004**, *38*, 126A–127A). About 156 million people in the United States live within 30 miles of a coal-fired power plant, points out John Stanton of the National Environmental Trust (NET), a nonprofit environmental group. He adds that about 460 U.S. coal-fired power plants burn more than 900 million tons (t) of coal every year, which produce 42% of all emissions reported under the Toxics Release Inventory. Indeed, these plants are the largest emitter of toxic gases, arsenic, and chromium, and are the second-largest source of lead and dioxin air pollution, NET notes in the 2004 report *Beyond Mercury*.

Still, CAMR presumably doesn't bar EPA from someday regulating other HAPs from power plants, says Amar Praveen of the Northeast States for Coordinated Air Use Management, an association of air quality control divisions. John Millett, an EPA spokeperson, agrees, saying that nothing in the new determination takes away EPA's authority to regulate HAPs under section 112, adding that such a move would require further study.

Nevertheless, air- and water-quality regulators in several states have strongly objected to the new CAMR. New Jersey's attorney general filed a lawsuit on March 29 on behalf of a coalition of eight northeastern states plus California.

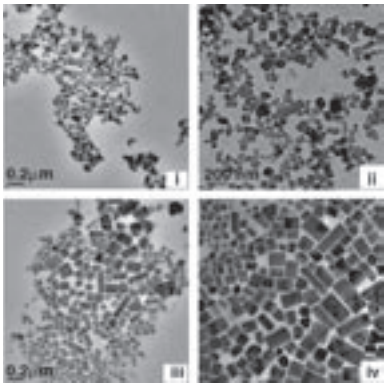
The mercury rule was welcomed by the industry because it offers plant operators flexibility in meeting the standards and doesn't require every plant to install controls. It sets a national cap on mercury emissions of 38 t beginning in 2010; an additional 15 t must be trimmed by 2018. Once up and running, the program will be fairly simple: Individual plants will receive a specific emissions cap. If emissions fall below the cap, the plant owner can sell the emission "credits" to another facility, where they can be used to increase emissions and still meet the second facility's cap.

CAMR had not been published at press time. For information on HAPs and CAMR, see www.epa.gov/mercury/control_emissions/decision.htm. —CATHERINE M. COONEY

## Buckyballs batter bacteria

For the first time, researchers have shown that aggregates of $C_{60}$—better known as fullerenes or buckyballs—can form nanosized, crystalline structures that inhibit the growth and respiration of certain bacteria. In a paper published in this issue of *ES&T* (pp 4307–4316), researchers at the Georgia Institute of Technology and Rice University have also found that these nanocrystals may be more mobile in water than expected.

Both results strengthen the argument that nanoparticles have different properties than their bulk counterparts, but those differences are not reflected in current procedures for safe handling.



ACS

**In water, buckyballs aggregate into nanocrystals, which have sizes and shapes that vary with water characteristics, such as pH. Nanocrystals prepared in water with pH of (i) 3.75, (ii) 5, (iii) 7, and (iv) 10.25 are shown in these transmission electron microscopy images.**

Hundreds of individual buckyballs compose a single nanocrystal, which can range in size from 25 to 500 nanometers, says corresponding author Joseph Hughes, a professor at Georgia Tech. "Depending on what the water characteristics were [when a nanocrystal formed], some [nanocrystals] are actually reasonably large when you compare them, say, to the size of a bacterial cell," he says.

Previous studies by other researchers have found that nanoparticles could prove harmful to human cells and large-mouth bass. In the new study, most *E. coli* and *Bacillus subtilis* died when exposed to the buckyball nanocrystals. These findings suggest that nanoparticles released in the environment could have widespread effects. "For environmental health, food-chain issues are very important, and bacteria are the base of many food chains," says Hughes.

Eva Oberdörster, a toxicologist at Southern Methodist University who conducted the bass

## News Briefs

### Nuclear fuel threat

The spent nuclear fuel stored in pools at some U.S. nuclear power plants may be vulnerable to terrorist attacks, says a new report from a committee of the U.S. National Academies' Board on Radioactive Waste Management. The report assesses the safety and security of the spent fuel at the country's 103 operating commercial nuclear reactors. The committee concluded that the likelihood is small that terrorists could steal enough spent nuclear fuel to make a dirty bomb, but an attack that partially or completely drains a plant's spent fuel pool might start a high-temperature fire that could release large quantities of radioactive material. To view *Safety and Security of Commercial Spent Nuclear Fuel Storage* go to www.nap.edu/catalog/11263.html?onpi_newsdoc04062005.


NOAA

### Trading oil for biomass

Enough biomass could be sustainably produced within the United States to replace 30% or more of the country's current petroleum consumption without affecting food, feed, or export demands, finds a report by the Oak Ridge National Laboratory and the U.S. Department of Agriculture. Biomass already provides more than 3% of the total U.S. energy consumption, according to the report. With "relatively modest changes in land-use and forestry and agricultural practices," more than 1.3 billion dry tons of biomass could be gleaned annually from forest and agricultural lands alone, the report finds. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply* can be accessed at http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf.

studies, complimented Hughes's group for nailing down the chemistry and antimicrobial activity in an area clouded by "anecdotal evidence". She notes, however, that the amounts of buckyballs used in the study "are actually pretty high concentrations to find out in the environment" and are unrealistic for long-term exposure, unless a spill occurs. But it's an important place to start, she adds.

Hughes et al.'s work is "starting to bring out the mechanism" of biological interaction and demonstrates that researchers need to think of nanomaterials on two levels: as single particles and as aggregate structures, says Ronald Turco, a professor of microbiology at Purdue University.

"One of the things we wanted to do in this work was not only to assess the effect on the bacteria, but we wanted to understand better [how] these $C_{60}$ materials [behave] in water," says Hughes. It is well accepted that individual buckyballs are not very soluble in polar solvents such as water, but nanocrystals were found to be stable colloidal aggregates. And Hughes and his colleagues found that water quality characteristics, such as pH and ionic strength, can make buckyballs more hydrophilic and thus alter the size and shape of these crystalline structures. He says the results show that nanocrystals would be mobile in the water environment, but using oxidants like chlorine "may be a way to protect [drinking] water supplies."

Currently, people who work with fullerenes rely on the material safety data sheet (MSDS) for handling procedures. According to Oberdörster, buckyballs have their own CAS number and "their own MSDS sheet, but it was created by copying the one from graphite."

Hughes's group is currently examining whether particle size is a component of toxicity. "We are starting to try and understand what size ranges are going to be the most important with regard to biological interaction," says Hughes of his group's latest, unpublished results. "And again, it points to the smaller that it is, the more important that it is." —RACHEL PETKEWICH

## The brain is defenseless against mercury

Researchers have long known that mercury increases mortality and decreases fertility in fish, but the underlying metabolic processes are still unknown. New research in this issue of *ES&T* (pp 3972–3980) helps uncover some of the mystery by examining which genes respond when fish are fed methylmercury (MeHg). Although multiple genes turn on in the muscle and liver to help store and detoxify the metal, the brain appears unresponsive and accumulates high levels of mercury. This leads researchers to believe that neural tissue might be unable to defend itself against this toxic compound.

"It was a big surprise when we found that genes in the neural system were not responding," says study author Jean-Paul Bourdineaud, a professor of biochemistry at the University of Bordeaux (France). Previous research has shown that mercury can cause lesions in the brain, and a recent study found that MeHg can decrease the density of neurotransmitters in some species that consume diets heavy in fish (*Environ. Sci. Technol.* **2005**, *39*, 218A).

The zebra fish in the study were fed diets that contain MeHg at concentrations similar to those found in wild fish (*Environ. Sci. Technol.* **2002**, *36,* 877–883). Thirteen different genes were then tested in liver, muscle, and brain tissue. These genes encode for proteins known to be involved in different functions such as antioxidant defense, metal chelation, DNA repair, and cell death. "Testing this range of genes gives us a toxicological survey of mercury's effects," says Bourdineaud.

ANTHONY FERNANDEZ

**Very few genes involved in cellular defense responded when diets of methylmercury were fed to zebra fish.**

For instance, the gene that codes for the protein superoxide dismutase produced more of this antioxidant in muscle, indicating that MeHg caused oxidative stress. Bourdineaud says that unpublished studies from his lab have also observed that MeHg can shrink the mitochondria in a cell and decrease muscle respiration by about 50%.

In the liver, MeHg accumulated rapidly during the first week, but concentrations later began to fall. "The demethylation in liver was not surprising," says Mark Sandheinrich, a professor of biology at the University of Wisconsin. "This suggests that mercury is being converted back to inorganic form and being secreted."

However, the brain showed levels sometimes twice as high as the other tissue but no gene activity. "I think this tells us that the neurological effect of mercury may be because the brain has no inherent ability to demethylate mercury and deal with metal toxicity," says Sandheinrich. —PAUL D. THACKER

# Hydrogen from a microbial fuel cell

An electrochemical boost enables bacteria in a microbial fuel cell (MFC) to convert waste to hydrogen. Research published in this issue of *ES&T* (pp 4317–4320) overcomes a biochemical energy barrier that prevents efficient conversion of organic matter to hydrogen (*Environ. Sci. Technol.* **2004**, *38*, 160A–167A), claims corresponding author Bruce Logan of the Pennsylvania State University.

BRUCE LOGAN

**With a small electrical boost, Pennsylvania State University researchers can generate hydrogen from wastewater.**

In earlier MFC research, Logan's group and others have demonstrated that when conventional microbial substrates, such as glucose and acetate, or even organic compounds in wastewater are fed to bacteria, electricity is generated. Only low power outputs have been reported to date, but researchers anticipate that with further design improvements MFCs can generate commercially viable amounts of electricity. Logan's group, however, offers an alternative path—MFCs that directly produce high yields of hydrogen gas.

Before enough hydrogen gas can be generated biologically, researchers must overcome a biochemical energy barrier that limits yield from bacterial metabolism. Hydrogen from bacterial fermentation is limited to 4 moles of hydrogen per mole glucose, with a practical yield of only 2–3 moles. That is because hydrogen formation from the end products of fermentation—acetate or butyrate—requires slightly more energy than the metabolic system possesses. Alternatively, electricity-generating MFCs can be used to generate hydrogen by electrolyzing water, but that process requires substantially more power.

In what Bruce Rittmann of Arizona State University calls a "clever experiment", Logan's group found that applying only a small voltage—just over 250 millivolts—to an MFC circuit degraded more than 95% of the acetate, with a concomitant recovery of 90% of the electrons as hydrogen gas in a completely anaerobic cell. After accounting for the energy spent providing the boost, this electrochemically assisted reactor could net 8–9 moles hydrogen per mole glucose, which is much closer to the 10–12 moles of hydrogen that the U.S. Department of Energy claims is required to make the production of "biohydrogen" from corn economically feasible, says Logan.

In theory, these MFCs can use any dissolved organic matter as substrate. Logan's group has already generated electricity from acetate, butyrate, ethanol, proteins, and even wastewater from pig farms. Logan believes that he can also make hydrogen from these materials. Whether hydrogen or electricity is produced, "our point is that . . . you don't need purified sugar anymore. . . . You can use wastewater, you can use fermentation end products, you can use almost anything that is biodegradable," says Logan.

Willy Verstraete of Ghent University (Belgium), another MFC researcher, praises Logan's work as "quite novel", but cautions that the "overall economic balance of it at this point is not certain." He adds that the net energy yield will be less than that when just electricity is made, because of the added boost needed to produce hydrogen.

Electricity or hydrogen? "What do we really want as output here?" asks Rittmann. "What do we prefer to have, what's more useful? . . . There isn't a generic answer. . . . What makes this paper good is it shows there are various ways, various outlets, and different combinations." —BARBARA BOOTH

## News Briefs

### Automakers help Canadians cut GHGs

In a unique agreement, Canadian automakers voluntarily agreed on April 5 to reduce the emissions of $CO_2$ and other greenhouse gases (GHGs) from cars by 5.3 megatonnes by 2010. The automakers say they will rely heavily on electric vehicles, "cleaner-burning diesel", and improving fuel efficiency in their light-duty cars and trucks to meet the target. Natural Resources Canada officials note that the industry's effort will play a key role in the country's plans to meet its commitments under the Kyoto Protocol on Climate Change. The agreement comes just as automakers press forward with a lawsuit against new rules in California that require them to shrink the GHG emissions from vehicles by 30% by 2016. The Canadian agreement illustrates that carmakers have the technology to reduce $CO_2$ emissions from their fleets, environmental groups say. The agreement can be found at www.nrcan-rncan.gc.ca.

RHONDA SAUNDERS

### U.S. conservatives call for renewable research

In late March, a group that included former government security officials and retired military officers sent a letter to President Bush urging the administration to "launch a major new initiative to curtail U.S. oil consumption through improved efficiency and the rapid development and deployment of advanced biomass, alcohol, and other available petroleum fuel alternatives." The letter writers are calling on the Bush Administration to devote $1 billion over the next 5 years, which they say is at a level "proportionate with other priorities for our nation's defense." The letter was drafted at the behest of the Energy Future Coalition, a bipartisan group, and is available at www.energyfuturecoalition.org.

# Are permafrost landfills safe for used drilling mud?

Dumping used drilling mud—the sludge-like material that lubricates oil and gas drilling shafts—into frozen pits in Arctic regions is a convenient way for the industry to dispose of their wastes, but experts are questioning whether the practice is safe for the environment. Studies under way in Canada, which were presented at the Assessment and Remediation of Contaminated Sites in Arctic and Cold Climates conference May 8 in Edmonton, suggest that new designs can keep these pits intact and the waste frozen. But global climate change is a wild card that could eventually lead to melting and erosion of even the redesigned pits.

The frozen pits or sumps are tennis-court-sized holes excavated 3–4 m deep into the permafrost, the Arctic's permanently frozen ground, says Steve Kokelj, a permafrost scientist with Canada's Department of Indian and Northern Affairs. After filling the holes with the drilling fluid, workers cap the pits with the excavated fill material, which may consist of ice-rich permafrost, he says. Over the past 30 years, 100–200 drilling waste sumps were carved out in the Mackenzie River delta region in Canada's Northwest Territory, primarily to support exploratory wells. Alaska's North Slope is home to about another 600 pits, says Judd Peterson, a geologist with Alaska's Department of Environmental Conservation.

Drillers operating on Alaska's North Slope no longer bury drilling mud in sumps. However, thanks to an impending oil and gas boom in the Mackenzie River delta, due to begin in 2009 with the construction of a pipeline, companies requesting permits to drill in this region are again considering sumps as the primary disposal option, says Chris Severson-Baker, director of the energy watch program for the Pembina Institute, an environmental think tank. "Since Conoco, Shell, and Imperial Oil haven't committed to not using sumps, it's likely to be an issue at the upcoming hearings on the projects," Severson-Baker says.

ENVIRONMENT CANADA

**Canada's Mackenzie River delta—an intricate network of river channels, lakes, and ponds—could be the site of new drilling waste pits. But will the delta remain cold enough to keep the wastes frozen?**

The industry knows there are concerns about sumps and is looking at alternatives, such as encapsulating waste or injecting it down deep drill holes, says Ian Scott, a general manager at the Canadian Association of Petroleum Producers. Meanwhile, companies have improved sump construction significantly since the 1970s, reducing waste volumes and no longer locating sumps next to water bodies, he adds.

Half of the sumps constructed in the 1970s have collapsed or are now collapsing. Faulty design and construction in the past have led to the melting and degradation of some sumps, Kokelj says. "If workers disturb the permafrost around the sump, it subsides and collects water, promoting thawing of the permafrost and collapse of the sump cover," he says. If the drilling mud is not completely frozen, potassium chloride (KCl), which is used in the mud as a freezing-point depressant, can seep up and out of the sump as the cap subsides. Some old sumps contain muds with as much as 10% KCl by weight, which can kill nearby plants, Kokelj adds.

Preliminary assessments of five sumps show that KCl is migrating hundreds of meters away from the pits, says Larry Dyke, an engineering geologist with the Geological Survey of Canada. Freeze–thaw cycles boost the concentration of KCl at the edge of the sumps, and thawing lenses of ice in the permafrost increase the hydraulic conductivity of soil, which moves the salt 10 times farther than by diffusion alone, he says. "These results suggest that permafrost cannot be expected to completely contain contaminants," he says.

In addition, global climate change is projected to hit the delta area early and hard, with increasing storm surges and flooding that could also erode or melt sumps, says Steve Harbicht, a biologist with Environment Canada. The dynamic nature of the Mackenzie River delta, an intricate network of river channels, lakes, and ponds, is a concern, he says. Moving river channels have already eroded some sumps on the Peel River.

In the very long term, the Mackenzie River delta will not remain cold enough to keep drilling mud frozen, says Chris Burn, Natural Sciences and Engineering Research Council of Canada Northern Research Chair at Carleton University. "It might become necessary to construct sumps with low-permeability liners, as we do in the South for landfill sites," he says.

—JANET PELLEY