

Do perfluoropolymers biodegrade into PFOA?

The scientific debate over how perfluorooctanoic acid (PFOA) and other perfluorocarboxylic acids (PFCAs) enter human blood and the environment is about to take an important new turn as researchers and regulators begin to focus on whether perfluorinated polymers can degrade to form PFOA in the environment. Potentially at stake is the future of some carpet and fabric stain repellants and paper coatings made from these polymers. If the polymers do degrade, then some currently being produced and some already in the environment will be sources of PFOA. If the polymers do not degrade, then those currently being produced are likely to have little effect on the environment or human health.

The debate now moves to center stage with the publication of the first peer-reviewed report of a long-term study on the degradation of perfluorinated polymers. The 2-year study by DuPont scientists, published in *ES&T* (pp 800–807), examines a fluoropolymer stain repellant solution under aerobic conditions in four different soils. Although the researchers measured formation of PFOA and other PFCAs, they conclude that the chemicals came from impurities, also known as residuals or precursors, in the stain repellant solution. As a result, they conclude that the polymer degrades very slowly, with a half-life of 1200–1700 years.

Their conclusion, applauded by some scientists, would appear to exonerate this polymer as a source of PFOA and other PFCAs in the

environment. This study “suggests that we can continue to use these polymers in such a way that environmental problems will not be arising, because the manufacturers have found ways to remove the impurities from their products,” says environmental chemist Don Mackay of Trent University (Canada).



Stain repellants help keep carpets clean, but what happens when they get into the environment?

da). But the results need to be confirmed by other studies, he adds. Fluorotelomer manufacturers have voluntarily agreed to remove residuals by 2015.

Other scientists in academia, industry, and government praise the effort but say the DuPont study has a major flaw related to the presence of residuals. “This study does not provide adequate data on rates of biodegradation. It is an important study, but it must not be overinterpreted,” says Cathy Fehrenbacher, chief of the U.S. EPA’s exposure assessment branch, which is investigating the fate and transport of PFOA as part of EPA’s overall investigation of the compound.

EPA, Environment Canada, other regulators, and environmental scientists are interested

in the sources of PFOA and other long-chain PFCAs because the compounds are persistent, ubiquitous, and linked to developmental problems and other adverse health effects in laboratory animals. In 2005, EPA’s science advisory board recommended that the agency classify PFOA as a “likely” human carcinogen. Canada has already banned some compounds that could break down in the environment to PFOA and other PFCAs.

Message in a bottle

DuPont conducted the biodegradation experiment on a fluorotelomer polymer solution that it markets as a stain repellant, according to DuPont scientist Bob Buck. The polymer has a hydrocarbon acrylate backbone. Attached to this via ester

linkages are fluorotelomer alcohols (FTOHs) with carbon-fluorine chains. If the ester linkages break and free these FTOHs, the FTOHs will degrade to PFOA. Ester linkages are known to be vulnerable to hydrolysis or cleavage by microbial enzymes, says environmental chemist Craig Criddle of Stanford University. But in fluoropolymers, the carbon-fluorine chains may protect the linkages from the enzymes.

The DuPont experiment was designed to determine whether degradation could occur for a particular polymer solution applied to soil under aerobic conditions. But free FTOHs also occur as residuals, and these complicate the experiment because they can degrade to PFOA. The polymer solution used in the study was a complex

mixture that contained fluorotelomer polymer, residual raw materials, hydrocarbon surfactants, and water. Buck acknowledges that the residuals decrease the study's ability to detect degradation of the polymer but says, "We used this because we wanted to make the experiment as realistic as possible."

The scientists mixed the polymer solution with four different soils, chosen because they collectively represent the bulk of U.S. soils, according to first author Mark Russell. They sealed the soil and polymer solution in glass vessels. At various time intervals over 2 years, the scientists measured levels of FTOHs, PFOA, and other fluorinated chemicals in the gas phase and in the soil.

The experimental setup troubles EPA's Fehrenbacher, who notes that the bottles leaked and may have released degradation products. The DuPont scientists also could not recover FTOHs that were added to sterile control bottles. They attribute this to the FTOHs' irreversible binding to the soil, but Fehrenbacher is not convinced. "The DuPont scientists make this claim with little or no evidence," she says. The soil experiments do not maintain mass balance—the scientists cannot account for all of the materials present at the beginning of the experiment, she notes.

Residual doubts

In the experimental vessels, FTOHs can come from two sources—the polymer itself, if the ester linkages break, and the residuals, many of which are FTOHs. Likewise, PFOA can originate from both polymer and residual breakdown. Determining how much PFOA comes from each source is difficult, however.

The DuPont scientists modeled the biodegradation rates for the polymer and residuals and then

compared the yield, or the percentage of the FTOH that degrades to PFOA, to that in other biodegradation studies to see whether the calculated yield fits with previous work. They argue that this modeling captures the crucial features of PFOA formation—an initial, relatively sharp increase that flattens out. "If polymer breakdown were significant, we wouldn't see this flattening," says Russell. As a result, the DuPont scientists are



Experiments to study biodegradation of fluoropolymers are difficult to design.

confident that their results are robust and that they are not missing any significant amount of polymer breakdown. Environmental chemist Linda Lee of Purdue University agrees with this interpretation of the data. "The model fits the data well enough that it would be hard to imagine that they are missing any significant amount of polymer breakdown," she says.

The DuPont team assumes a yield from FTOH to PFOA of about 28%. Previously published studies estimate this yield to be less than 10%. These estimates are compatible, according to Buck, because the low values are estimates based on a monthlong experiment. Extrapolating these yields to 2 years gives the higher values, he says. Environmental chemist Scott Mabury of the University of Toronto takes issue with such extrapolation. He

notes that the 10% yield was obtained in an experiment with microbes from sewage sludge that were continuously conditioned to degrade precursors. "More reasonable assumptions regarding the potential yield of PFOA from the identified precursors would yield a conclusion opposite that of the authors. Namely, it appears that the polymer, even under nonideal test conditions, yielded at least three times as much PFOA as the residuals," says Mabury.

Analytical uncertainties and assumptions about residual degradation rates also concern chemist Bill Reagan of 3M Corp. "It is very difficult to determine the breakdown rate for the polymer, because of the relatively large amount of residuals. There is the potential to overestimate the half-life of the polymer," he says. A longer study or a study with significantly lower residuals would be useful to verify the estimated half-life.

Reagan tells *ES&T* that he has seen fluoropolymer breakdown in biodegradation experiments conducted by 3M in support of new-product registrations. The polymers also contain fluoroacrylate ester linkages, he says. "We see relatively rapid fluorochemical polymer breakdown." However, Reagan notes that each polymer is different and it may be misleading to apply data from one test situation to others.

The right place?

Although scientists are divided about how to interpret this first published fluoropolymer degradation study, they all agree that the study should not be given too much weight. "We believe that the pathways we have described will be the same in other situations, but we do not want to interpret these results as representative of all potential degradation processes," says Buck. Reagan agrees. "These exper-

iments involve the solution that is applied during processing, not what might exist on products in people's homes or discarded products in the environment. The authors assert that this represents the worst case, but there is no evidence for that," he says.

Perhaps more importantly, the scientists should examine a more relevant environment, such as activated-sludge systems used for wastewater treatment, instead of soil, says Criddle. "Hydrolysis rates will likely be greater, resulting in more rapid release of the alcohols, and stripping of the alcohols to the

atmosphere would be expected," he adds.

Scientists are still learning how to conduct these studies, says Fehrenbacher, but EPA has already started to list characteristics of a definitive study.

First, scientists need to fully describe the polymer and any residuals present—using a radiolabeled polymer would be ideal but is expensive. Next, scientists need to maintain the mass balance; use of aggressive extraction methods should help meet this goal. "The DuPont study is useful but by no means definitive," and lacks these

characteristics, Fehrenbacher adds.

The study has sparked vigorous debate on how and under what conditions to study biodegradation of fluoropolymers. Says Mackay, "I think that we are really trying to find out how to use fluorochemicals without suffering environmental harm. Obviously, applying the polymer to soil is different from what happens during the lifetime of dirty carpets or what happens in a wastewater treatment plant. This should be the first in a series of studies that will figure this out."

—REBECCA RENNER

Ceramic filter makes water treatment easy

The technology sounds simple: fire a ceramic pot, perhaps coat it with a fine layer of silver, and let the water percolate through. In regions where water carries millions of microbes, this relatively inexpensive treatment method has its attractions. For about a decade, the nonprofit organization Potters for Peace has been teaching communities to manufacture their ceramic water filters, which retail for \$5–15. Although they have been used widely from Nicaragua to Thailand, no scientific data have been published to prove their efficacy or to show how these ceramic filters work.

Now, in *ES&T* (pp 927–933), researchers from the University of Virginia report that clay water filters from Mexico and the U.S. can remove more than 98% of the test organism *E. coli*. With an added layer of silver, the filters remove all *E. coli*. "Without the silver—just the ceramic filter—it seems like it works well, but adding the silver further improves the performance," says coauthor James Smith.

"Until this report, there have been very little data on how [the filters] work and what the specific mechanisms are," says Kara Nelson, an environmental engineer



Clay pots, made in a press such as the one shown here (left) in a Guatemalan factory, fit inside plastic buckets for filtering water.



**JAMES SMITH (LEFT)
VINKA OYANDEL-CRAVER (RIGHT)**

who studies a variety of low-cost point-of-use water treatments at the University of California Berkeley. "Without an understanding of the fundamental mechanisms behind [a technology], we have to take a black-box approach," she says. "That's not efficient. There are so many different pathogens, so many environmental conditions, so many different things that could be in water."

Lead author Vinka Oyanedel-Craver and Smith examined the

ceramic filter materials in the lab and found that commercial pottery material from the U.S. was the most successful at removing *E. coli*. The authors hypothesize that the industrial material has many

more and much smaller pores than the coarser clays from Mexico. In addition, the pathways between the pores where water flows are more interconnected, allowing water to speed through more

quickly, whereas the smaller pore sizes block *E. coli* from getting through. Added silver—purchased by local pottery manufacturers as a relatively inexpensive slurry, facilitated by Potters for Peace—could actually be killing the remaining *E. coli* through direct toxic contact, the authors posit.

The results suggest that more sieving at on-the-ground manufacturing sites could lead to finer-grained ceramic filters and more effective water treatment. Although the filters' \$5–15 cost may be insurmountable for some households, it is a worthwhile investment for several years' worth of filtration, the authors argue. The next step is to test how these filters "behave under real-world, long-term use," Smith says.