Research Brief 147: Microbial and Photolytic Transformations of Environmental Contaminants

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Background: Researchers at the Duke University SBRP are studying the effects of microbial and photolytic processes on transformations of polycyclic aromatic hydrocarbons (PAHs) and organophosphate pesticides (OPs). Their goals are to better understand natural transformation processes occurring at Superfund sites and to develop systems to accelerate the destruction of chemical contaminants.

Much of this research focuses on intermediate products of the degradation processes. These products are of particular interest for several reasons:

- Intermediate products of microbial and photolytic processes can be more bioavailable and/or more toxic than the parent compounds. It is important to acknowledge that removal of a parent compound alone may not be the best measure of site cleanup.
- Intermediate products may affect other microorganisms involved in bioremediation of the parent compound or other contaminants.
- Combined microbial and photolytic processes may be synergistic. The Duke researchers are working to assess biodegradability of photolytic end products and photodegradability of biodegradation end products. For example, high molecular weight PAHs tend to be recalcitrant to microbial degradation but are susceptible to photolytic degradation. Thus, combined photochemical and microbial treatment could be used to transform high molecular weight PAHs to more biodegradable forms.

Advances: Drs. Andrew Schuler and Karl Linden are studying the degradation of PAHs and microbial population dynamics in mixed bacterial cultures established by enrichment from creosote-contaminated sediments from a salt-marsh tidal inlet along the Elizabeth River adjacent to the Atlantic Woods Industries Superfund site in Virginia. The researchers are focusing on degradation of the sulfur-containing PAH dibenzothiophene (DBT) by a mixed bacterial culture. They monitor: a) DBT degradation rates; b) intermediate product formation; c) microbial population dynamics of 10 taxonomic groups using quantitative PCR (qPCR) assays; and d) changes in toxicity via luminescence inhibition in the bioluminescent bacterium *Vibrio fischeri*.

Without pH control, pH dropped substantially and DBT degradation was greatly reduced. When pH was maintained at 7.5, degradation proceeded steadily and over 90% DBT reduction was achieved. The Schuler/Linden research team determined that the formation of toxic intermediate products is an important concern, as toxicity initially doubled and stayed at relatively high levels even after the DBT was degraded. According to qPCR results, *Flavobacteriaceae* and *Chromatiales*- groups were dominant regardless of pH control, while *Rhizobiales*-like bacteria were a major group under no pH control. None of these organisms have been previously implicated in DBT degradation, but *Chromatiales* is known to accumulate sulfur and may be of particular interest in the degradation of DBT.

The researchers also investigated photolytic process. They constructed a simulated natural sunlight system to study natural photolysis of the PAHs fluorene (FLU), dibenzofuran (DBF) and DBT alone and in mixtures. They observed no direct photolysis during 8 hours of exposure to natural sunlight, but did find that there was decay in the presence of hydrogen peroxide, suggesting that oxidative degradation is a significant environmental pathway. The researchers studied UV-based oxidative processes (UV photolysis and hydrogen peroxide assisted photodegradation) of the same group of PAHs and found a synergistic effect during photolysis with higher degradation rates within the mixture as compared to photodegradation as single components in an aqueous solution.

The researchers have also determined the kinetics and mechanisms of the photodegradation of the organophosphate pesticides chlorpyrifos, parathion, and diazinon under engineered and natural UV decay conditions. They have developed fundamental parameters of UV-based decay to allow modeling and design of a treatment system for destruction of these chemicals. In natural systems, the sunlight itself did not result in appreciable decay of the contaminants, but the enhancement due to photolysis in the presence of naturally occurring photosensitizers is currently under study.

Significance: These studies are some of the first using qPCR to monitor microbial populations in a mixed culture during degradation, and the results suggest that the combined contributions of the microbial consortium are important to understanding and improving biodegradation of even simple PAH containing systems.

This work is yielding important information regarding the fundamental processes affecting toxic exposures in natural systems. Very little work has been done on the interaction between microbiological and photodegradation processes, yet this combination may be particularly important in estuary systems, where chemicals suspended in the water column are exposed to microbes and to sunlight, and it may hold promise for the development of new engineered systems for remediation.

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To learn more about this research, please refer to the following sources:

Shemer, Hilla and Karl G. Linden. 2007. Aqueous photodegradation and toxicity of the polycyclic aromatic hydrocarbons fluorene, dibenzofuran and dibenzothiophene. Water Research (http://www.elsevier.com/inca/publications/store/3/ 0/9/index.htt). 41(4):853-61.

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