

Doctoral Dissertation Defense

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## *Non-Target Analysis of Bioremediated Soil*

December 6, 2017 | MHRC 2005 | 9:00am

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants of environmental concern. Bioremediation, relying on stimulation of natural microbial degradation processes, is a well-established technology to clean up PAH-contaminated soils. However, bioremediation does not necessarily lead to a reduction in soil toxicity. PAH-contaminated sites are affected by extremely complex mixtures, such as coal tar or creosote. Many biotransformation products or co-occurring compounds can also contribute to the overall toxicological effects of the soil before and after bioremediation, but their identities and abundances remain unknown. Therefore, the objective of this dissertation was to use non-target analysis workflows to identify the genotoxic transformation products, important co-occurring pollutants, and the unrecognized biotransformation pathways that could contribute to explain the toxicological effects observed beyond parent PAHs.

First, a non-target analytical approach was developed, combining effect-directed analysis (EDA) and metabolite profiling, to identify a novel PAH metabolite (2H-naphtho[2,1,8-*def*]chromen-2-one, NCO) that increased the toxicity and genotoxicity in the contaminated soil subjected to lab-scale bioremediation. NCO was determined to be a bacterial metabolite of pyrene, and it was found in samples from three other PAH-contaminated samples after biostimulation in microcosms.

Second, high resolution mass spectrometry (HRMS) and mass-defect filtering were applied to four PAH-contaminated samples to analyze the diversity, abundance, and biodegradation behavior of N-heterocyclic polyaromatic pollutants (azaarenes). The diversity, relatively high concentrations, and persistence of high-molecular-weight azaarenes were highlighted, and isomer-selective biodegradation was observed.

Third, the stable isotope-assisted metabolomics (SIAM) workflow was tested and applied to a PAH-contaminated soil. Uniformly  $^{13}\text{C}$ -labeled fluoranthene, pyrene, or benzo[*a*]anthracene were spiked into the soil and incubated in microcosms. With SIAM, known and unknown metabolites such as ring-cleavage products and conjugates were detected, and the transformation pathways leading to their formation proposed.

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