

Abundance, Diversity and Biodegradation Patterns of Azaarenes in Polycyclic Aromatic Hydrocarbon Polluted Soils

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Background/Objectives. Current risk assessment approaches for soils contaminated with polycyclic aromatic hydrocarbons (PAHs) only refer to the U.S. EPA list of 16 regulated compounds. However, recent investigations highlight that those soils may also contain significant levels of other co-occurring contaminants, such as oxygenated PAHs (oxy-PAHs) and azaarenes (N-PACs). Despite the demonstrated toxicity and higher water solubility of these compounds, which confers increased environmental mobility and bioavailability compared to their PAH counterparts, their presence and fate in polluted soils is generally neglected. In this work, we focus our attention on N-PACs with the aim to demonstrate their prevalence and abundance in PAH-contaminated soils, and determine their potential for bioremediation.

Approach/Activities. Total organic extracts from four soil samples with different geographical origins and distinctive type (e.g., manufactured-gas plant, creosote) and level of PAH contamination were analyzed by high resolution LC-ESI-QTOF-MS. The presence and distribution of N-PAC homolog series was determined using Kendrick mass defect plots based on the detection of their exact mass, and their abundance quantified using standard calibration curves for selected isomers. In order to identify the potential of endogenous soil communities for N-PAC biodegradation, these analytical tools were also applied during six-week lab-scale slurry incubations of the four soils under biostimulated (aeration plus nutrients) conditions.

Results/Lessons Learned. Kendrick mass defect plots identified an unprecedented diversity of azaarenes in the four analyzed samples, including N-PAC homolog families ranging from two to five aromatic rings, and with different extents of methylation (mono-, di- and trimethyl derivatives). Of significant relevance was the detection of N-containing analogue families for high molecular weight PAHs, such as aza-fluoranthenes/pyrenes, aza-benz[*a*]anthracenes/chrysenes or aza-benzo[*a*]pyrenes. Only considering their non-methylated homologs, the concentrations for these families in the four soils ranged between 1.5 and 24.0 $\mu\text{g}\cdot\text{g}^{-1}$, 4.6 and 33.2 $\mu\text{g}\cdot\text{g}^{-1}$ and 1.9 and 31.0 $\mu\text{g}\cdot\text{g}^{-1}$, respectively. The concentration ratios of representative azaarene families relative to their counterpart PAHs (N-PAC/PAH) were as high as 0.14, indicating their high relative abundance. Under stimulated biodegradation conditions, significant degradation was observed for most three- and four-ring N-PAC families, with a preference for the non- and mono-methylated compounds. Among these groups, microbial attack was homolog-specific; this selectivity is attributed to potential limitations due to structural hindrance and/or the involvement of distinctive microbial communities.