

## **The effect of soil moisture and oxygen content on naphthalene biodegradation**

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Petroleum hydrocarbon (PHC) contamination of soil and groundwater can impact ecosystems and natural resources. Biodegradation is a key process contributing to the natural attenuation and remediation of PHCs in the subsurface, but the rates and pathways of PHC biodegradation depend on various environmental factors including soil moisture. Soil moisture exerts an important control on porewater dissolved O<sub>2</sub> availability and solute transport, and by extension, on microbial biodegradation activity. To investigate the effect of soil moisture and oxygen availability on naphthalene biodegradation, we performed a microcosm incubation experiment under soil moisture conditions ranging from 60% to 100% water-filled pore space (WFPS), with oxic or anoxic headspace conditions, at a constant temperature of 25°C. Naphthalene-spiked soil microcosms were incubated for 44 days and sampled weekly. Time series data were generated for headspace gas concentrations, porewater chemistry, and total soil naphthalene concentrations. Analysis of total soil naphthalene over time revealed that net biodegradation rates were fastest under 60% WFPS conditions, and slowest under fully saturated conditions. Total soil naphthalene data were fit to a first order kinetic rate equation. These data exhibited two distinct regimes: a fast regime, characterized by an apparent first order rate constant of 0.43 day<sup>-1</sup>, followed by a slow regime, characterized by an apparent first order rate constant of 0.035 day<sup>-1</sup> – approximately an order of magnitude of difference. Within the fast and slow regimes, the order of magnitude of the apparent first order rate constant was similar between different soil moisture treatments. Porewater chemistry data indicated that the fast regime was dominated by microbial respiratory processes, while the slow phase was dominated by fermentative processes; thus, the order-of-magnitude change in the apparent first order degradation rate constant of naphthalene coincided with the onset of (slower) fermentative biodegradation. Our findings show that the apparent first-order rate constant of naphthalene biodegradation varies by one order of magnitude across the soil moisture and O<sub>2</sub> treatments tested in this study, representing conditions found in the vadose zone. Our work implies that spatial and temporal variations in soil moisture – and resulting O<sub>2</sub> availability – could bring about large variations in the effectiveness of PHC natural attenuation at contaminated field sites. Results such as those presented here can help inform how we represent PHC biodegradation in fate and transport models for the vadose zone and the underlying groundwater compartment. We are currently complementing this study with temperature-controlled incubation experiments to investigate temperature-dependence of fast and slow apparent first order rate constants of PHC biodegradation.