Toxicity Assessment of Groundwater Contaminated by Petroleum Hydrocarbons at a Well-Characterized, Aged, Crude-Oil Release Site

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Background/Objectives. A growing body of evidence suggests that partial transformation products found in waters impacted by petroleum hydrocarbons may have adverse effects on laboratory animals, wildlife, and humans. The goal of this project is to screen petroleum–impacted waters for the ability to activate human nuclear receptors (hNRs), and to integrate the results with biogeochemical data in order to improve understanding of the effectiveness of long-term natural attenuation. NRs often represent the first point of interaction of a chemical with the organism, and also control a variety of biological processes (e.g., development, endocrine function). Screening of the water samples for NR interaction can be used to prioritize/identify chemical drivers of toxicity, and potential mechanisms of toxicity. A groundwater-wetland system impacted by an oil pipeline spill in 1979 near Bemidji, MN, USA was chosen to conduct our experiments. This oil spill resulted in the release of 10,700 barrels of crude oil that flowed over land and percolated through the unsaturated zone, settling on the water table. The fate and transport of this oil has been studied by the USGS and university researchers for over 30 years. The site has an abundance of existing spatial and temporal water chemistry data and sampling infrastructure.

Approach/Activities. Water samples were collected from various contamination concentrations within the hydrocarbon plume including areas of methanogenic and iron-reducing biodegradation from hydrologically different areas within the groundwater, wetland and lake, as well as background waters upgradient from the spill site. Both field and laboratory analyses were conducted to determine the physical and biogeochemical properties of the samples, including dominant redox zonation, organic, and inorganic chemistry. The samples were also assessed for: 1) acute toxicity (in situ, raw samples, Microtox®, N=30), and 2) human nuclear receptor (hNR) activity (solid phase extracted samples, 48 hNRs evaluated using *in vitro* Trans-FACTORIAL™ Attagene Inc. platform, N=5).

Results/Lessons Learned. Field analyses revealed a substantial acute toxicity (51% reduction in bacterial luminescence - a proxy for the disruption of metabolic activity) in samples taken from more contaminated, methanogenic zones with relatively high concentrations of nonvolatile dissolved organic carbon (NVDOC) (e.g., 29.7 mg/L C). Acute toxicity was not observed in less contaminated or background samples from iron reducing zones with NVDOC concentrations of 3.3 mg/L C and 1.7 mg/L C respectively. The most highly activated hNRs in the water collected from beneath the oil body included ERa, PXR, PPARa, PPARg and RXRb. Increased activation of these receptors may lead to developmental toxicity, endocrine disruption, and metabolic dysfunction (glucose and/or lipid). Those same NRs responded with the highest magnitude in the waters collected from within the contaminant plume in methanogenic zones. Samples collected upgradient from the main oil body in iron-reducing zones activated fewer nuclear receptor targets. The background sample only activated PXR, which “senses” the presence of foreign or toxic substances. These results indicate a potential of petroleum-impacted waters to impact NR-modulated biological processes, and have implications for decisions involving effective remediation of petroleum-impacted waters to protect ecosystem function and services.