Potential Human and Aquatic Toxicity of Petroleum Biodegradation Metabolites in Groundwater at Fuel Release Sites

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Background/Objectives. Petroleum biodegradation produces the formation and degradation of oxygenated intermediate metabolites such as organic acids and esters, alcohols, phenols, ketones and aldehydes. The organics plume may last for decades or longer due to the continuing biodegradation of the petroleum source. Non-targeted GCxGC-TOFMS analyses of groundwater sample extracts from 22 upland biodegrading fuel release sites has tentatively identified the mixtures of oxygen-containing compounds (assumed herein to be metabolites) in these plumes. The potential toxicity of these metabolite mixtures to human and aquatic receptors has been investigated using constituent-specific and whole-mixture approaches.

Approach/Activities. Toxicity evaluation of complex mixtures is challenging. A disadvantage to the constituent approach is that we may never identify all chemicals in a mixture. Directly testing the whole mixture overcomes the potential analytical limitations, but presents challenges including selection of appropriate assays that are suitable for testing mixtures present in unconventional media such as groundwater. To evaluate the potential toxicity to aquatic receptors, upgradient (representing local background conditions) and downgradient groundwater samples (intended to contain metabolites but not hydrocarbons) were collected from 14 representative sites and submitted to a laboratory for chronic toxicity testing using EPA Methods 1000 (Fathead Minnow), 1002 (Daphnid) and 1003 (Green Algae). Evaluation of potential human toxicity of the metabolites was initially assessed using a constituent-specific approach by reviewing available agency-derived Reference Doses (RfDs) for individual potential metabolites, and then developing an RfD-based toxicity ranking system for each of the 22 molecular structural classes of potential metabolites. Source area and downgradient area groundwater samples were collected at 22 sites, and this ranking system was applied to all metabolites identified by GCxGC in each sample. To supplement the constituent-specific approach, whole-mixture testing with in-vitro assays for genotoxicity (gamma-H2AX assay) and endocrine disruption (ERTA assay) was conducted with groundwater samples collected from upgradient and downgradient locations at 12 representative sites.

Results/Lessons Learned. Aquatic toxicity test results show that there is generally no difference in observed toxicity between upgradient groundwater samples free of metabolites and downgradient samples containing metabolites. This suggests that any aquatic toxicity observed primarily arose from background groundwater quality, and not from metabolites. The human RfD-based ranking system results show that the vast majority of the identified metabolites are in structural classes ranked "Low" toxicity to humans (RfDs≥0.1 mg/kg/day), and that the proportion of Low toxicity compounds increases with increasing biodegradation of the metabolites plumes. Results of in-vitro testing of upgradient and downgradient groundwater samples using the gamma-H2AX assay and the ERTA assay showed no response in any sample, indicating the metabolite mixtures do not appear to have the potential to cause significant genotoxic or endocrine disruption effects. Overall, the complex mixtures of metabolites in groundwater at fuel release sites are unlikely to present a significant risk to human health or aquatic life.