Lifecycle of Extractable Organics in Groundwater at Biodegrading 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. These metabolites are found in groundwater due to their high solubility, and the organics plume may last for decades or longer due to the continuing biodegradation of the petroleum source. This work was conducted specifically to address regulatory questions regarding the nature and potential toxicity of the polar organics that are commonly measured as "total petroleum hydrocarbons" unless a SGC is used to separate polars from hydrocarbons. This presentation demonstrates the lifecycle of "extractable organics" groundwater plumes at sites with biodegrading fuel sources, and updates Zemo et al., 2016 (DOI 10.1002/ieam.1848).

Approach/Activities. Groundwater samples collected from source and downgradient (but within the organics plume) areas from 22 upland fuel release sites were extracted using methylene chloride and extracts were analyzed using targeted (GC-FID and GC-MS) and non-targeted (GC-MS, and GCxGC-TOFMS) methods. Metabolites identified using GCxGC in each sample were classified according to one of 22 molecular structural classes, and assigned an oral reference dose-based toxicity ranking. In addition, upgradient (background) samples were collected from 16 of the 22 sites to support whole-mixture toxicity testing (described in separate paper) and were analyzed using the same methods.

Results/Lessons Learned. If a petroleum source is an active source of dissolved hydrocarbons (e.g., GRO is present), the associated "Stage 1" extractable organics plume consists of dissolved C10+ hydrocarbons and biodegradation metabolites, dominated by alcohols (per-sample average of 36% of identified metabolites) and ketones (32%). For sources weathered such that dissolved hydrocarbons are no longer present, the "Stage 2" extractable organics plume within the smear zone consists of 100% metabolites, dominated by acids/esters (42%) followed by alcohols (26%) and ketones (25%), with very few aldehydes or phenols. The "Stage 3" plume, which is the combination of smear zone and downgradient areas, consists of 100% metabolites, dominated by acids/esters (70%). The "Stage 4" plume, downgradient of the smear zone, is composed of 100% metabolites dominated by organic acids/esters (about 78%), with n- and alkyl- structures the most commonly identified. Very few saturated cyclic acid or alkylphenol structures were identified. The identified metabolites naturally attenuate in a predictable manner with an overall trend toward simpler molecular structures and a higher proportion of organic acids/esters. The overall human toxicity ranking of metabolites identified in these plumes is "Low" with an increasingly lower profile as the plumes biodegrade from Stage 1 (78% Low) to Stage 4 (95% Low). These findings are consistent with the natural attenuation paradigm adopted by many regulatory agencies for petroleum release sites. Although we have assumed that the organics in the downgradient samples were metabolites, review of the upgradient data indicates that about 60% of the most commonly detected compounds in downgradient wells were also detected in upgradient wells. A majority of these were fatty acids or fatty acid esters, which are known to be ubiquitous components of DOC in aquatic systems.