Life-Cycle of Extractable Organics in Groundwater at Biodegrading Fuel Release Sites

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Abstract

This poster summarizes the results of a multi-year research study of the nature and toxicity of petroleum biodegradation metabolites in groundwater at fuel release sites that are quantified as diesel-range "Total Petroleum Hydrocarbons" (TPH; also known as TPHd, diesel-range organics (DRO), etc.), unless a silica gel cleanup (SGC) step is used on the sample extract prior to the TPH analysis. This issue is important for site risk management in regulatory jurisdictions that use TPH as a metric; the presence of these metabolites may preclude site closure even if all other factors can be considered "low-risk." Previous work has shown that up to 100% of the extractable organics in groundwater at petroleum release sites can be biodegradation metabolites. The metabolites can be separated from the hydrocarbons by incorporating a SGC step; however, regulatory agency acceptance of SGC has been inconsistent because of questions about the nature and toxicity of the metabolites. The present study was conducted to answer these specific questions. Groundwater samples collected from source and downgradient wells at fuel release sites were extracted and subjected to targeted gas chromatography-mass spectrometry (GC-MS) and nontargeted two-dimensional gas chromatography with time-of-flight mass spectrometry (GCXGC-MS) analyses, and the metabolites identified in each sample were classified according to molecular structural classes and assigned an oral reference dose (RfD)– based toxicity ranking. Our work demonstrates that the metabolites identified in groundwater at biodegrading fuel release sites are in classes ranked as low toxicity to humans and are not expected to pose significant risk to human health. The identified metabolites naturally attenuate in a predictable manner, with an overall trend to an increasingly higher proportion of organic acids and esters, and a lower human toxicity profile, and a life cycle that is consistent with the low-risk natural attenuation paradigm adopted by many regulatory agencies for petroleum release sites. Zemo et al 2016 (DOI 10.1002/ieam.1848).

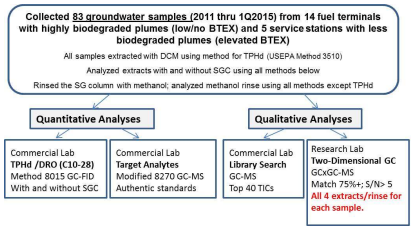
Study Methods and Results

- Identified 22 potential classes of metabolites
- Developed an RfD-based toxicity ranking system for the classes using existing regulatory approaches.
- Identified 76 individual metabolites for quantitative analysis.
- Collected more than 100 groundwater samples from fuel release sites
- Classified all tentatively identified compounds (TICs) in each sample by chemical structure and human toxicity potential; about >1200 unique TICs identified

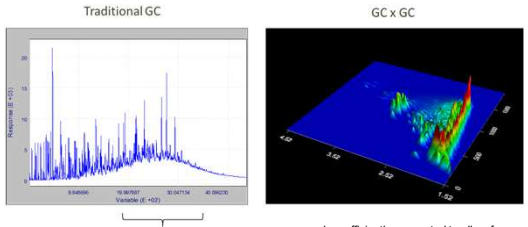
Polar Family and Specific Chemical Class	Expected Chronic Oral Toxicity to Humans
Alcohols (and diols)	
(Alkyl) alcohols	Low (RfD ≥0.1)
(Alkyl) cyclic alcohols	Low
(Alkyl) polycyclic alcohols	Low
(Alkyl) aromatic alcohols	Low
(Alkyl) polyaromatic alcohols	Low to moderate (0.1>RfD≥0.01)
Acids (and esters)	
(Alkyl) acids/esters	Low
(Alkyl) cyclic acids/esters	Low
(Alkyl) polycyclic acids/esters	Low
(Alkyl) aromatic acids/esters	Low
(Alkyl) polyaromatic acids/esters	Low to moderate
Ketones	
(Alkyl) ketones	Low to moderate
(Alkyl) cyclic ketones	Low
(Alkyl) polycyclic ketones	Low
(Alkyl) aromatic ketones	Low to moderate
(Alkyl) polyaromatic ketones	Low to moderate
Aldehydes	
(Alkyl) aldehydes	Low to moderate
(Alkyl) cyclic aldehydes	Low to moderate
(Alkyl) polycyclic aldehydes	Low to moderate
(Alkyl) aromatic aldehydes	Low to moderate
(Alkyl) polyaromatic aldehydes	Low to moderate
Phenols	
(Alkyl) phenols	Moderate* (0.01>RfD≥ 0.001)
Phenol	Low

Alkylphenol DTBP was classified as low toxicity based on EPA 2009.

Groundwater analysis: "targeted" quantitative and "non-targeted" methods



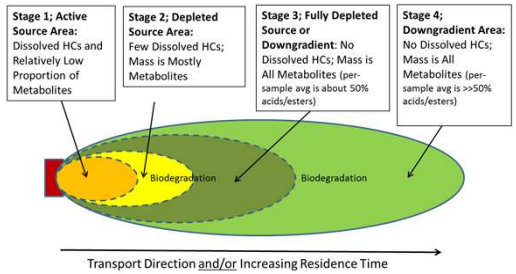
Benefits of GCXGC-MS



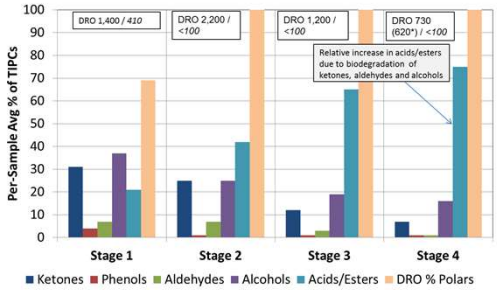
This unresolved complex mixture….

…can be sufficiently separated to allow for tentatively identifying compounds using mass spectrometry

Proposed Life Cycle of Extractable Polar Organics at Biodegrading Fuel Release Sites

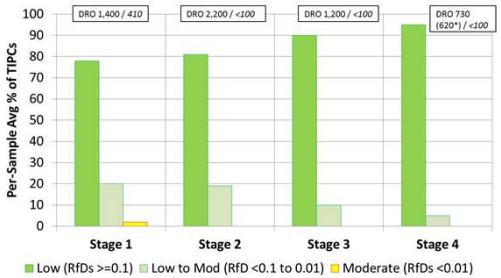


Average Distribution of Metabolite Families: *Acids/esters proportion increases as biodegradation continues*



TIPCs = tentatively identified polar compounds (metabolites only). DRO concentration (ug/L) without/*with* SGC is the average for the population representing the stage. Results are for samples without entrained product collected 2011-1Q2015.

Average Distribution of Human Health Toxicity Profile: *"Low" toxicity proportion increases as biodegradation continues*



TIPCs = tentatively identified polar compounds (metabolites only). DRO concentration (ug/L) without/*with* SGC is the average for the population representing he stage. Results are for samples without entrained product collected 2011 – 1Q2015.

Aquatic Toxicity Testing

- **Overall, the metabolites did not increase the toxicity of the groundwater above site background.**
- Tested groundwater samples collected from upgradient (free of polars) and downgradient wells (containing polars but no hydrocarbons) from 10 sites.
- Tested 3 species using EPA Methods (96-hour green algae test USEPA 1000 (growth); 7-day water flea test USEPA 1002 (survival and reproduction); 7-day fathead minnow USEPA 1003 (survival and growth).
- Analyzed groundwater samples for general water quality parameters.
- Toxicity observed was primarily due to background water quality.
- Toxicity was not correlated with the concentration of metabolites in the sample (no dose-response).

Life Cycle Summary

- 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.

Lessons Learned

- The human toxicity ranking of extractable polar compounds 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).
- Petroleum metabolites naturally attenuate in a predictable manner with an overall trend toward simpler molecular structures and a higher proportion of organic acids/esters.
- These findings are consistent with the natural attenuation paradigm adopted by many regulatory agencies for petroleum release sites.
- 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 dissolved organic carbon (DOC) in aquatic systems.
- Although we have assumed that the organics in the downgradient samples were degradation intermediates, they may be microbial products that are consistent with DOC found in unimpacted aquifers.

Acknowledgements

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