

Measurement of Signature Metabolites at Hydrocarbon Release Sites as Components of Natural Attenuation

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OBJECTIVES

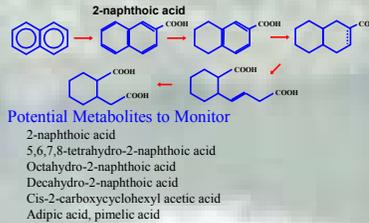
- Identify *signature metabolites* of MGP and hydrocarbon waste degradation
- Develop target analyte list
- Identify and verify analytical methods
- Demonstrate at two or more MGP sites

LINES OF EVIDENCE FOR NA

- Primary, secondary, and optional
 - Primary
 - Decreasing chemical concentrations
 - Secondary
 - Geochemical measurements
 - Optional
 - Modeling
 - Microbiological studies

Signature metabolites are primary evidence that chemicals are degrading

ANAEROBIC NAPHTHALENE DEGRADATION



Potential Metabolites to Monitor

2-naphthoic acid
5,6,7,8-tetrahydro-2-naphthoic acid
Octahydro-2-naphthoic acid
Decahydro-2-naphthoic acid
Cis-2-carboxycyclohexyl acetic acid
Adipic acid, pimelic acid

SAMPLE PREPARATION

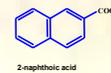
- Solid phase extraction (SPE) of water
 - Reversed-phase SPE cartridge (Waters Oasis HLB)
 - Sample pH <2
 - Elution with MTBE/methanol
 - Concentration
- Standard soil extraction methods

STUDY DESIGN

- Develop general compound list
 - Use published and in-house data
 - Generate short list (TCL) of representative compounds
- Demonstrate analytical methods
 - GC/MS, HPLC, LC/MS
 - Verify methods on TCL
 - Establish detection limits (ppt range?)
- Verify proper sampling and preservation methods
- Monitor signature metabolites at one or more MGP sites
 - Well selection based on MAHs, PAHs, and geochemical levels
- Conduct parallel microcosm study

MODEL COMPOUNDS

1-benzylsuccinic acid 1-naphthalenemethanol
2-naphthol 1,2,3,4-tetrahydronaphthoic acid
2-naphthoic acid 9-fluorenone
2,3-naphthalenedicarboxylic acid



Model compounds were chosen for method verification. Their structures were similar to anticipated signature metabolites and standards were available.

RESULTS – TARRY SEDIMENT

- Site description
 - Shallow MGP tar-impacted sediments
- 3.1 to 270 mg/kg total MAHs/PAHs
- High NO₃ or NO₂ and SO₄
- 5 sediment and assoc. pore water samples collected
- Parallel microcosm study conducted
- Compounds detected
 - Confirmed in pore water and microcosms
 - 2-Naphthoic acid 4 µg/L
 - Tetrahydro-7-naphthoic acid 0.2 µg/L
 - 1-Methyl-2-naphthoic acid 0.2 µg/L
 - Benzylsuccinate 0.7 µg/L
 - tentative
 - 2-Naphthoic acid

by LC/UV and SPE/LC/MS

RESULTS – SITE 24 REVISITED

- Samples description
 - 8 groundwater samples
 - 0.5 - 3 mg/L naphthalene
 - Low MAHs
 - Very low DO
- Samples analyzed for:
 - 3 isomers of hydroxynaphthoic acid by deriv/GC/MS
- DL ≈ 5 µg/L
- No hydroxynaphthoic acids detected
- Tentatively identified:
 - Naphthoic acid isomer
 - Phenanthrene carboxylic acid isomer
 - Naphthalene acetic acid isomer
 - Methyl naphthalene acetic acid isomer

DATA QUALITY OBJECTIVES

- Detection limits
 - Low parts per trillion
- Minimize interferences from:
 - high parent compound concentrations
- Good recovery and precision

QUALITY CONTROL RESULTS FOR LC/UV METHOD

Quantitation limit (2 L sample) 25 ppt
Detection limit ~10 ppt
Spike recovery at 5 ppb ~80%

Results for LC/MS were similar

CONCLUSIONS

- Natural biodegradation of MGP tar generates organic acids
 - Aerobic and anaerobic
 - Not present in source tar
 - At measurable concentrations
- SPE with LC/UV and LC/MS effective tools for metabolite identification and measurement to 25 ppt
- Microcosm studies provide controlled conditions for metabolite formation and time studies.
- Metabolites provide primary evidence of natural attenuation

ABSTRACT

Recently, natural attenuation (NA) has gained technical and regulatory acceptance as an appropriate remedial approach at some sites. A "lines of evidence" approach is commonly used for proving that natural attenuation of contaminated soil and groundwater is occurring at a site. The "evidence" is based on showing the disappearance of contaminants by field monitoring and laboratory tests, as well as showing the existence of attenuation mechanisms in the field. Another line of evidence is the presence of microbial degradation products of selected parent compounds in groundwater.

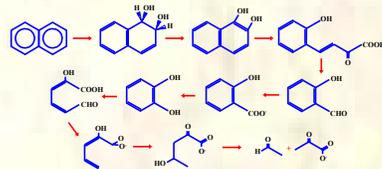
Utilities can be responsible for releases of hydrocarbons such as manufactured gas plant (MGP) tars, gas pipeline condensates, and gasoline and fuel oils, petroleum solvents. These materials contain chemicals such as monocyclic aromatic hydrocarbons (MAH), polycyclic aromatic hydrocarbons (PAH), their alkylated homologs, and aliphatic hydrocarbons. Recent studies have identified several transient metabolites of hydrocarbons in laboratory microcosm tests and in groundwater containing high concentrations of parent chemicals. This presentation reports on work to develop a target compound list for hydrocarbon contaminated sites (signature metabolites) and to identify and test appropriate chemical analysis methods for those compounds. The results of the method development and the analyses of groundwater and sediment pore water samples will be presented. Potential applications of this research in the development of appropriate protocols for sediments are contemplated by EPRI and these will also be discussed briefly.

MGP PARENT COMPOUNDS

Benzene	Alkylated naphthalenes
Toluene	Phenanthrene
Xylenes	Other PAHs
Alkylated benzenes	Some alkanes/naphthenic compounds
Naphthalene	Some S, N, O compounds

The biodegradation products of these compounds should be present in MGP-impacted groundwater

AEROBIC NAPHTHALENE DEGRADATION



ORGANIC ACIDS IN COAL TAR

Phenols/alkylphenols	Naphthols
Alkylphenols	Hydroxybiphenyl
Acetic acid	Hydroxyindan
Trihydroxynaphthalene	Hydroxybenzoic acid

Signature metabolites cannot be present in the unaltered tar