Evaluation of Bio-oxidation to Mitigate Long-Term Dissolution and Mass Discharge of Contaminants from Coal Tar and Creosote

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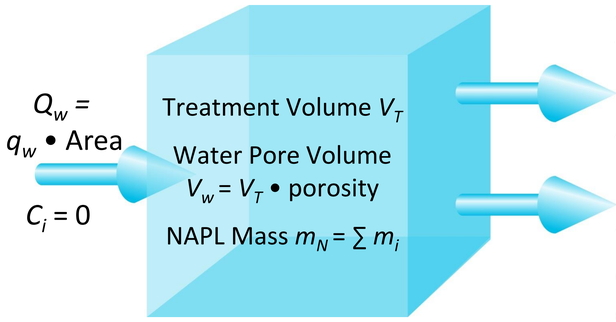
OVERVIEW

Enhancing NAPL composition change is a viable risk-based remediation strategy at coal tar and creosote sites to mitigate dissolution and mass flux to groundwater.

The following information will be discussed:

- NAPL depletion modeling requires NAPL effective solubility model
- Raoult's Law NAPL solubility model
- EPRI-developed laboratory-based NAPL equilibration method
- Applications to water-gas tar (MGP site) and creosote (wood-treating site)

NAPL DEPLETION MODEL



Δm_i = mass loss of compound *i* from the NAPL

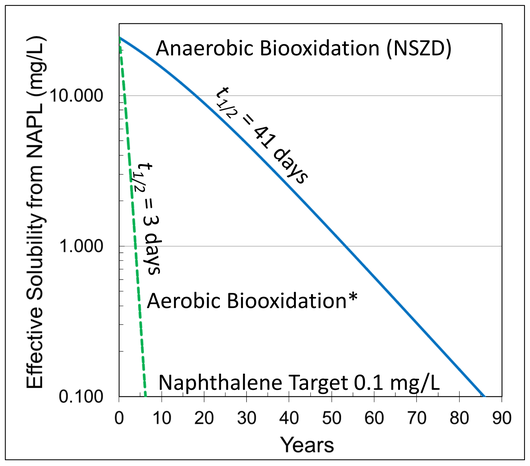
Dissolution and Advection
$\Delta m_{i,d} = Q_w \bullet C_i$

Dissolution and Biooxidation
$\Delta m_{i,b} = V_w \bullet C_i \bullet (1 - e^{-k \bullet \Delta t})$

C_i = effective aqueous solubility C_{eq}^i of compound *i* from the NAPL

- Excel-based numerical model
- Groundwater discharge, Q_w (homogeneous)
- Biooxidation rates of compounds, k (constant)
- Models NAPL composition change with time
- Solubility Model determines effective solubility
- Assumes instantaneous equilibrium dissolution

Naphthalene Depletion from Creosote



** Aerobic biooxidation rate from biosparge pilot study*

ANALYTICAL METHODS

The NAPL samples were analyzed by GC/FID (EPA 8015M) for fingerprinting, alkanes, and total petroleum hydrocarbons and by GC/MS/SIM (EPA 8270M) for PAHs, alkyl PAH homologues and other selected compounds.

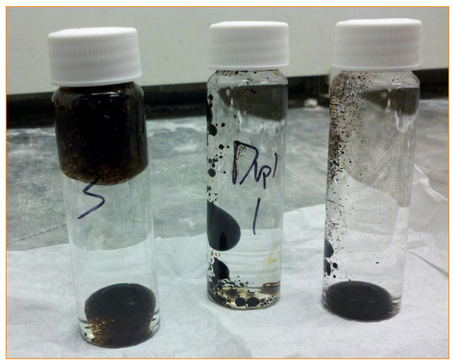
1. 2.0 g of each NAPL sample was equilibrated with water in 40 ml VOA vials in duplicate.
2. Samples were equilibrated for 5 days on an end-over-end rotator at ambient temperature.
3. At the end of 5 days, about 30 ml of the aqueous portion (water weights were recorded) were transferred to new 40 mL VOA vials, taking great care to not collect any of the NAPL.
4. Water samples were prepared by solvent extraction (EPA 3511) using DCM. The extracts were spiked with internal standard and analyzed by GC/MS/SIM-SCAN (EPA 8270M) for MAHs and PAHs.

EPA Method 3511 for Water Analysis

- Developed by META for EPRI, initially for use at MGP sites
- Small volumes of water are extracted for volatile and semivolatile compounds in one run
- 76 target compounds included benzene, toluene, xylenes, and alkylated benzenes, PAHs, alkylated PAHs, and several heterocyclic compounds
- Detection Limit was 0.6 µg/L
- Pentachlorophenol was analyzed for with EPA 3511 in creosote samples

SAMPLING METHODS

- A two-phase NAPL/water equilibration test was conducted using the method described in EPRI (2004) and Brown et al. (2005)
- Following equilibration, NAPL is separated into LNAPL, DNAPL, and various smears and blebs according to the relative aliphatic and aromatic content
- To prevent NAPL from being collected with the equilibrated water, a double needle sampling approach is used



1. Insert pipet with parafilm plug into the sample.
2. Carefully insert syringe needle through the parafilm plug.
3. Withdraw 25 to 30 mL of water sample and transfer to a clean vial for analysis.

SOLUBILITY MODEL

From Raoult's Law, the effective aqueous solubility of compound *i* from the NAPL is (Brown et al. 2005):

$$C_{eq}^i = \frac{C_s^i}{FR_i} \frac{\overline{MW}_{ct}}{MW_i} C_{ct}^i = G_i \overline{MW}_{ct}$$

C_s^i = pure phase aqueous solubility of compound *i*

FR_i = solid-liquid fugacity ratio of compound *i*

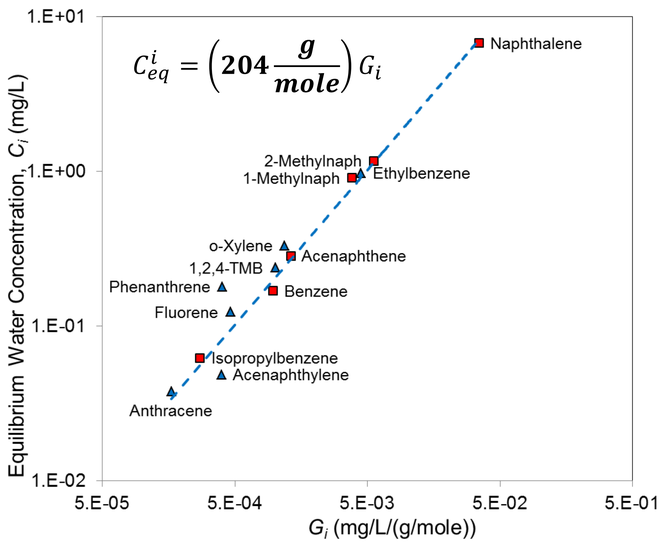
C_{ct}^i = mass fraction of compound *i in NAPL*

MW_i = molecular weight of compound *i*

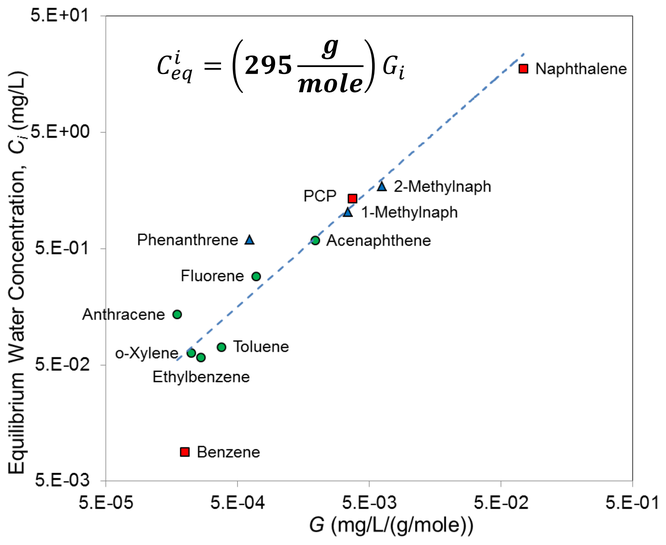
$\overline{MW}_{ct}$ = average molecular weight of the NAPL

- Fugacity ratios and pure phase aqueous solubilities from Brown et al. (2005)
- Average molecular weight of NAPL is the slope of line fit to C_{eq}^i versus G_i for compounds (G_i>0.0001)
- Slope is from a linear regression of the log-transformed data

MGP Site



Creosote Site



SUMMARY

- A Raoult's Law solubility model provided good fits to the laboratory analytical data from NAPL-water equilibration batch tests
- EPA Methods 3511/8270M provide the full range of volatile and semivolatile coal tar compounds to less than a part per billion using only 25 mL to 30 mL of sample
- The average molecular weights determined by this method were consistent with other reported MWs for MGP tar and creosote
- The solubility models were used to model NAPL depletion and weathering for dissolved-phase remediation strategies (aerobic biooxidation and natural attenuation)

References

EPRI. 2004. Laboratory Assessment of Leaching Potential Coal Tar at MGP Sites. 1009425.

Brown, E. et al. 2005. "Raoult's Law-Based Method for Determination of Coal Tar Average Molecular Weight," Env. Toxicology and Chemistry, 24:1886-1892.