Measuring Diesel-Range Organic Concentrations in Groundwater

Edward Heyse, PhD, PE
Bruce Henry, PG
Brian Blicker, PE

PARSONS

DRO in Groundwater

- DRO concentrations in groundwater at former Galena FOL are high and fluctuate, and drive timeline to achieve cleanup complete
- Possible causes
  - Partially oxidized polar metabolites (result of bioremediation) with higher solubility than original DRO components
  - Polar micelles, NAPL “blebs” or sheen in low flow submersible pump samples (exacerbated by ~25 ft water table fluctuation at Galena)
- Objective:
  - Use different sampling techniques to better understand DRO results
  - Expedite sites to efficient closure

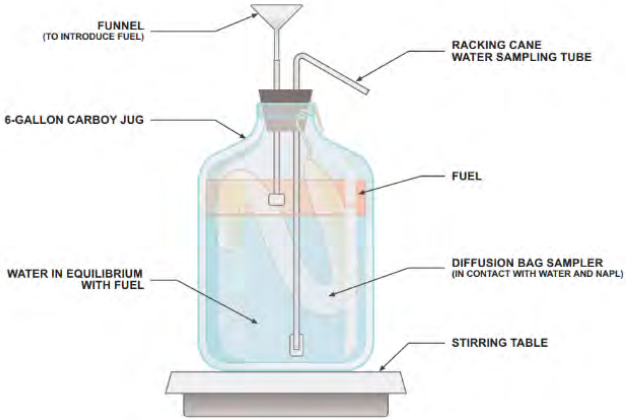
Method AK102

- Basis of Alaska DEC Cleanup Level for DRO
  - Gas chromatographic method for detection of semi-volatile petroleum products such as diesels. Other non-petroleum compounds with similar characteristics and boiling points, may also be detected with this method.
  - Method uses capillary column gas chromatograph equipped with a flame ionization detector (FID), which has been temperature programmed to facilitate separation of organic compounds.
  - Quantitation compares the total chromatographic area between and including the peak start of C10 to the peak start of C25, including both resolved and unresolved components, based on FID response compared to a diesel calibration standard.

Evaluation of Monitoring Techniques for DRO in Groundwater

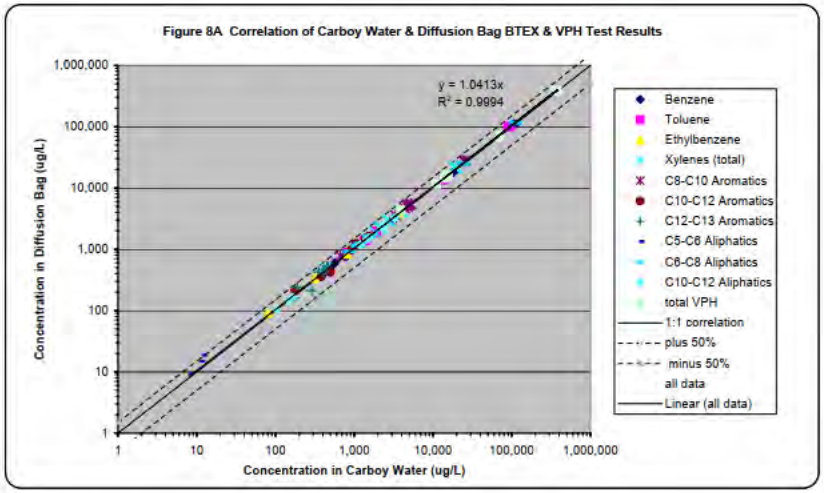
- Evaluated three sampling techniques:
  - Low flow sampling – DRO analysis using AK102
  - Low flow sampling with Silica Gel Cleanup (SGC) prior to AK102 analysis – removes dissolved polar components
  - Passive Diffusion Bag Samplers – non-polar dissolved components diffuse into PDB
- Used data to estimate dissolved polar, dissolved non-polar, and NAPL fractions
  - Non-polar dissolved = PDB sample result
  - Polar compounds (dissolved and micelles) = Low Flow – SGC results
  - NAPL = SGC – PDB results

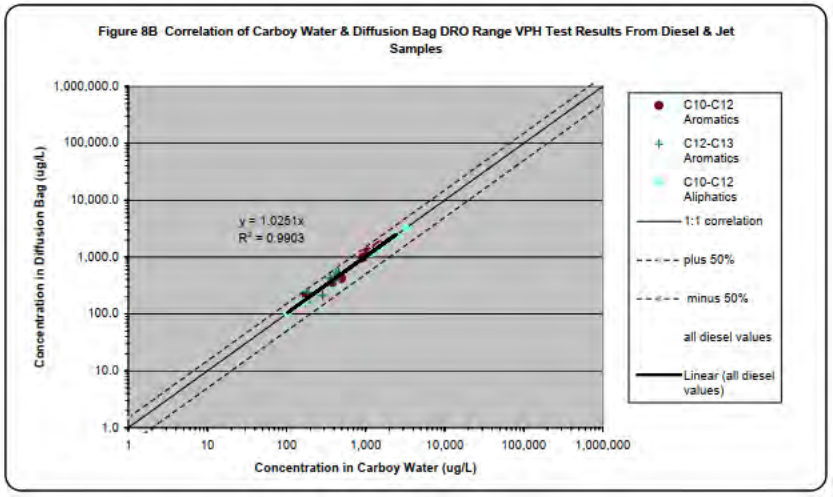
BTEX and VPH Sampling With PDB Confirmed through Laboratory Studies



- Top graph is gasoline-range BTEX/VPH results ($C_6 – C_{12}$, $R^2 = 0.9994$)
- Bottom graph is diesel-range VPH results ($C_{10} – C_{13}$, $R^2 = 0.9903$)

Source: *Groundwater Sampling Techniques for Site Characterization and Hydrocarbon Risk Calculations* (Geosphere and CH2M HILL, 2006) prepared for Alaska Statement of Cooperation Working Group





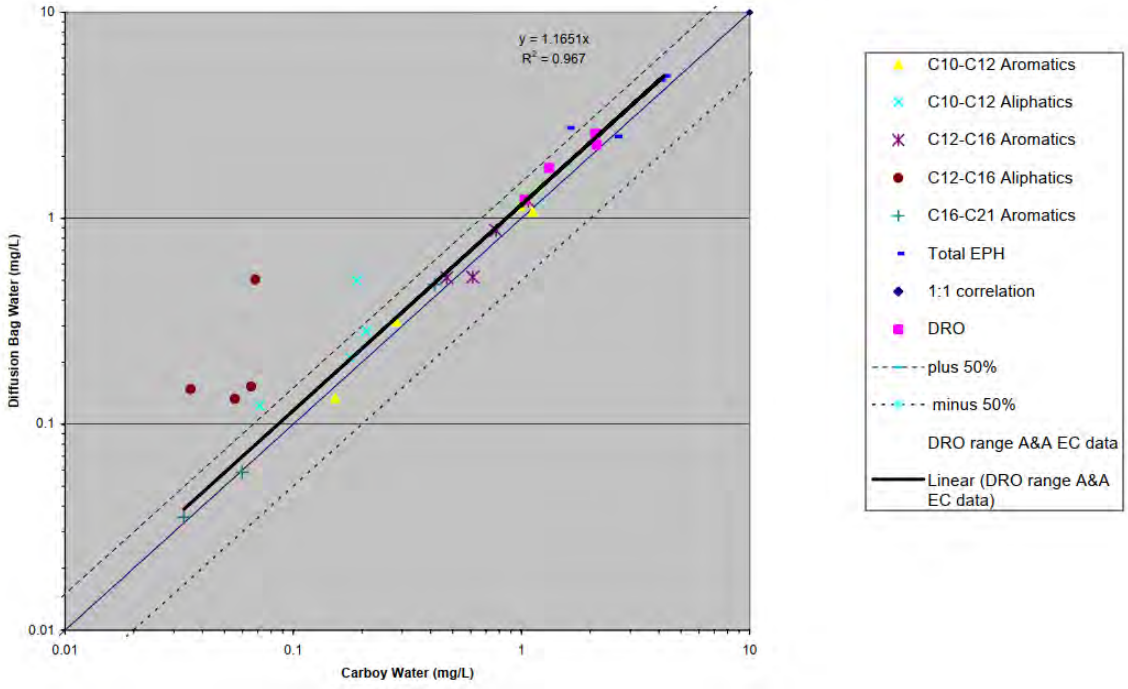
PARSONS

DRO Sampling with PDB Validated through Laboratory Studies

- Diesel-range DRO and EPH results ($C_{10} – C_{21}$, $R^2 = 0.967$)

Source: *Groundwater Sampling Techniques for Site Characterization and Hydrocarbon Risk Calculations* (Geosphere and CH2M HILL, 2006) prepared for Alaska Statement of Cooperation Working Group

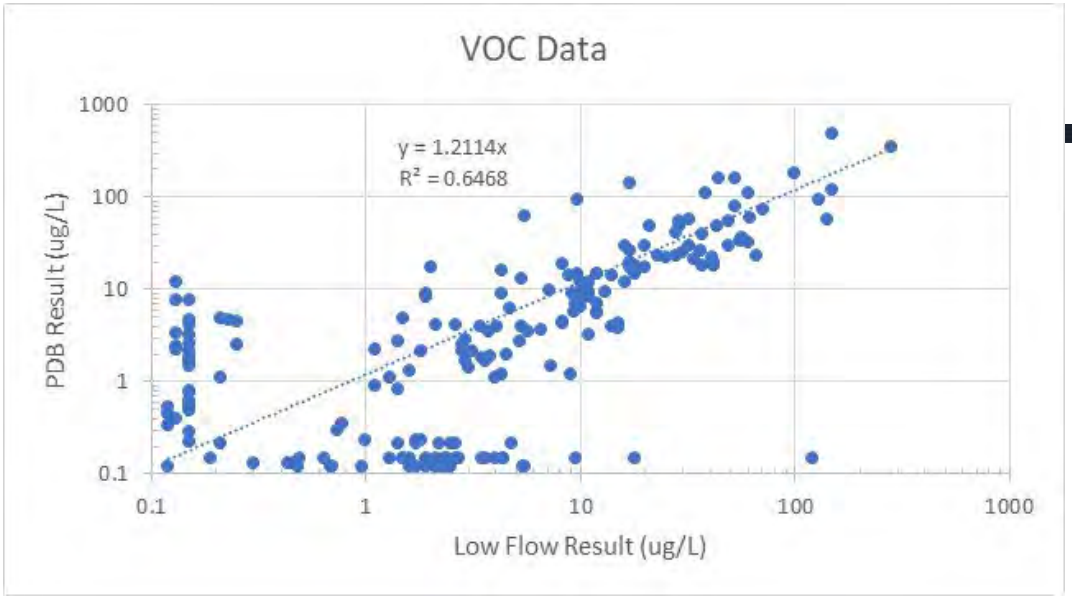
Figure 9 Correlation of Carboy Water & Diffusion Bag EPH Test Results

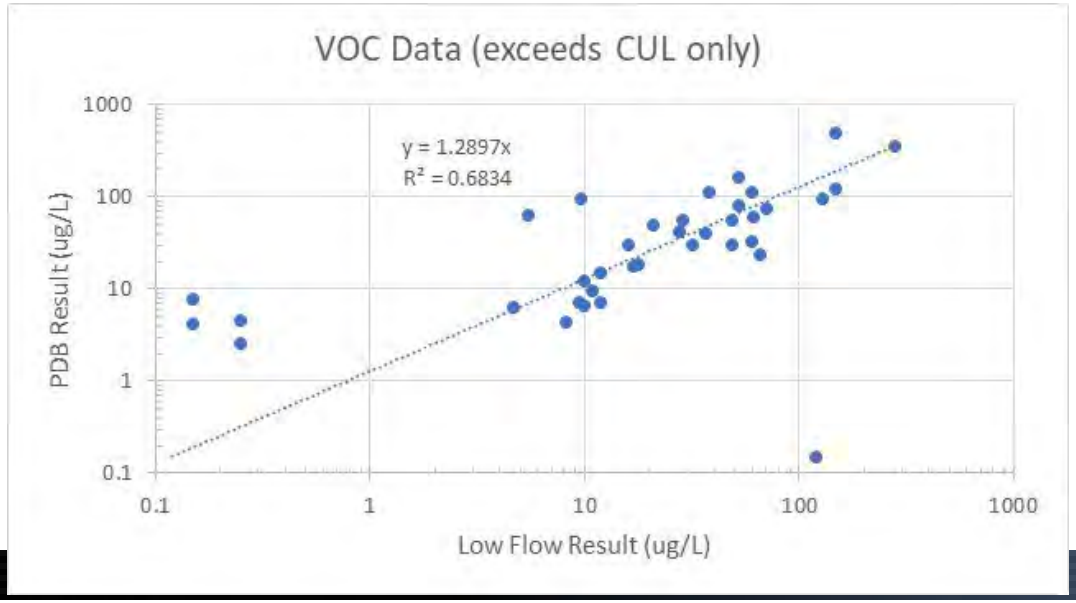


Polar “Blobs” in Weathered DRO

- Vials of weathered jet fuel with black specks of polar “blobs” (micelles) in the water phase below the NAPL phase

Groundwater Monitoring QC Testing

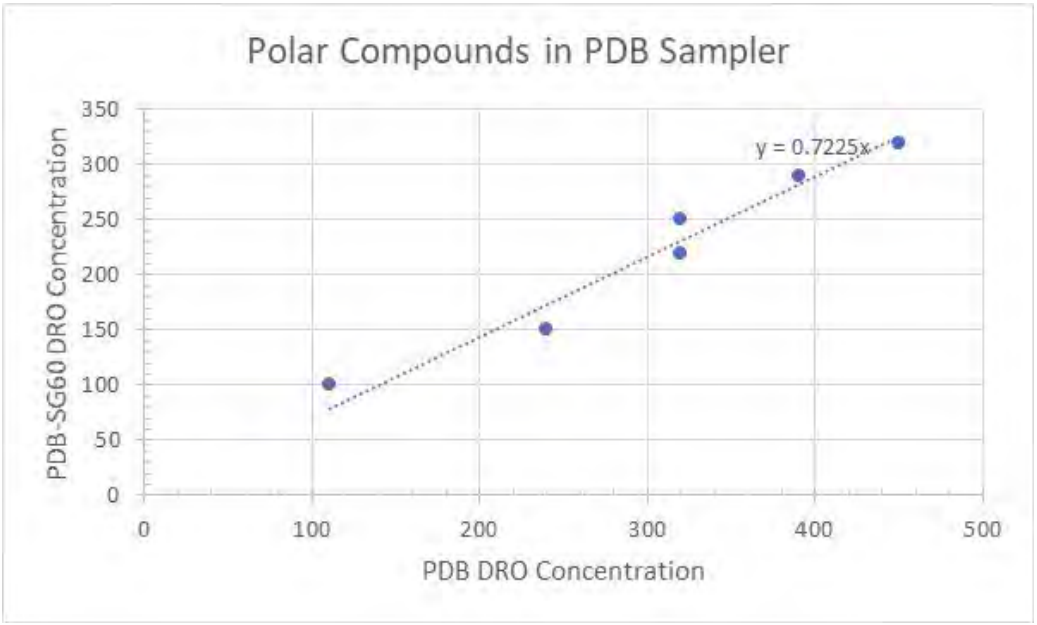




- Compare PDB and low flow result for petroleum aromatics and chlorinated ethenes
- Good correlation; PDB result is slightly higher (conservative)

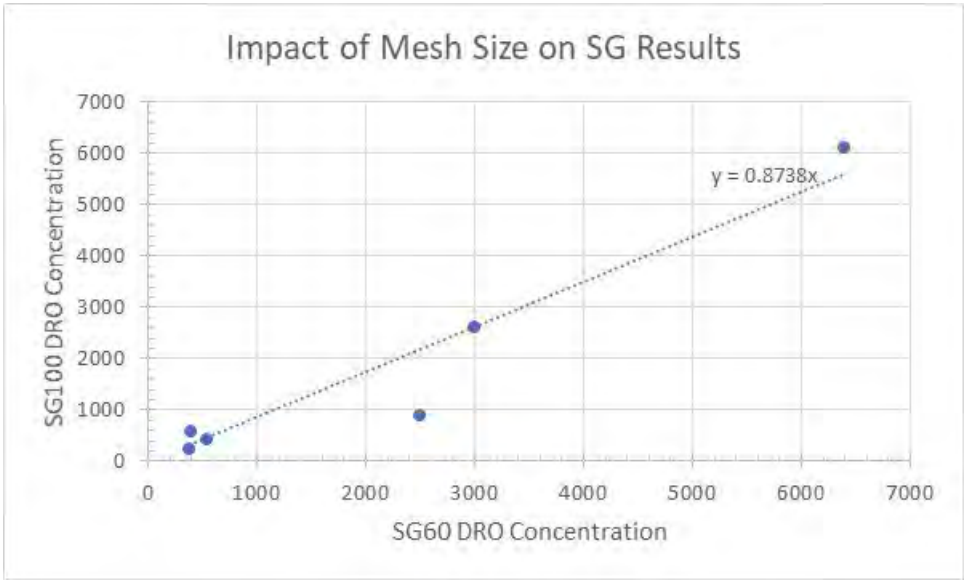
PARSONS

Groundwater Monitoring QC Testing



- PDB sample was split, a portion for AK102 analysis and a portion for AK102 with SGC
- Some polar compounds may be diffusing into PDB
  - Only 0.5% to 3% of polar compounds in groundwater enter the PDB
  - Because polar compounds are >> non-polar in groundwater, polar compounds are nearly 30% of AK102 result in PDB
  - Non-polar dissolved fraction may be overestimated and NAPL underestimated

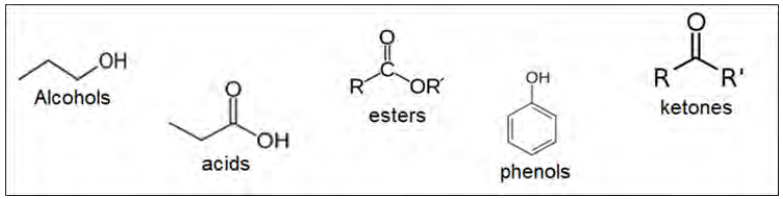
Groundwater Monitoring QC Testing

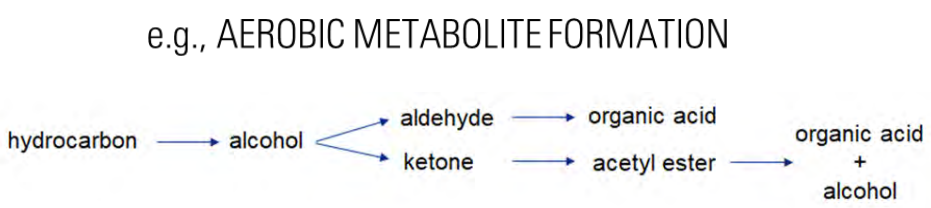


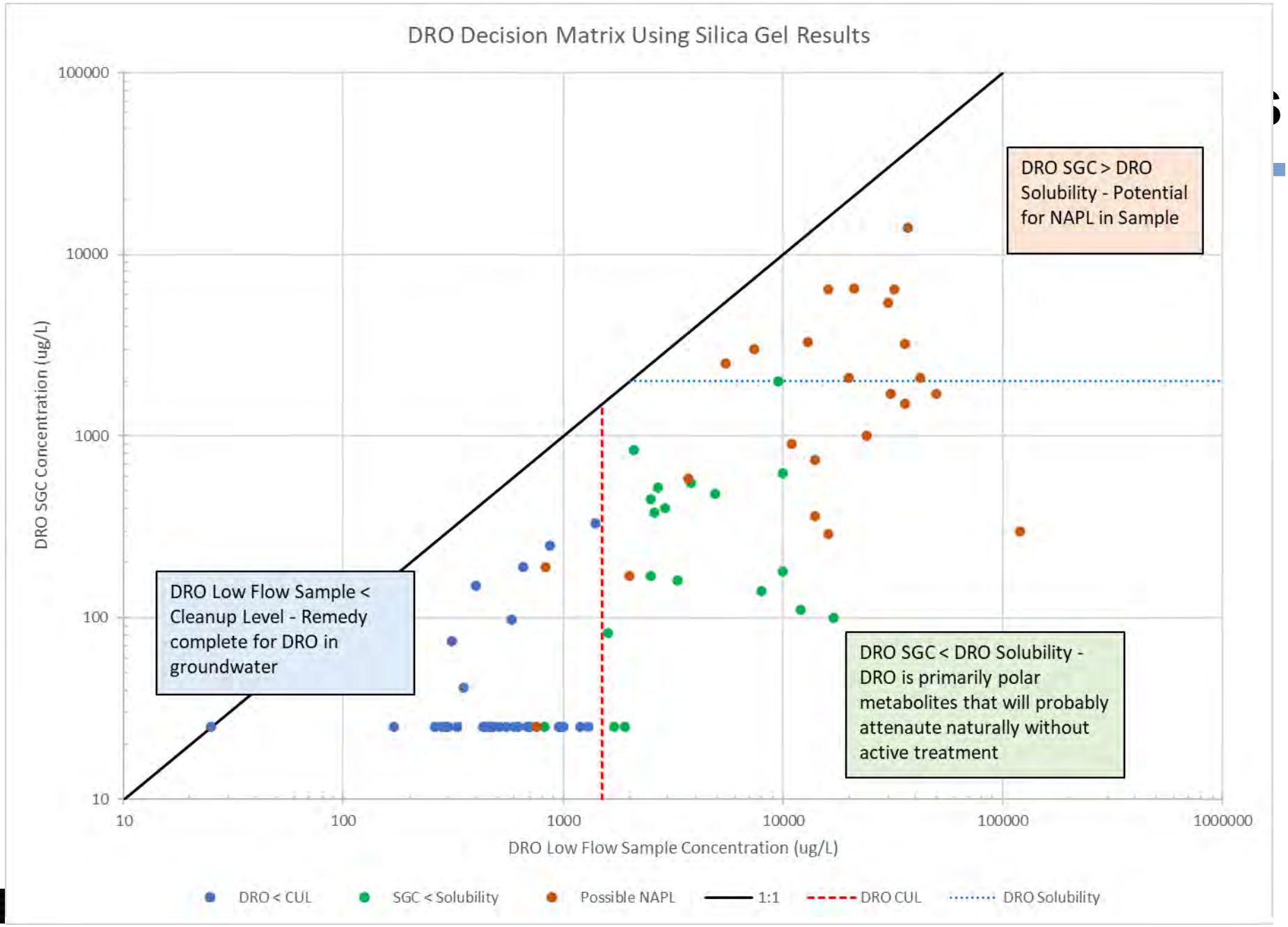
- ADEC SGC Method (Dec 2021) allows 60-100 mesh size for silica gel
- Most SGC samples were run through a column with a 60-mesh size
- Some duplicate samples were analyzed with a 100-mesh size column (denser size)
- Concentrations run through 100-mesh column were slightly lower (87%) compared to 60 mesh column
- 60-mesh column gives a higher concentration
  - Dissolved polar fraction may be underestimated
  - NAPL fraction may be overestimated

Sample Results

- DRO in Galena groundwater is heavily weathered:
  - Source area wells – AK102 DRO is 84% polar, 9% NAPL, 7% non-polar
  - Downgradient wells – AK102 DRO is 89% polar, 0% NAPL, 11% non-polar
- Weathering of diesel fuel causes compositional change in the hydrocarbons
  - Abiotic and biotic degradation transforms DRO into polar metabolites that includes alcohols, acids, esters, phenols, and ketones
- Estimation of NAPL portion is uncertain due to high concentrations of polar compounds impacting PDB and SGC results






DRO Decision Matrix Using Silica Gel Results
DRO SGC Concentration (ug/L)
DRO Low Flow Sample Concentration (ug/L)
100000
10000
1000
100
10
10
100
1000
10000
100000
1000000
DRO SGC > DRO Solubility - Potential for NAPL in Sample
DRO Low Flow Sample < Cleanup Level - Remedy complete for DRO in groundwater
DRO SGC < DRO Solubility - DRO is primarily polar metabolites that will probably attenaute naturally without active treatment
DRO < CUL
SGC < Solubility
Possible NAPL
1:1
DRO CUL
DRO Solubility

Conclusions

- Active treatment and natural weathering create partially oxidized, polar metabolites that are more soluble than original fuel components
  - Accounts for increased DRO concentrations observed after initiating bioventing, air sparging and other treatment processes
  - After petroleum constituents (BTEX, naphthalene, trimethylbenzenes, etc.) have been treated to below cleanup levels, more active treatment is not going to reduce DRO concentrations as measured by AK102 to the cleanup level in a reasonable timeframe
- SGC results can be used to help decide when to transition to natural attenuation
  - Low Flow Result < CUL – Cleanup Complete
  - SGC result < CUL – DRO is primarily polar metabolites; transition to MNA
  - SGC result > CUL – More active treatment may be necessary
  - SGC result > DRO Solubility – Evaluate for possible NAPL in sample