Mobility of a Highly Weathered Mixed Bunker Fuel and Diesel NAPL

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Background

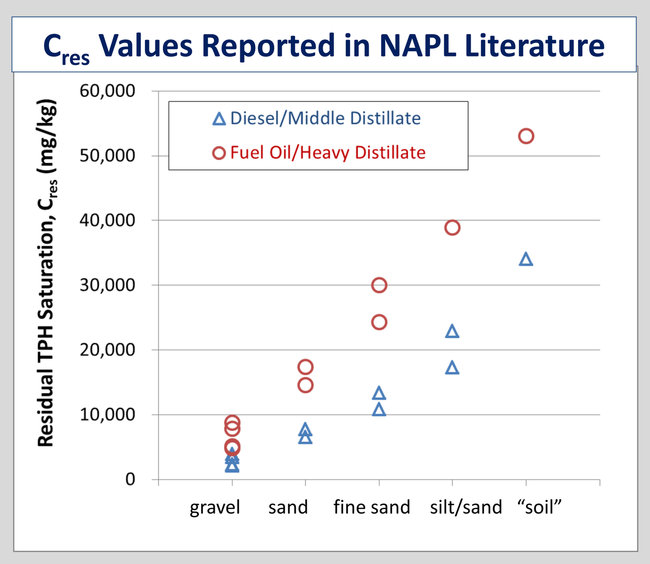
- Soil excavation at a former fuel depot was selected as the key component of a remedial strategy to prevent petroleum hydrocarbon sheens from forming on the adjacent estuary.
- Hydrocarbon sheens were potentially caused by mobile non-aqueous phase liquid (NAPL) migrating from soil within approximately 300 feet of the shoreline.
- The NAPL consists of a mixture of varying proportions of highly weathered bunker fuel and diesel, with bunker fuel being predominant in most areas.
- NAPL is present in discontinuous pockets in soil types ranging from silts and clays, to loose sand and gravel.
- Historical operation of deep sump ponds resulted in smearing of NAPL below the current groundwater table.

Objectives

- **Develop a field testing and screening approach to facilitate real-time decisions during soil excavation and limit excavation to soil containing mobile NAPL.**
  - ➢ define a range of total petroleum hydrocarbon (TPH) concentrations in soil above which mobile NAPL is likely to be present
  - ➢ develop "action levels" to screen soil during excavation, thereby limiting the excavation extent to areas where NAPL is potentially mobile.
  - ➢ develop a correlation between laboratory and field TPH analytical methods, to allow for real-time field measurements of TPH concentrations

NAPL Mobility Defined

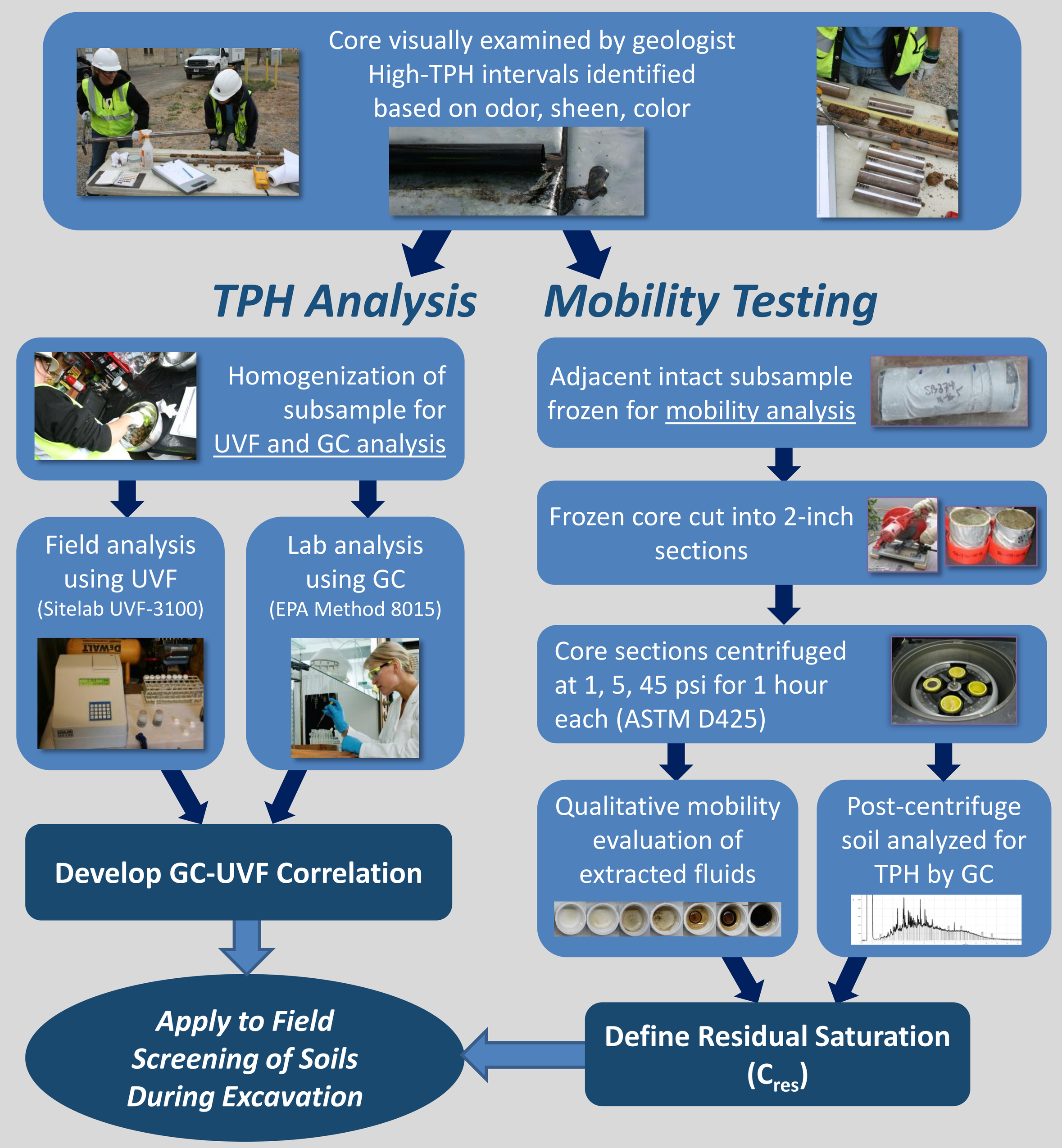
- NAPL mobility depends on properties of both the NAPL and soil, and is governed by the same equations as groundwater flow, with conductivity and gradient controlling the rate of flow.
- NAPL concentration (saturation) must be sufficiently high to overcome capillary forces to be mobile. NAPL present in soil at a lower saturation is immobile, or "residual."
  - ➢ Residual concentration, C_{res}, defines a TPH concentration **below which NAPL is not mobile**



Sources: Brost and DeVaull, 2000; Fussell et al., 1981; Schwille, 1970

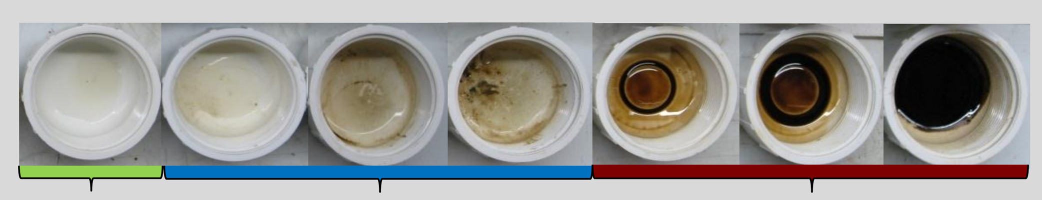
- C_{res} measurements reported in the literature vary with soil texture and NAPL composition, but also by measurement method
- C_{res} for fuel oils (including bunker fuel) reported as high as 54,000 mg/kg
- C_{res} for diesel reported as high as 35,000 mg/kg
- Laboratory measurements may not represent field mobility, which may be limited due to discontinuities in soil texture and variable NAPL distribution

Approach



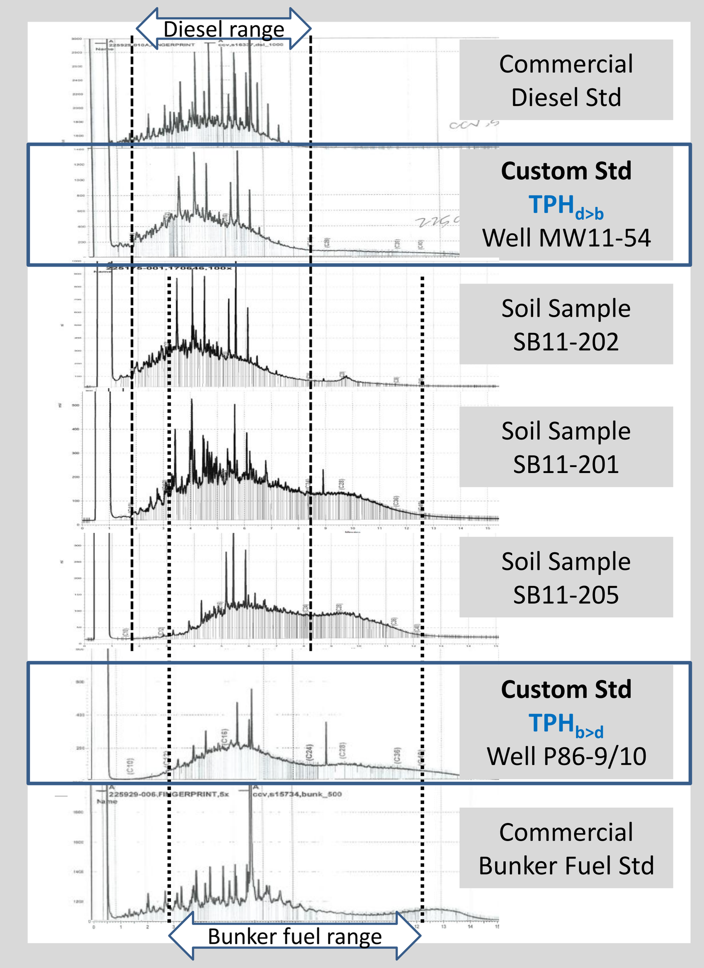
Qualitative Mobility Evaluation

- Presence of free product evaluated qualitatively in fluids extracted after centrifugation at 45 psi (ASTM D425)
- Method is conservative because pressure of 45 psi is equivalent to approximately 1,000xG or a head differential of 104 feet of water, far greater than would be encountered in soil.



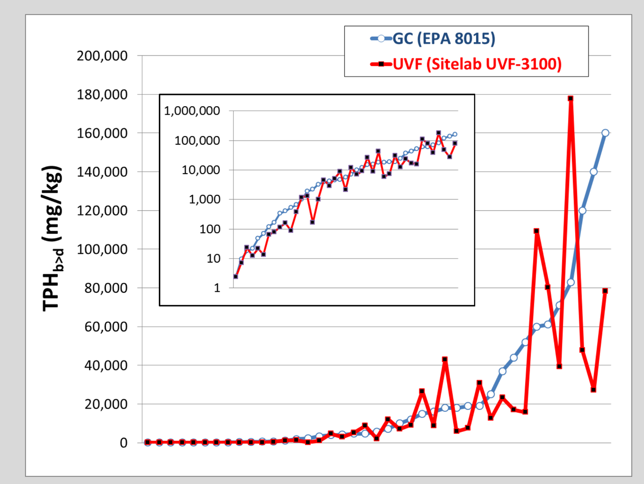
None	**Trace**	**Mobile Phase**
No visible LNAPL	LNAPL sheen	Separate LNAPL phase

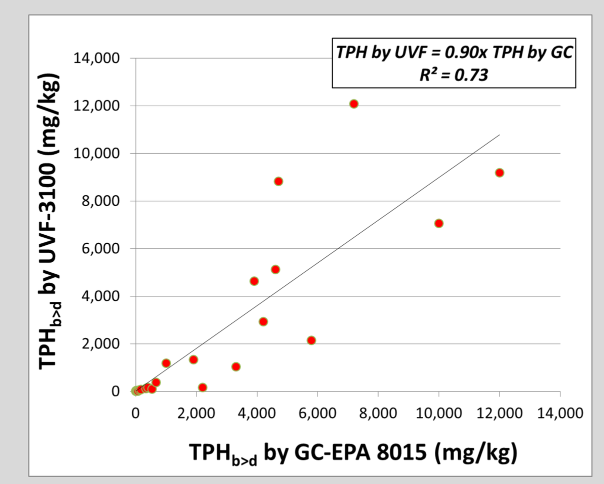
Custom TPH Calibration Standards



- Wide range of bunker/diesel proportions observed
- Chromatograms did not match commercial calibration standards
- Two custom calibration standards established:
  - ➢ ***"$TPH_{b>d}$" – representing a "mostly bunker" NAPL***
    - *based on well P86-9/10*
  - ➢ ***"$TPH_{d>b}$" – representing a "mostly diesel" NAPL***
    - *based on well MW11-54*
- Same standards used for GC and UVF calibration
- GC – UVF correlation improved when custom calibration standards used

GC – UVF Correlation

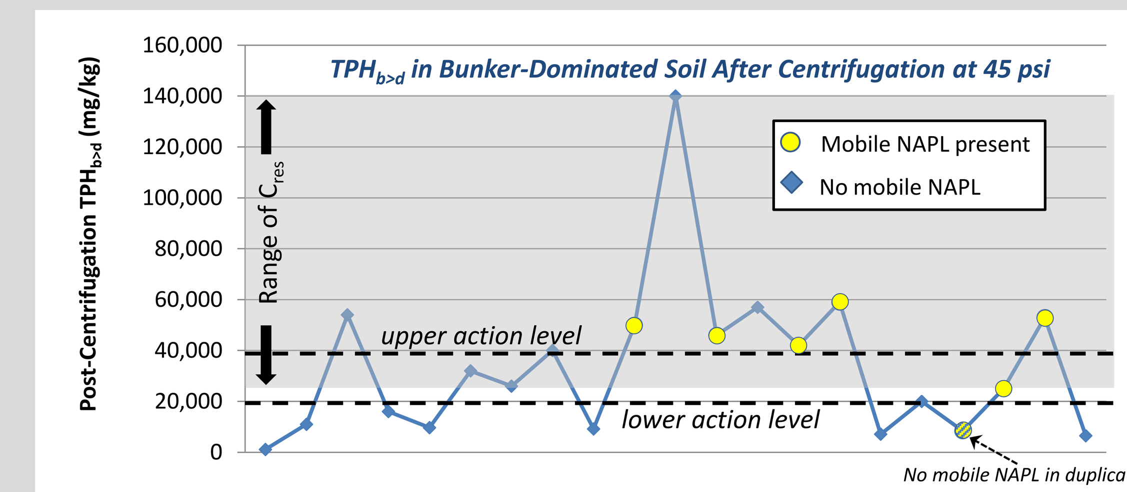




- GC – UVF correlation for $TPH_{b>d}$ was generally poor ($R^2 = 0.42$)
- GC – UVF correlation improves when only considering samples with $TPH_{b>d}$ <12,000 mg/kg ($R^2 = 0.73$)
- Too few data points to define GC-UVF correlation for $TPH_{d>b}$
- Poor correlation at high concentrations may be related to pore-scale variability in the distribution of NAPL ganglia
  - ➢ ***UVF can be reliably used at the Site when $TPH_{b>d}$ <12,000 mg/kg***
  - ➢ *Soil with $TPH_{b>d}$ >12,000 mg/kg will be analyzed by GC (EPA 8015), based on custom calibration standards*

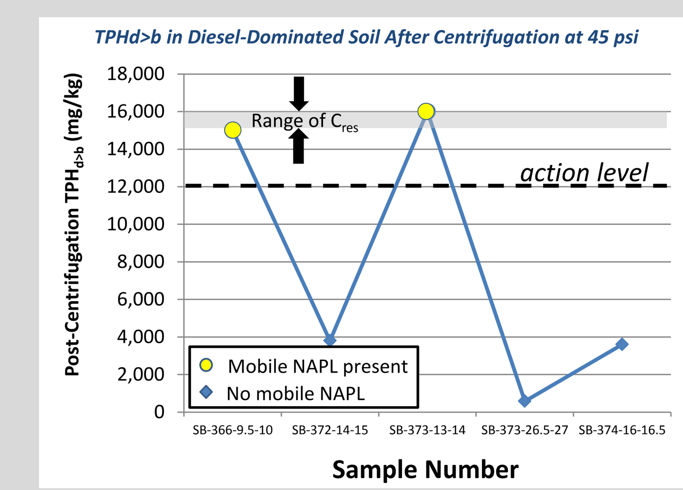
NAPL Mobility & Action Levels

NAPL Mobility in Soil Containing Primarily Bunker Fuel



- Mobile NAPL was most frequently observed (visually and based on mobility testing) in sandy/gravelly soil, which was consistent with expectations.
- Wide range of C_{res} **measured in bunker-dominated soil: 25,000 to >140,000 mg/kg**
- Most of the measured C_{res} values are > 40,000 mg/kg.
- **Upper action level** of **40,000 mg/kg** represents a $TPH_{b>d}$ concentration above which Site soil is likely to contain mobile NAPL in bunker range.
- **Lower action level** of **20,000 mg/kg** represents a $TPH_{b>d}$ concentration above which a small percentage of Site soil may contain mobile NAPL in the bunker range.
- Lab mobility testing will be performed for soil with TPH > 20,000 mg/kg

NAPL Mobility in Soil Containing Primarily Diesel



- Mobile NAPL present in two out of five diesel-dominated soil samples
- C_{res} **measured in diesel-dominated soil: 15,000 and 16,000 mg/kg**
- This concentration range is consistent with C_{res} values for diesel and diesel/bunker compositions from the literature.
- Due to small number of data points, a conservative **action level was established at 12,000 mg/kg**.

Acknowledgements

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Key References

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