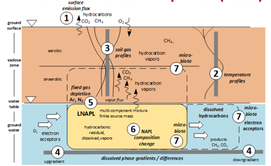
NAPL Depletion Estimates from Changes in Petroleum Chemical Composition

Method Overview

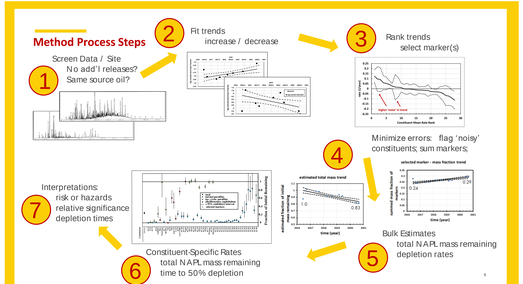
Natural Source Zone Depletion (NSZD)



- Many applied NSZD methods evaluate gaseous / vapor emissions (mostly methane) and quantify the surface emission flux (of CO_2) or heat generated in aerobic reaction. (NSZD Yield is a "bulk rate")
- Here we evaluate NSZD by evaluating source zone NAPL directly by measuring composition change over time.
- Both bulk and composition -specific depletion rates are estimated.

Methods 1 to 6 see: Standard Guide for Estimating Natural Attenuation Rates for Non-Aqueous Phase Liquids in the Subsurface DRAFT (ASTM WK76688)

NSZD from Composition Change

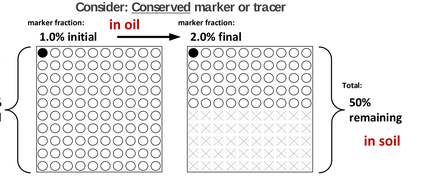


Method Details in:
George E. DeVaull, Ileana A. L. Rhodes, Emiliano Hinojosa, Cristin L. Bruce, [etroleum NAPL Depletion Estimates and Selection of Marker Constituents from Compositional Analysis, *Groundwater Monitoring & Remediation* 40, 4, 2020, 44–53. https://doi.org/10.1111/gwmr.12410 (open access)

Relating Concentration in NAPL (Oil) to relative Soil Concentration

Consider: Conserved marker or tracer

Example: Simple Application for two samples



$$\frac{\text{initial}}{\text{final}} = \frac{1\%}{2\%} = 50\% \text{ of initial total is remaining}$$

[total mass] = [total soil concentration] - [soil averaging volume]

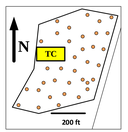
In practice: analysis of many NAPL samples over time and fit a trend

- **How to choose the best 'marker'?**
- Look at each constituent trend in NAPL – one by one
- Select the constituent(s) that shows the greatest increase over time for concentration in NAPL (g-chemical/g-NAPL) {or mass fraction in NAPL}.
- This is the 'best' marker chemical for a specific NAPL
- Multiple markers can be summed (to improve confidence limits)
- If the selected marker(s) depletes, the remaining mass estimate is conservative (an overestimate)

Applied Case Example

Site Description and Overview

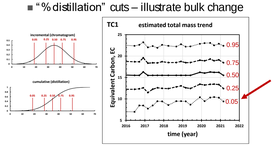
- Former refinery and product distribution terminal
  - all surface infrastructure removed
  - delineated petroleum LNAPL at/ near water table
- Geology / Groundwater
  - Water table < 4m bgl, confined/ semiconfined
  - Periodic fluctuations ~ 1m, higher winter/ spring, lower summer-autumn
- LNAPL
  - Gasoline/ Diesel mix
  - Apparent NAPL thickness 0.25 to 2 m nominally, varies. Average ~ 0.05 m. 40 acres total.
  - Similar composition across the site and over time
  - Varied degrees of weathering across the site
- Remediation (in progress).
  - Pumped LNAPL recovery. manifolded and consolidated into six chambers
- NAPL samples from chambers (TC)
  - 18 NAPL analyses over 4.7 years (approx. 4 times / year) in this example (other TC results are similar)
- Analysis
  - 72 Hydrocarbon constituents
  - Selected chemicals and narrow equivalent hydrocarbon ranges
  - Direct injection, Methods ASTM D3328-06, USEPA methods 8015 & 8260



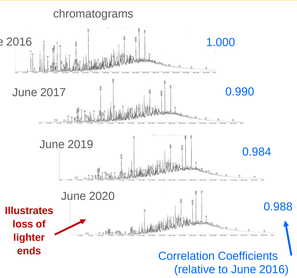
NAPL from Multiple wells consolidated and sampled from one collection chamber (TC)

LNAPL Analysis and Preliminary Evaluation

- GC/ FID & GC/ MS analysis
  - Qualitative chromatogram comparisons
  - Similar composition, not identical
  - Expert check: peak baseline and integration
- Chromatogram (non-polar separation)
  - Integrate: simulate a batch distillation
  - "% distillation" cuts – illustrate bulk change



chromatograms

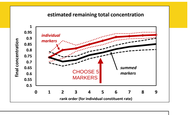


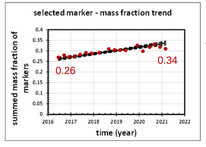
Illustrates loss of lighter ends

Correlation Coefficients (relative to June 2016)

Bulk Depletion Estimates

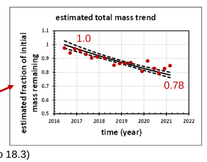
- Fit trend (each constituent mass fraction in oil)
  - Select markers from increasing constituent mass fraction
  - Sum 'best' markers to improve confidence (top 5 – this example)
    - >nC12<=nC13, >nC23<=nC24, >nC13<=nC14; nC14<=nC15; nC20<nC21





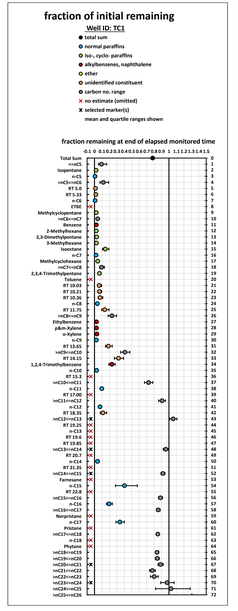
Increasing marker mass fraction

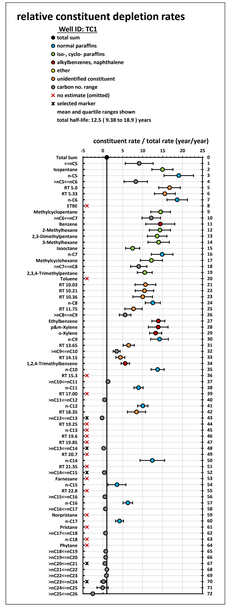
Decreasing relative NAPL mass



- Results: Estimated time for 50%total depletion (years) 15.1 (12.9 to 18.3)
  - Initial Total half life 12.5 (9.4 to 18.9)
  - Fraction of Initial NAPL Remaining 0.78 (0.76 to 0.8) after 4.7 years
    - Similar (bulk) results across this site; different evolution in different areas of the site

Composition – Specific Results





depletion of:
Volatiles
BTEX
other constituents

depletion of:
n-paraffins
other constituents

plotted constituent rates are relative to bulk rate (12.5 year half-life)

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Pittsburgh, PA

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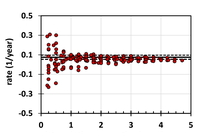
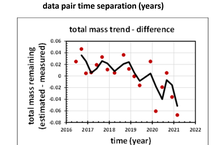
Trend analysis detail: How much data is needed?

- Linear regression, non-parametric, etc., average rates are weighted sum (or distributional values) of unique multiple terms:
  - rate = $[\ \ln(c_{n+1}) - \ln(c_n)\ ] \ / \ (t_{n+1} - t_n)$
  - n = 18 samples, n (n-1)/ 2 =153 unique combinations
  - Examine source of variability in short term differences
  - Apparent annual repeating cyclic residual error between measured data and long-term trend
- Points:
  - Long-term trend evident in long-term data
  - Shorter term variability probably due to Seasonal water table fluctuations and sampling of different NAPL zones in different season





This Data Suggests:

Minimum data record > 2 years

More scatter for differences < 1 year