Estimates of Hydrocarbon NAPL Depletion from Compositional Change over Time

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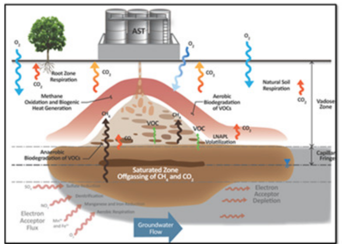


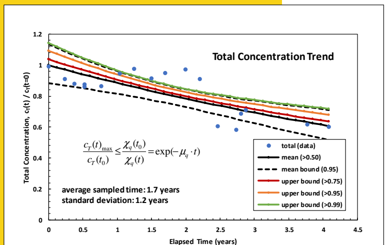
Figure credit: Quantification of Vapor Phase-related Natural Source Zone Depletion Processes, American Petroleum Institute, Publ. No. 4784, May 2017

Method Review: Garg, S., et al., Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change, Groundwater Monitoring and Remediation, 37,3,2017, 62-81.

- Various methods are available for directly estimating total LNAPL depletion.
- Here we show methods for estimating both total and constituent LNAPL depletion based on measured compositional changes in source-zone oil over time.

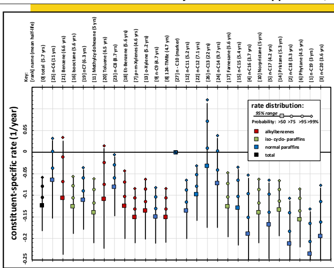
Example results – test case #1

MW4B (LNAPL from well). Oil sampled and analyzed
4 years of data, quarterly, 29 chemicals, Diesel-like (C5-C20)
Omit n-C5, i-C5 [noisy]. No pumping, skimming
Total Rate: -0.12 ± 0.06 /year
Half-life: 5.7 (3.8 to 11) years
Remaining Oil Mass:
61% (63%, 68%, 72%) of initial (Prob > 0.50, 0.75, 0.95, 0.99)



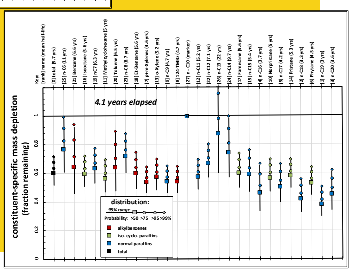
- Bulk oil depletion estimate (proportional to concentration in soil) based on quarterly LNAPL analysis from a single monitoring well. Data points, trends, and error bounds shown.
- Zero- and first- order trends are very similar in this application; the estimated half-life is longer than the data record.

Rate Estimates

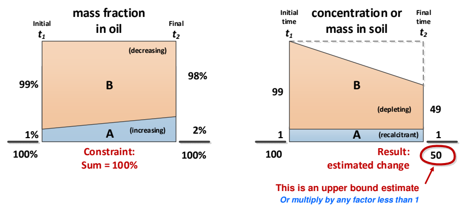


Limited marker chemical selection

Depletion Estimates



Source Depletion Example: Simple 'Binary' Mixture



- Constituent measurements are *mass fractions* in oil
- Relate *oil mass fractions* to *oil mass in soil* (soil concentration)

Key Idea: • The most recalcitrant chemical has the greatest increasing trend in oil mass fraction

- For an assigned marker chemical in the oil, depletion estimates are often based on relative changes in the concentration of the marker chemical in the oil.
- Selected marker chemicals may be present at low concentrations, may be absent, or may deplete from the oil over time.
- The illustration is for a binary mixture. If the assigned tracer depletes the estimate of remaining oil is an upper bound.

Many Constituents

How to identify / select a (conserved) marker chemical?

With data:
- constituent mass fraction versus time

Find rate-of-change in mass fraction:
- from regression (parametric or non-parametric)
- rank order the ln rate(s)-of-change (high to low)

Identification
- The most positive increasing rate(s)-of-change is:
  - The most conserved constituent (it may still attenuate)
  - Can be summed with similar constituents (based on statistical tests) for improved error bounds

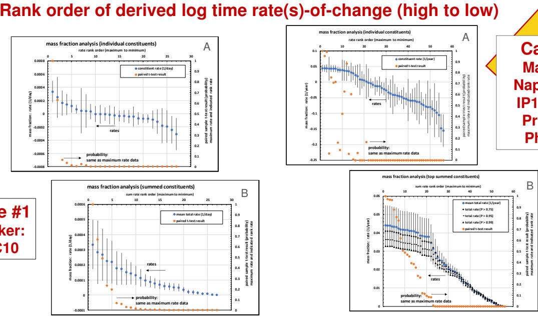
Estimated Mass Depletion

Proportional to total LNAPL soil concentration

$$\frac{c_T(t)_{\max}}{c_T(t_0)} \le \frac{\chi_q(t_0)}{\chi_q(t)} = \exp(-\mu_q \cdot t)$$

Total LNAPL depletion rate over time:
c_T - total LNAPL concentration in soil (equality holds if marker is conserved)
χ_q - mass fraction for constituent q, for maximum increasing trend

Rank order of derived log time rate(s)-of-change (high to low)



Case #1 Marker: n-C10

Case #2 Markers: Naph, IP13, IP14, IP15, Pristane, Phytane

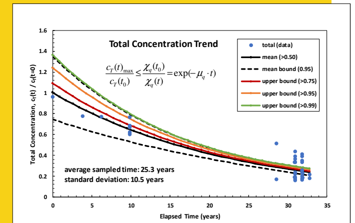
'A' plots:
- Ranked rates for individual constituents, indicated error bounds

'B' plots:
- Ranked rates for summed constituents [sum 1 (max) to *i*]
- identifies sensitivity of including more constituents as 'marker' chemicals

Example: Select top range summed constituents as marker/tracer
- Constituent relation (to maximum) shown with paired sample t-test

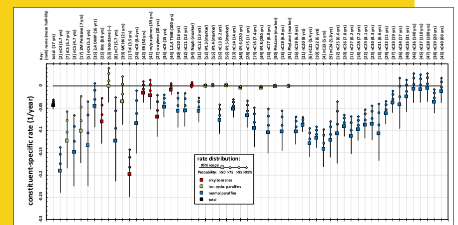
Example results – test case #2

Bemedji MN Pipeline release North Pool (USGS)
33 years of data, 39 sample times, 56 chemicals, crude oil (C4 to C40)
Total Rate: -4.2% per year (-3.2% to -5.2%)
Total Half-Life: 16.6 years (13.3 to 21.9)
Remaining Oil Mass (less than):
23% (25%, 26%, 27%) of initial mass (Prob > 0.50, 0.75, 0.95, 0.99)

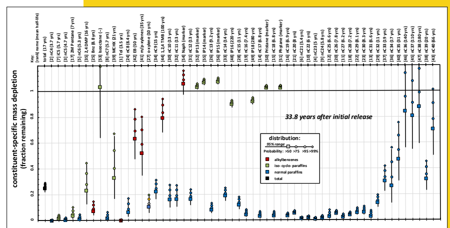


- Bulk oil depletion estimate (proportional to concentration in soil) for data from the Bemedji, MN release site. Data: Lundy, D. A., PhD thesis. University of Georgia, Athens, 2015.

Rate Estimates



Depletion Estimates



- Method for estimating total and constituent LNAPL depletion shown
- Similar and varied results
- Applied use options
  - Remediation and risk evaluation
    - Comparing natural & engineered removal rates
    - Chemical-specific risk evaluations
- This suggests a benefit to more consistently sample and analyze oil (over time) at petroleum release sites
  - This may be simpler and more direct than some other proposed and applied depletion assessment methods
- May also be applied for other environmental media
  - evaluation of attenuation relative to mixing / dilution
  - sediments, soil, water