An Evaluation of Natural Source Zone Depletion Versus Active Remediation Rates

IPEC 22 November 2015

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Drivers and Objective

- Measurement of natural source zone depletion (NSZD) rates (aka loss rates) of petroleum hydrocarbon LNAPL is an emerging science
 - To receive broader support, it is important to ground-truth the results
- To provide perspective, a survey consisting of 51 diverse sites/systems was performed to improve understanding of rates of remediation (in consistent units) for various petroleum remediation approaches
- This presentation will compare NSZD remediation rates to active remediation systems, and show that measurements of NSZD rates are comparable



Agenda

- Conceptualization of LNAPL in Subsurface
- Overview of NSZD
- Rates of NSZD as Measured by CO₂ Efflux
- Rates of Active Remediation
- NSZD vs Active Remediation Rates
- Conclusions

LNAPL Setting

• LNAPL exists in 4-phases



• Pore fluid profile often at <30% pore volume



LNAPL Quantification

- Integrating specific volume over an area provides an estimate of the volume of LNAPL in the subsurface
 - A 1-ft mobile LNAPL smear zone profile with specific volume of 0.05 ft³/ft² roughly equates to 16,000 gallons of LNAPL per acre (gal/ac)
- Removal of 5,000 gallons from this area, reduces the in situ LNAPL volume by 30%
 - Reduces in situ LNAPL pore fluid saturations in smear zone profile to a maximum equal to the residual LNAPL saturation
 - Non-recoverable, immobile fraction will remain in situ



Natural Source Zone Depletion - Petroleum



Natural Source Zone Depletion - Petroleum

- LNAPL is degraded by the intrinsic processes of volatilization, dissolution, and biodegradation
- Results in significant and measurable losses of source material





Carbon Dioxide (CO₂) Efflux Measurements

- Estimated NSZD (aka LNAPL loss) rates based on stoichiometric conversion of sitewide CO₂ efflux measurements
- 8 diverse sites (E-Flux CO₂ Traps 3 sites and LI-COR_® 8100A soil flux system – 6 sites)
 - Total of 86 CO₂ trap and 290 LI-COR® event-locations
- Site conditions included:
 - Natural gas well site
 - Operating gas plant and compressor station
 - Pipeline
 - Terminal
 - Railyard
 - Remote maintenance camp
- Urban and rural areas with predominantly pervious, but variable ground cover
- Consolidated and unconsolidated subsurface soil



E-Flux CO₂ Trap



LI-COR® 8100A Soil Flux System



Example Results from a NSZD Evaluation

- Collected CO₂ efflux measurements
- Corrected for background
- Performed stoichiometric conversion
- Plotted NSZD rates
- Integrated the results to estimate a sitewide NSZD rate
- Sites with multiple rounds of measurements were seasonally adjusted to estimate an annual rate



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Summary of NSZD Rates



 \cancel{N} <u>Note</u>: Recall a site with LNAPL specific volume of 0.05 ft³/ft² contains 16,000 gals/ac.



Summary of NSZD Rates

• Recall: 1-ft mobile LNAPL smear zone profile with specific volume of 0.05 ft³/ft² roughly equates to 16,000 gallons of LNAPL per acre (gal/ac)



• Removal of 700 gallons per acre equates to less than an inch removal, with the same assumptions



Assessment of Comparable Rates of Remediation

- Surveyed projects to compile real site monitoring data
- 43 systems

LNAPL Skimming	6
Groundwater drawdown-enhanced Skimming	5
Bioventing/Biosparging	4
Soil Vapor Extraction	5
Air Sparging/Soil Vapor Extraction	10
Multiphase Extraction	13
Total Number of Active Systems in Survey =	43

- Sites in survey include a variety of:
 - petroleum products
 - source zone dimensions
 - remedial design bases
 - operation and maintenance routines (i.e., zones, pulsing, etc.)

	Median	Range
Treatment Area Size (acres)	2.0	0.1 - 108
Total Volume Removed (gallons)	4,500	18 - 6,000,000
Mass Removal Rate (pounds/year)	7,339	4 - 5,000,000
Years of Operation (years)	5.0	0.6 - 24
Remediation Rates (gallons/acre/year)	1,057	0.1 - 11,790



Active Remediation Rate Survey Results



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 Survey indicates that NSZD rates fall within the range of other remedial approaches

Evaluation of Early and Late Stage Rates NSZD Median = 700 10,000 ☆ Remediation Rate (gal/ac/yr) gal/ac/yr 1,000 100 10 1 Air Sparging Soil Vapor Extraction GN-drandown LNAPL Skinning Soil Vapor Extraction SVE Multiphase Extraction (MPE) LNAPL Skinning BioventingBiospatging

Early Stage Median Median Late Stage Median

Midway into remediation, NSZD may become stronger than some remedies

<u>Note</u>: 10 of the 13 MPE systems had no difference in early and late remediation rates, thus were excluded from this early/late data sets



Approximate Efflux Monitoring Costs

- LI-COR soil flux system
 - Rental ~\$1,700/month for the first month and ~\$900/month for subsequent months
 - 20 beveled 8" PVC collars ~\$300
 - Mobilization, 8 hrs onsite/visit, 2 field technicians install collars and perform four rounds of daily measurements
 - ~\$500/location
- E-Flux CO₂ traps
 - Field components (~\$320/location)
 - CO_2 and ¹⁴C analysis of traps ~\$1,700/location
 - Two site visits, start and end of 2 week deployment period (install and retrieve/ship traps, 4 hrs onsite, 1 field technician)
 - ~\$2,000/location



Conclusions

- In general NSZD rates measured using CO₂ efflux methods are reasonable
 - They fall within the spectrum of the surveyed remedial systems (~200-4,000 gal/ac/yr)
 - Are consistent with plausible rates of remediation for sites with >10,000 gal/ac present in the subsurface
- NSZD rates are significant and are competitive with remediation rates of some active systems
- There appears to be a point during remediation when the effectiveness of active remediation may fall below NSZD
 - The NSZD rate is a useful metric for optimization of active remediation



Thank You

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