

A Comparison of Natural Source Zone Depletion and Active Remediation Rates

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Innovation that Provides Sustainable Solutions to Complex Local Challenges, Worldwide

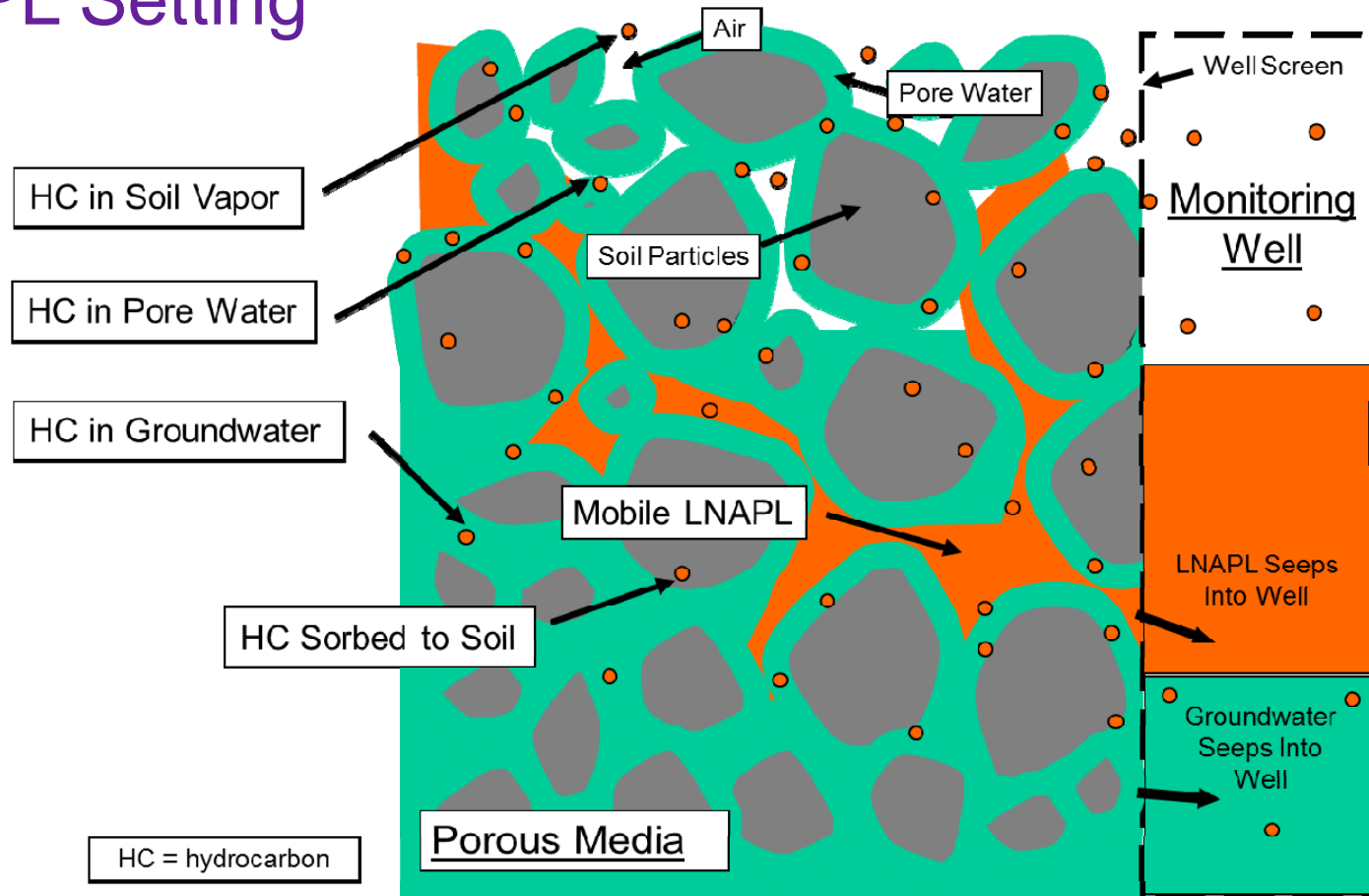
Drivers and Objective

- 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 ~55 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 other approaches, and show that measurements performed to date are within a valid spectrum

Agenda

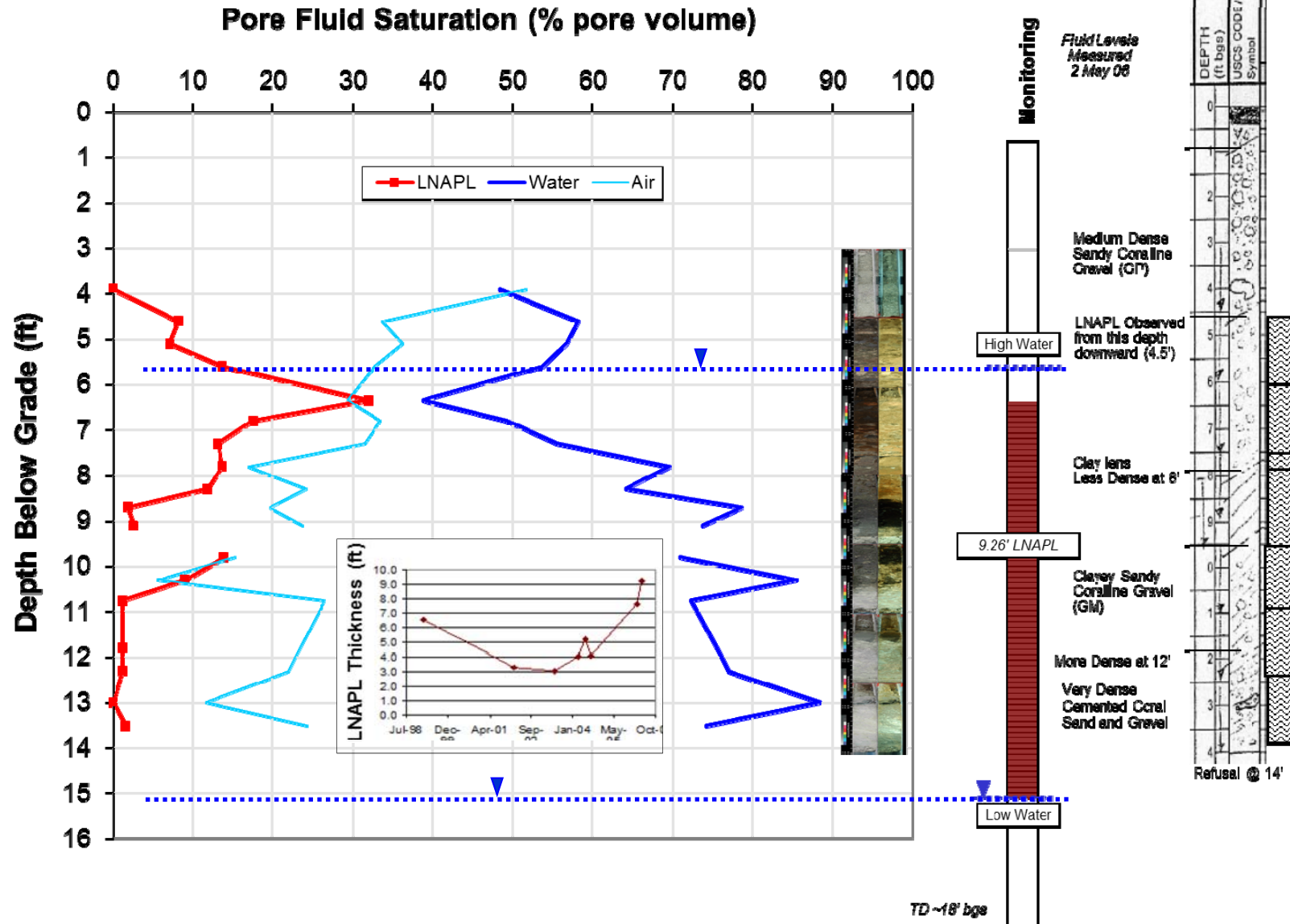
- Conceptualization of LNAPL in Subsurface
- Overview of NSZD
- Rates of NSZD as Measured by CO₂ Efflux
- Comparable Rates of Active Remediation
- Conclusions

LNAPL Setting



- LNAPL exists within a 4-phase variably saturated pore fluid profile often at <30% pore volume

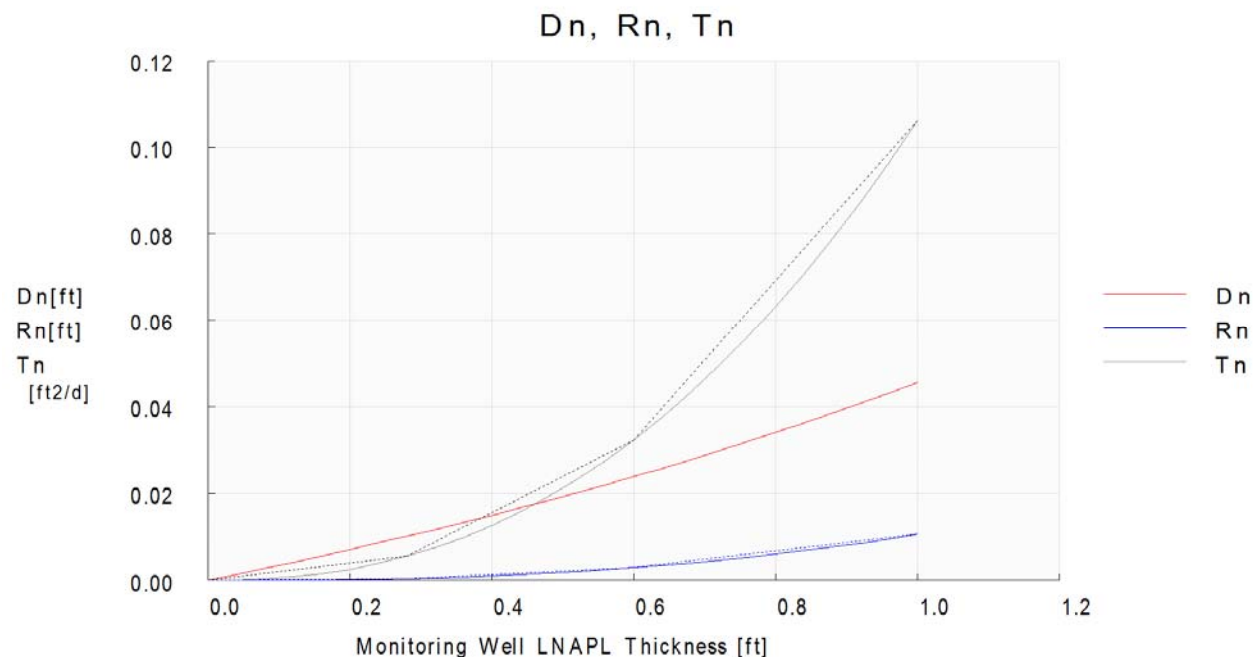
Example LNAPL Smear Zone Profile



LNAPL Quantification



- Specific volume is a useful measure of the quantity of LNAPL in a unit volume of soil (m^3/m^2 or L/m^2), or (ft^3/ft^2 or gal/ft^2 for our American friends)
- LDRM output for a well-graded fine to coarse sand with gravel

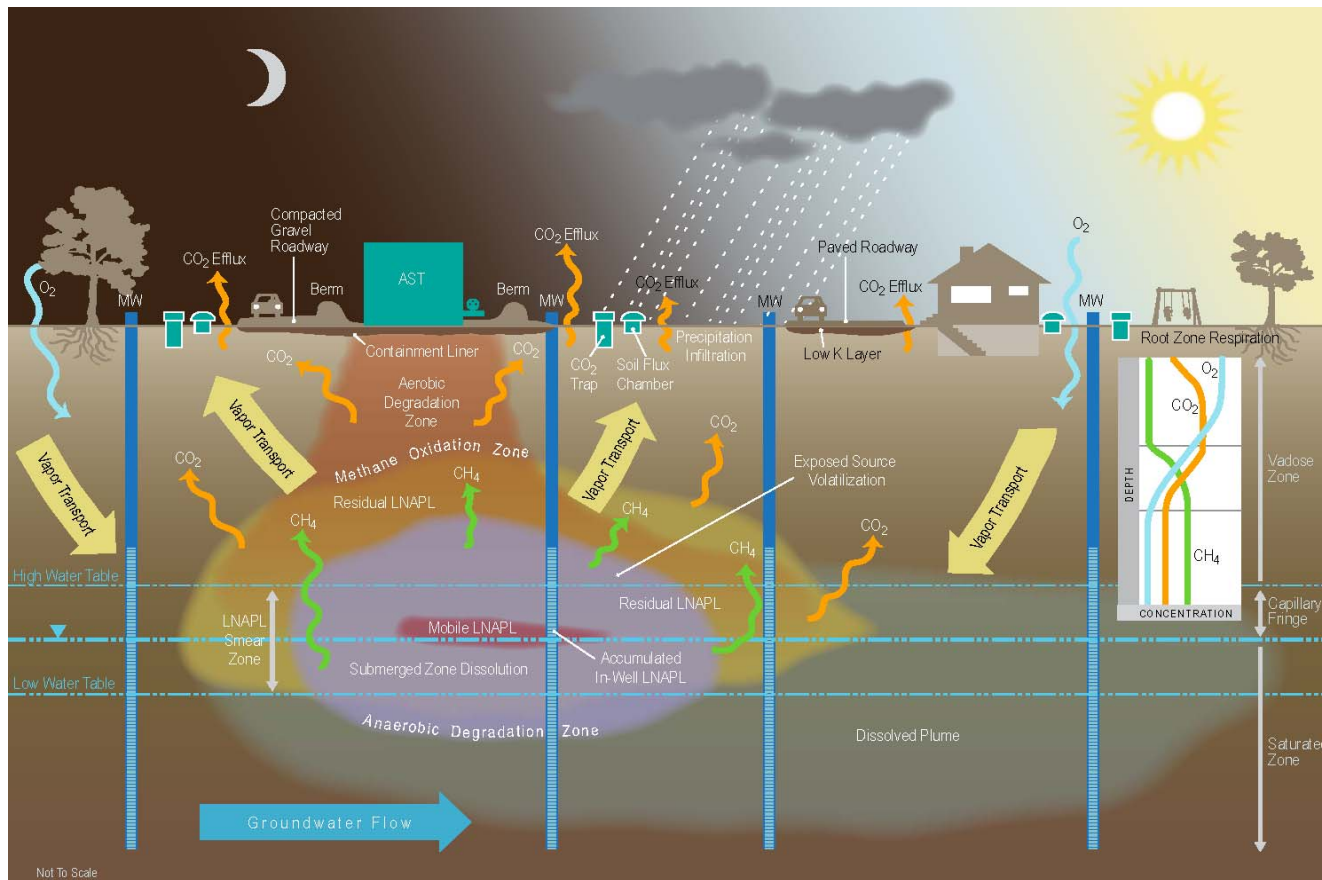


LNAPL Quantification (continued)

- A plot and geospatial integration of specific volume allows an estimate of the volume of LNAPL in the subsurface
 - A 30 cm mobile LNAPL smear zone profile with specific volume (D_n) of $0.05\text{ft}^3/\text{ft}^2$ ($T_n \sim 0.1\text{ft}^2/\text{d}$) roughly equates to 16,000 gal (equal to 149,545 L/ha) of LNAPL per acre (gal/ac)
- Removal of 5,000 gallons (18,927 L) 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

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



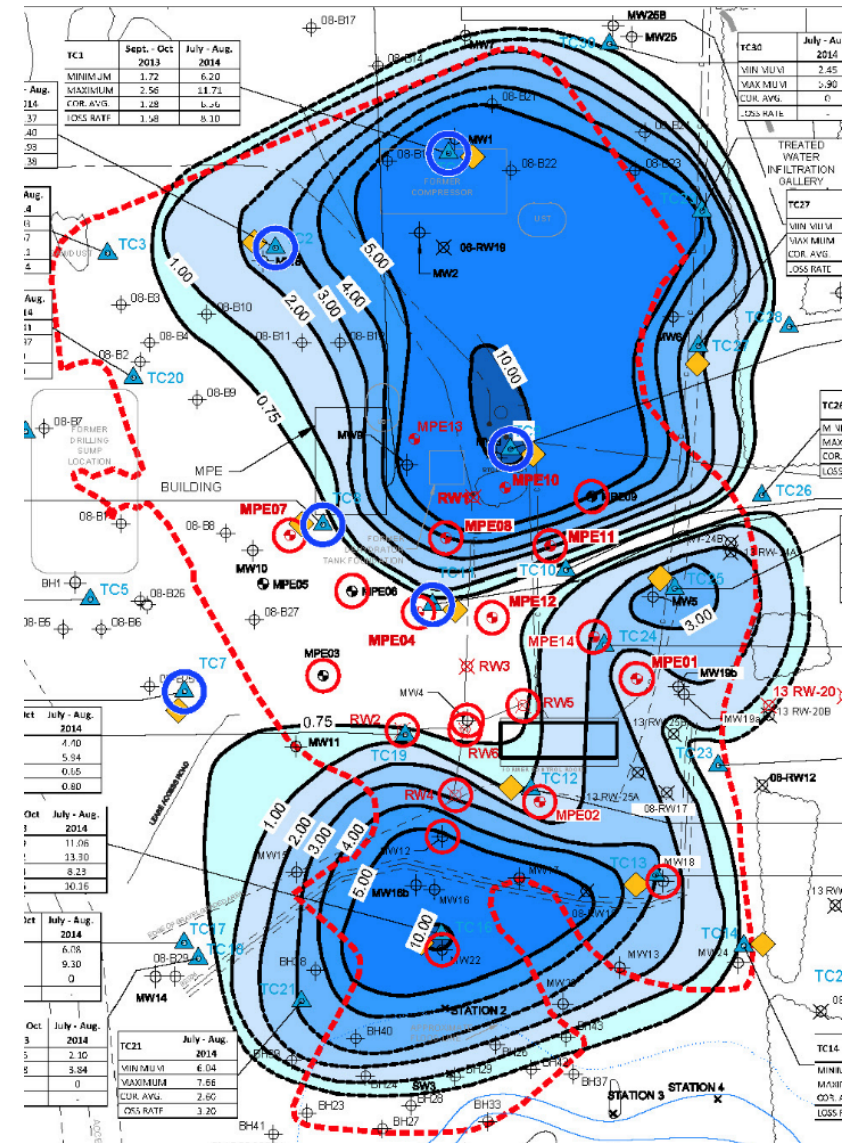
Carbon Dioxide (CO₂) Efflux Measurements

★ Note: Only sites with site-wide CO₂ efflux surveys were considered.

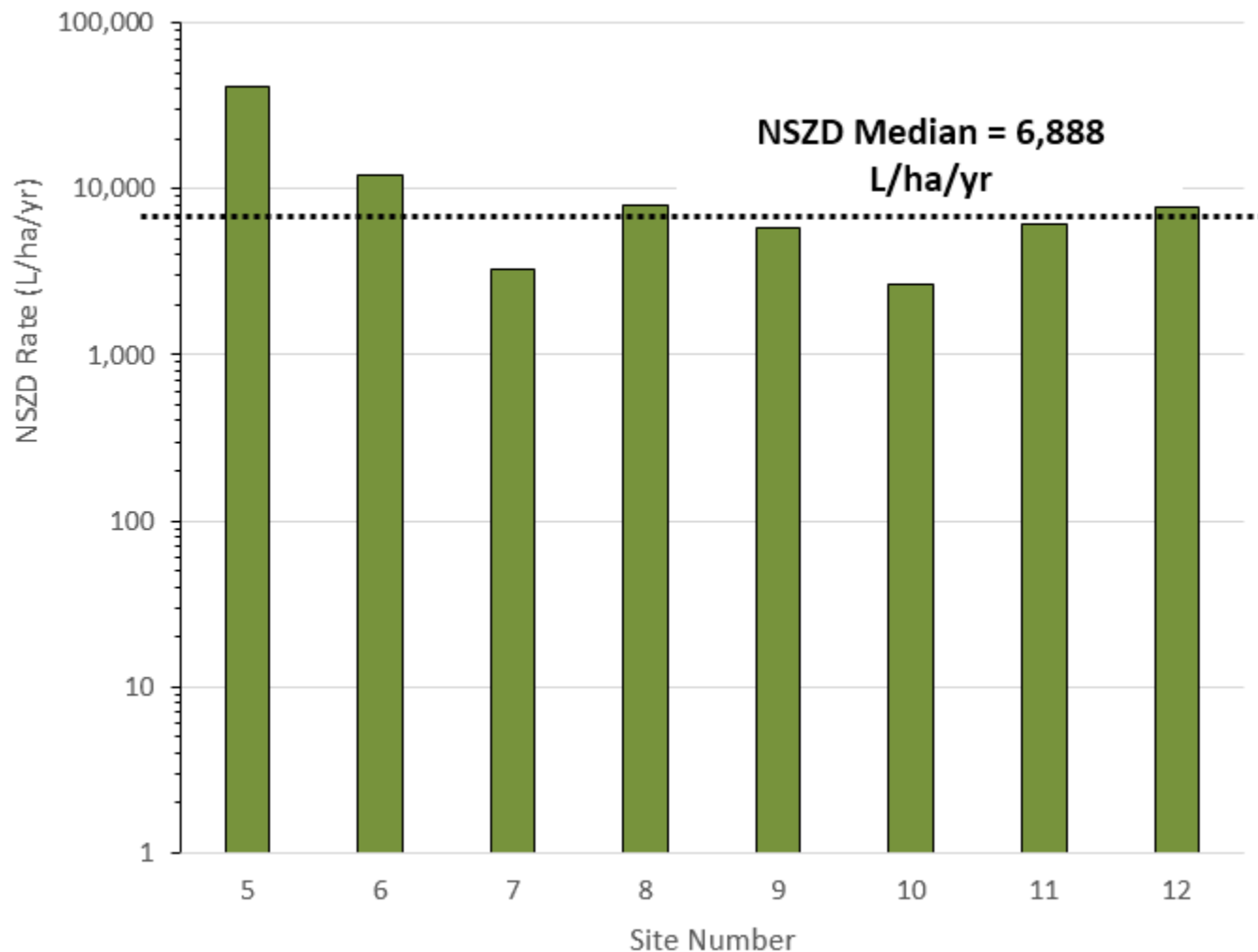
- Estimated NSZD (aka LNAPL loss) rates based on stoichiometric conversion of sitewide CO₂ efflux measurements
- 8 diverse sites including 3 sites by E-Flux CO₂ Traps and 6 by LI-COR® 8100A soil flux system
 - Total of 86 CO₂ trap and 290 LI-COR® event-locations
- Site conditions included:
 - Natural 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

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



Summary of NSZD Rates



★ Note: Recall a site with LNAPL specific volume of $0.05 \text{ ft}^3/\text{ft}^2$ contains 16,000 gals/ac.

Assessment of Comparable Rates of Remediation

- Surveyed projects to compile real site monitoring data

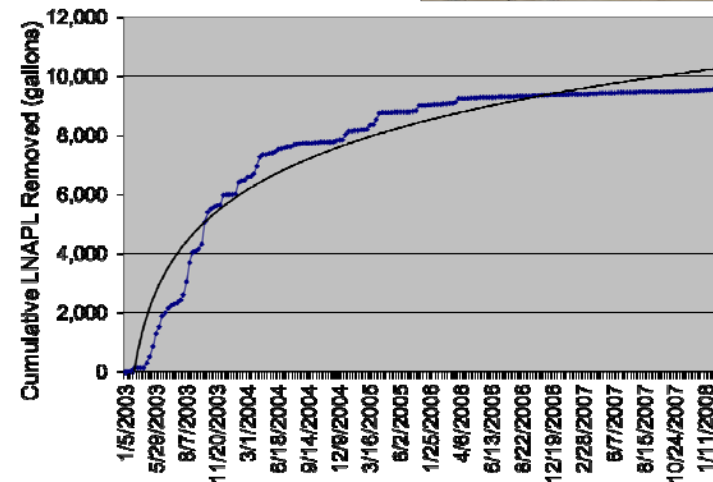
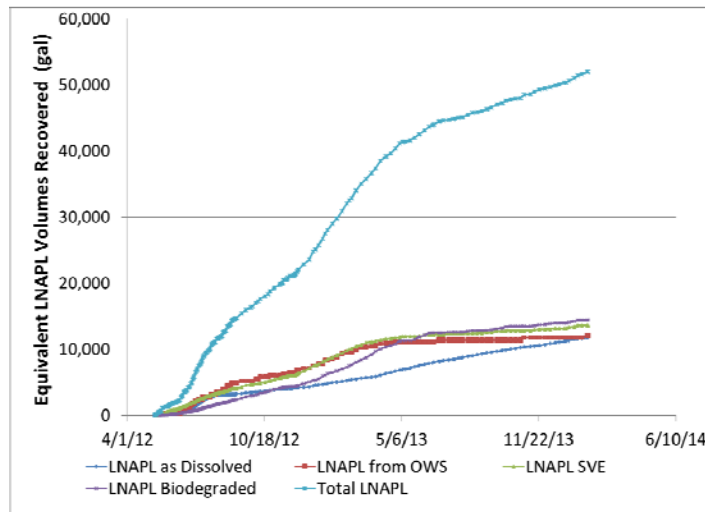
- 43 systems

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 broad range of:
 - petroleum products
 - source zone dimensions
 - remedial design bases
 - operation and maintenance routines (i.e., zones, pulsing, etc.)

Remedial System Summary

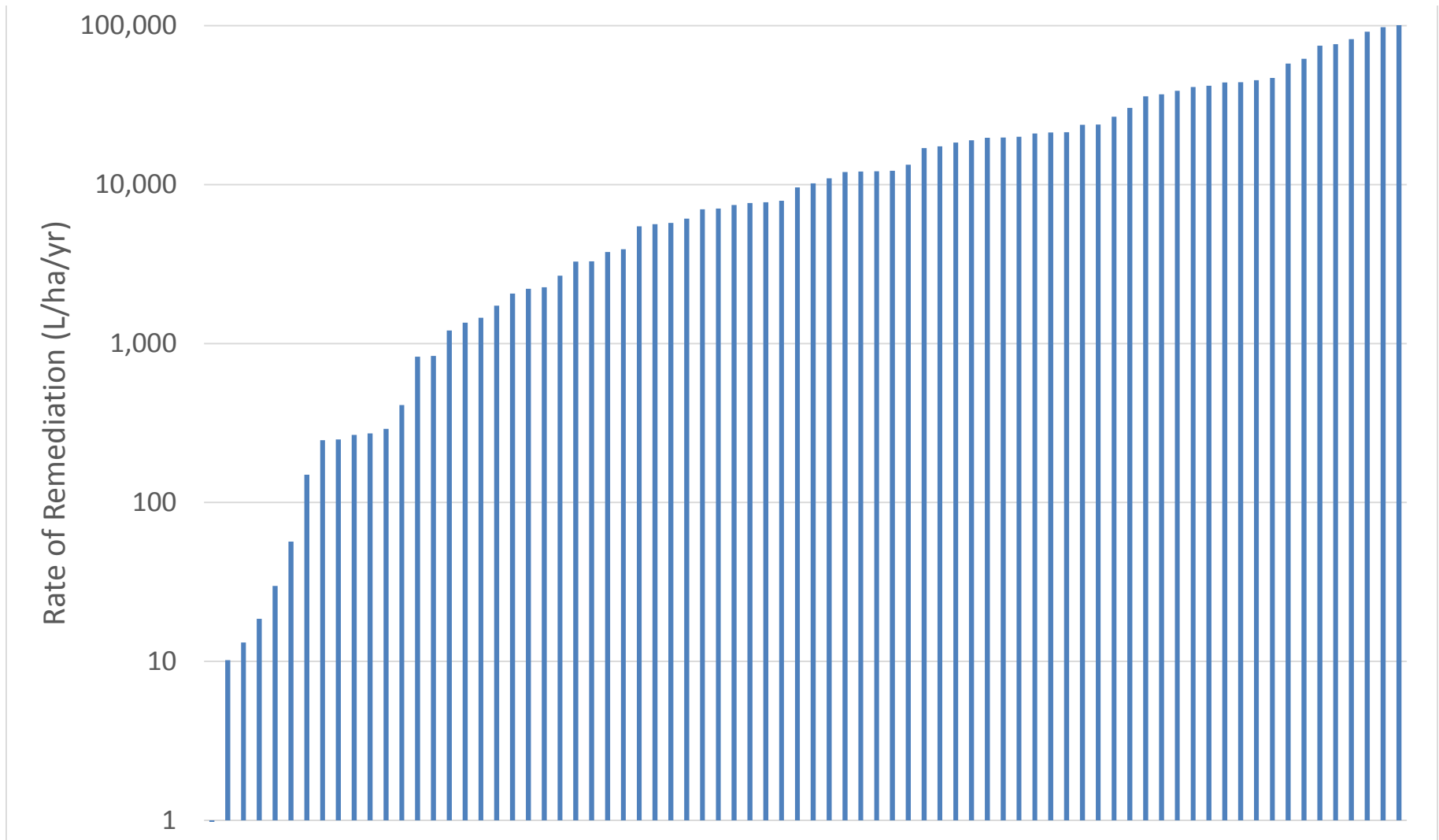
- Required detailed mass removal tracking



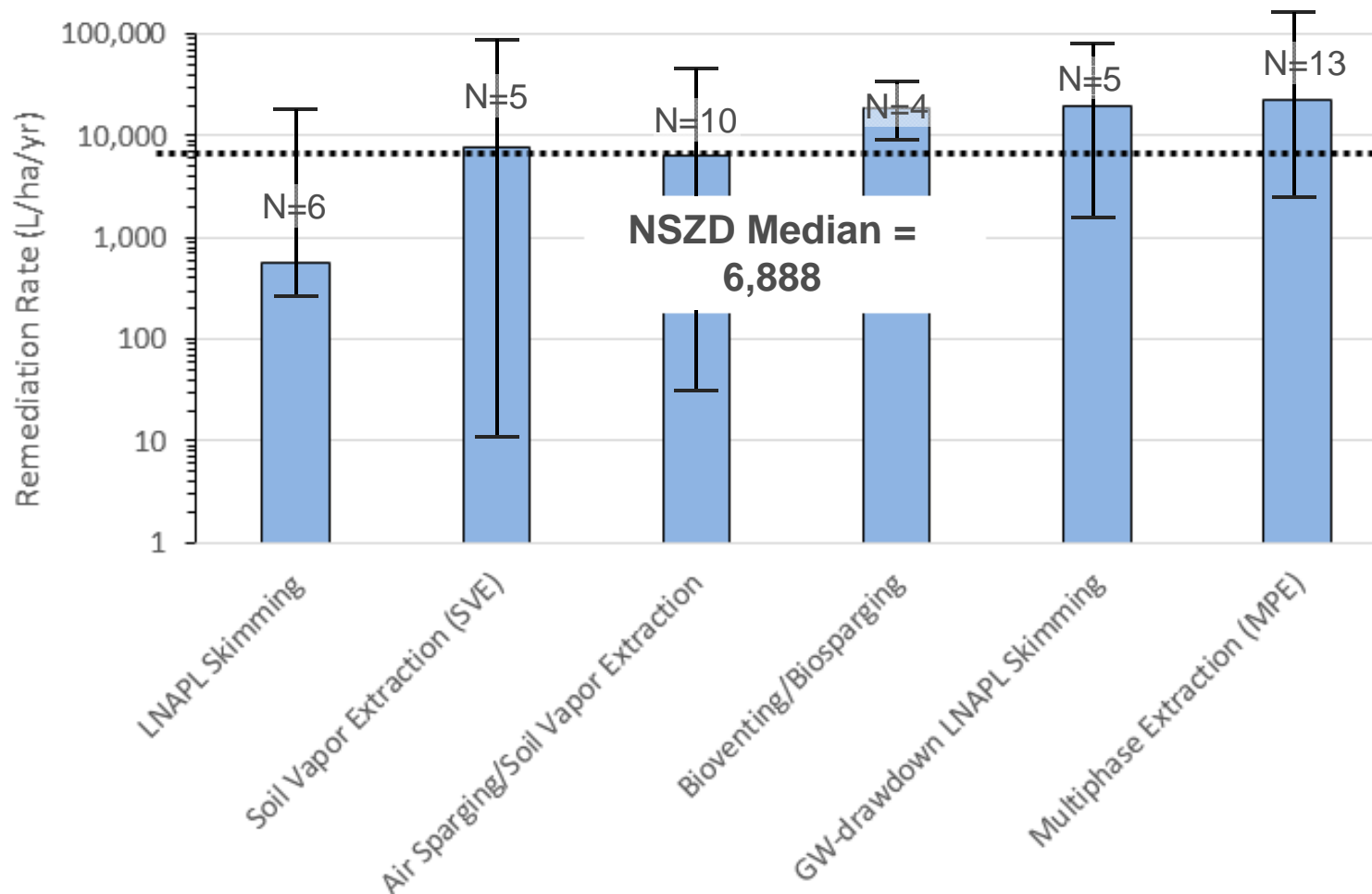
	<u>Median</u>	<u>Range</u>
Range in Treatment Area Size (acres)	1.7	0.1 - 108
Range in Total Volume Removed (gallons)	3,125	18 - 6,000,000
Range in Mass Removal Rate (pounds/year)	7,137	4 - 5,000,000
Range in Years of Operation (years)	5.0	0.6 - 24
Range in Remediation Rates (gallons/acre/year)	936	0.1 - 11,790

★ Note: Survey included only petroleum LNAPL remediation sites.

Active Remediation Rate Survey Results

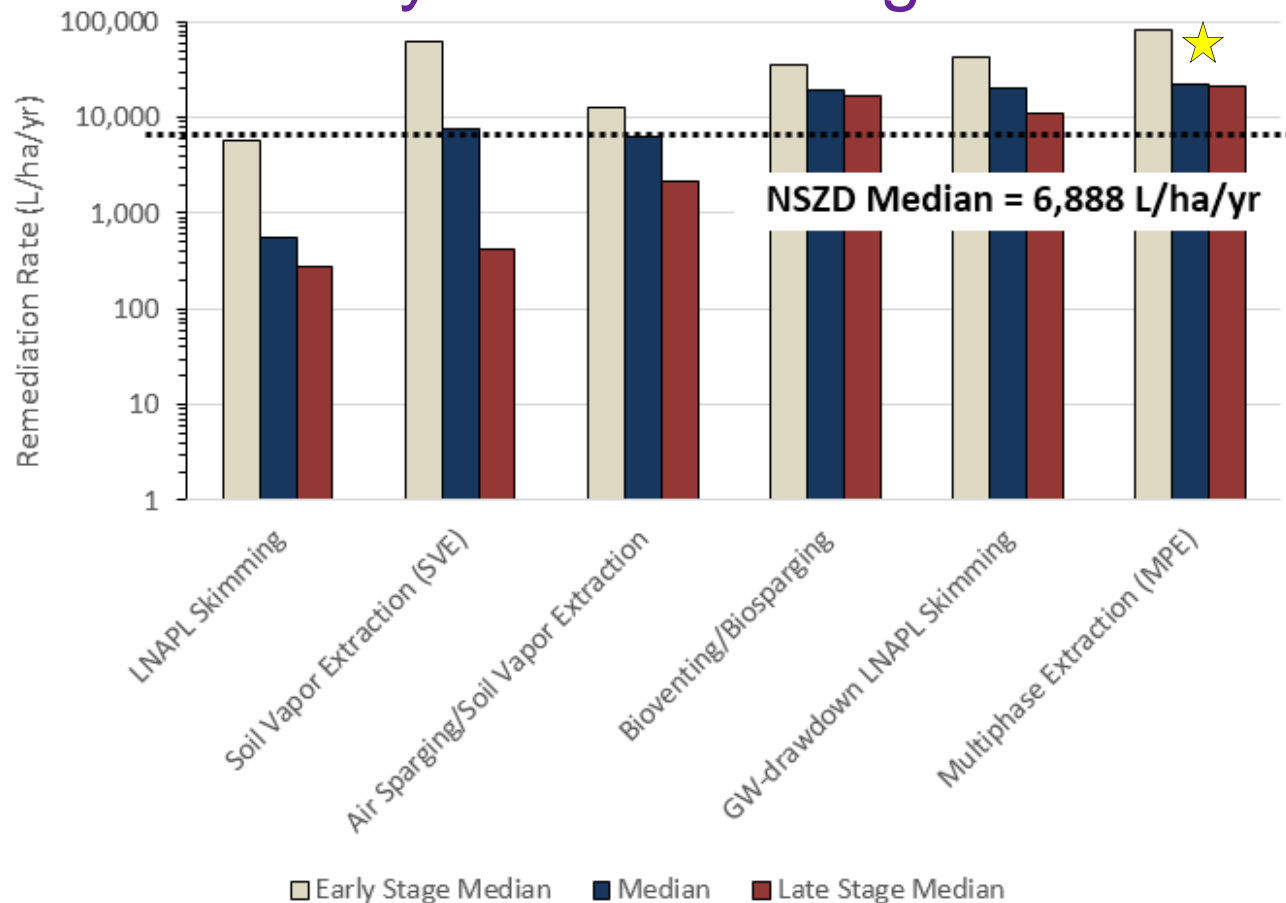


Comparison of Median Rates of Remediation



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

Evaluation of Early and Late Stage Rates



- Midway into remediation, NSZD may become stronger than some remedies



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

Conclusions

- In general, within this survey scope, the NSZD rates measured using CO₂ efflux methods are reasonable
 - They fall within the spectrum of the surveyed remedial systems roughly from 100-2,000 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
- Of interest is an inflection 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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