# **Quantifying Natural Source Zone Depletion Rates for Confined LNAPL**

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#### Background

#### **NSZD** Introduction

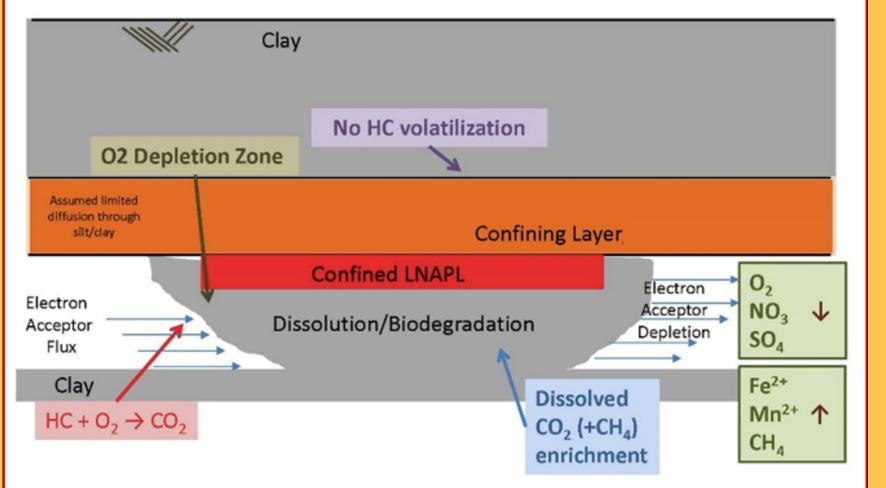
- NSZD measurements quantify naturally occurring degradation rates of LNAPL in the subsurface
- Established methods available for unconfined LNAPL, depending on site conditions
- Quantifying NSZD rates for confined LNAPL is not well established and requires use of multiple methods

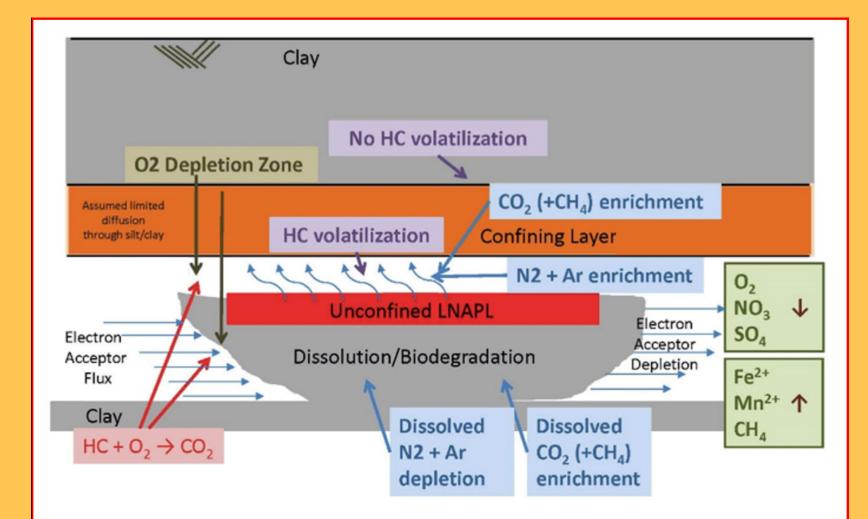
#### Benefits of NSZD



- LNAPL NSZD satisfies source reduction and "MEP" as the only process that removes remaining NAPL
- Monitored NSZD is a transition remedy; at the end of hydraulic recovery
- By quantifying the NSZD process and monitoring the NSZD occurrence, MEP and/or specific regulatory requirements can be achieved, and the site can be closed

### NSZD under Unconfined and Confined Conditions





LNAPL NSZD processes in a confined condition.

LNAPL NSZD processes in unconfined condition.

- Saturated clay layer impedes upward gas transport migration under confined condition
- Hydrocarbon volatilization occurring in zone above LNAPL body in unconfined condition

## Contact Information

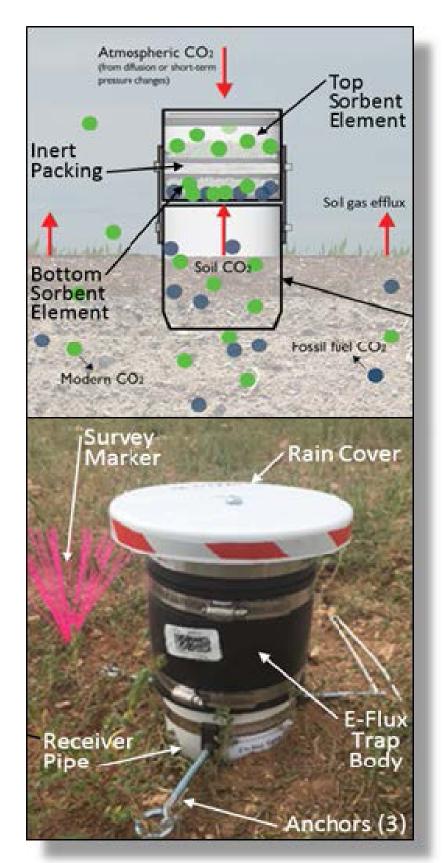
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#### Methods

#### Confined Conditions NSZD Testing Methods

- Thermal profiles within existing monitoring wells
- Dissolved gas samples in groundwater
- Quantify NSZD by trending changes over time or distance
- Geochemical parameters in groundwater
- Electron acceptors
- Anaerobic reduction parameters
- CO<sub>2</sub> flux

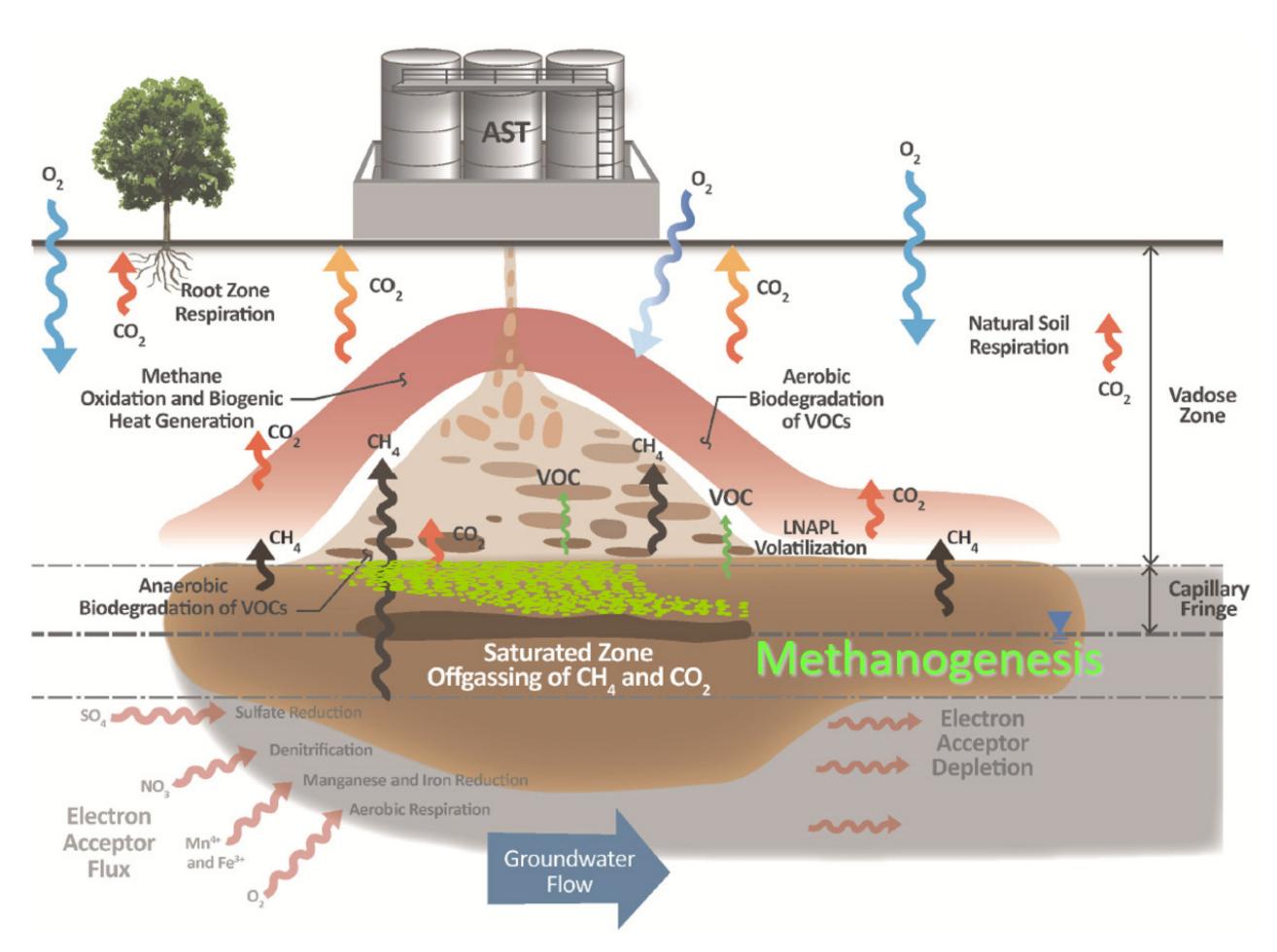
#### NSZD Vadose Zone Estimation Methods



American Petroleum Institute (API) 2017. Quantification of Vapor Phase-Related NSZD Processes.



### How do Methods Fit Together



American Petroleum Institute (API), 2017. Quantification of Vapor Phase-Related NSZD Processes.

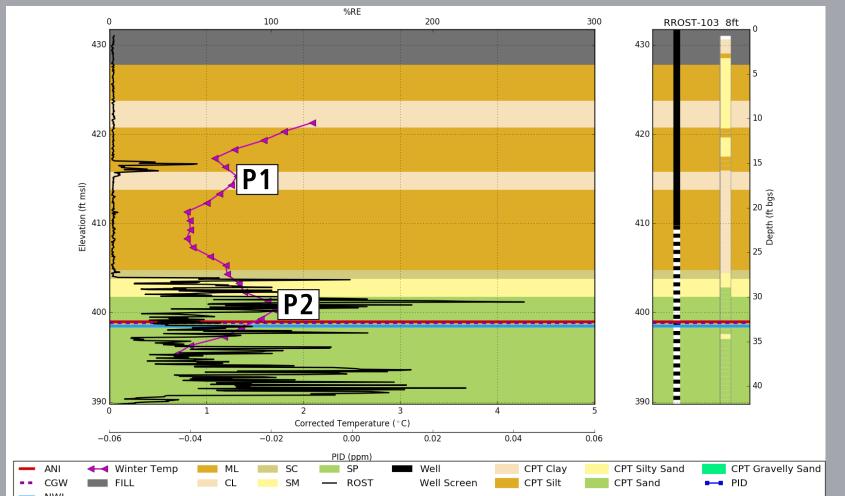
#### Site Background

- Former petroleum facility located in the Midwest
- LNAPL body is not generally hydraulically recoverable
- Using NSZD rates to meet specific regulatory requirements
- Two water saturated units:
- "Shallow interval"
- "Deeper interval"

#### Results

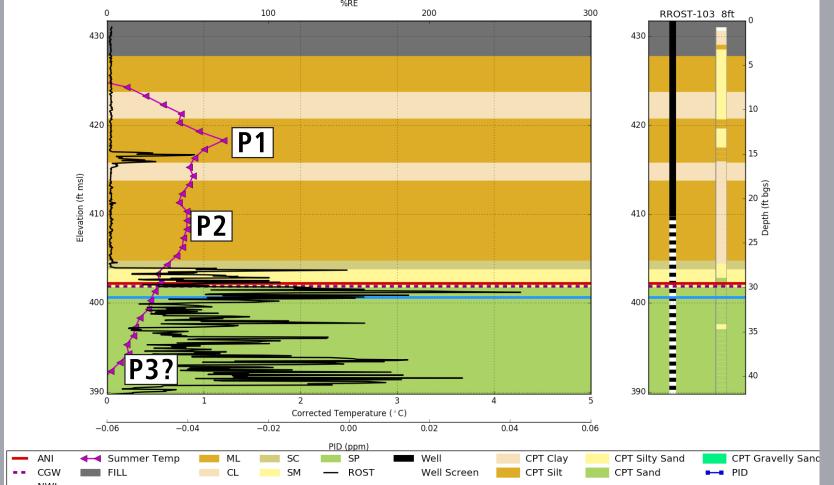
### Confined vs. Unconfined Conditions at Well A

Winter



- Groundwater is unconfined
- Peak in shallow interval (P1)
- Peak in sand above water table (P2)

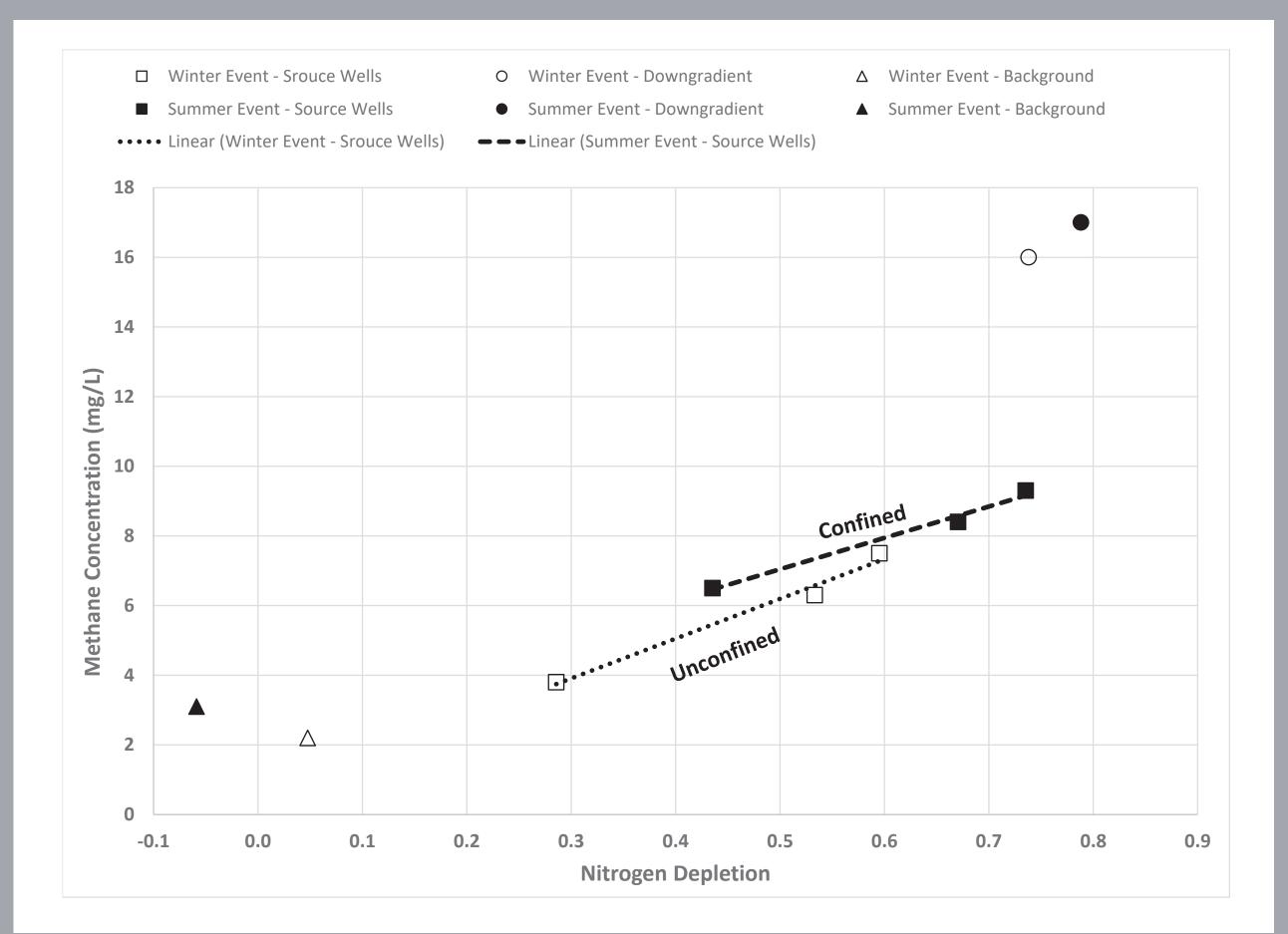
Summer



- Groundwater is confined
- Peak in shallow interval (P1)
- Peak above clay (P2)
- Peak in deeper interval (P3)

Multiple biodegradation zones and confined conditions = multiple thermal response zones

#### Nitrogen-Methane Behavior



- Less methane enrichment and less nitrogen depletion under unconfined compared to confined conditions
- Downgradient anomalies related to transport of methane



# Group 2

### Geochemical, Dissolved Gas, and CO<sub>2</sub> Trap Results

#### **GEOCHEMICAL PARAMETERS**

• Results consistent with ongoing methanogenesis and/or sulfate reduction.

#### **DISSOLVED GAS**

- Nitrogen depletion and methane enrichment identified
- LNAPL samples showed poor correlation with groundwater samples

#### CO<sub>2</sub> TRAP

- Carbon traps are measuring shallow NSZD only (shallow interval)
- Under estimates NSZD compared to temperature profile if we only use vadose zone results

### Results at Well A

Zone	Winter Event (unconfined)		Summer Event (confined)		
	Thermal	Dissolved Gas	Thermal	Dissolved Gas	Carbon Trap
P1	700		700		100
P2	1,000		500		
P3		500	1,200	1,100	
Total	1,700	500	2,400	1,100	

Rates are in gal/acre/year

#### Conclusions

- CO2 traps not recommended for confined conditions.
- Temperature profile method was not reliable in estimating NSZD under confined conditions in the deep interval.
- Temperature profile method demonstrated the occurrence of NSZD in shallow interval.
- Dissolved gas method can be used to estimate NSZD rates under confined and unconfined conditions.
- Seasonal variation affects estimated NSZD rates.