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Estimating natural attenuation rates at hydrocarbon contaminated sites using closed and open flux chambers

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Bioremediation techniques: a challenge for slightly contaminated soil and mine tailings
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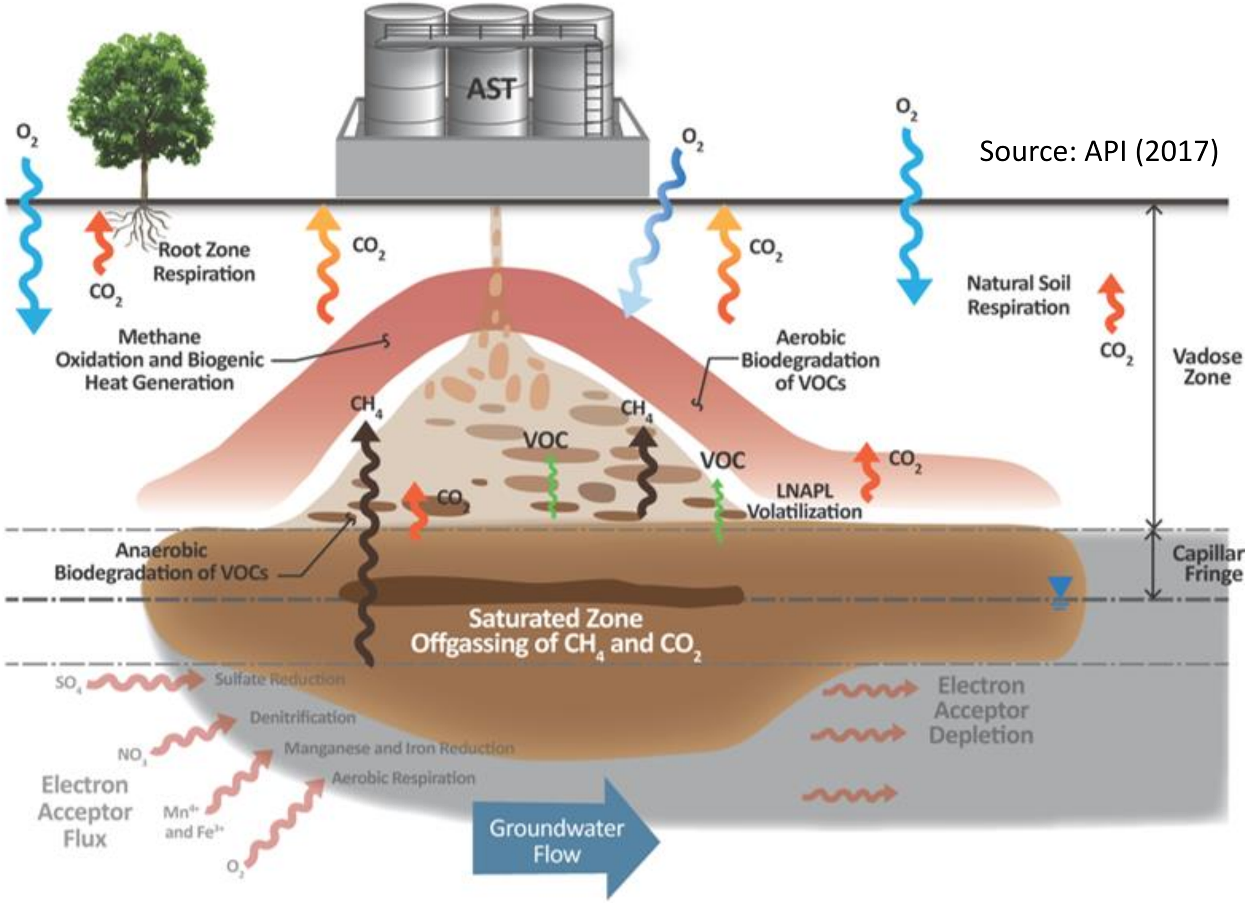
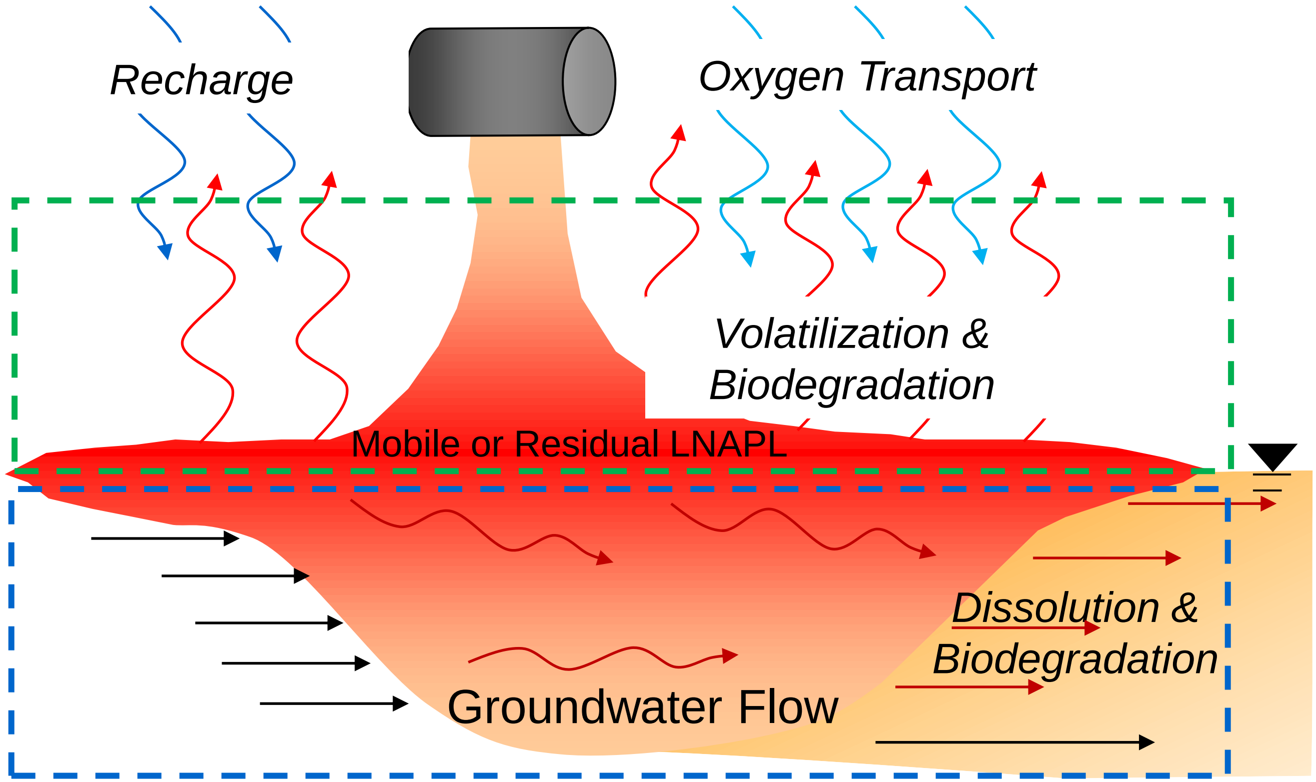
Natural attenuation of petroleum hydrocarbons



Source: API (2017)

Petroleum hydrocarbons in the subsurface are subjected to a series of natural attenuation phenomena that lead to a substantial reduction in the mass of contaminants over time

Natural source zone depletion (NSZD)



Source: Modified from ITRC (2009)

Two primary natural LNAPL mass loss processes:

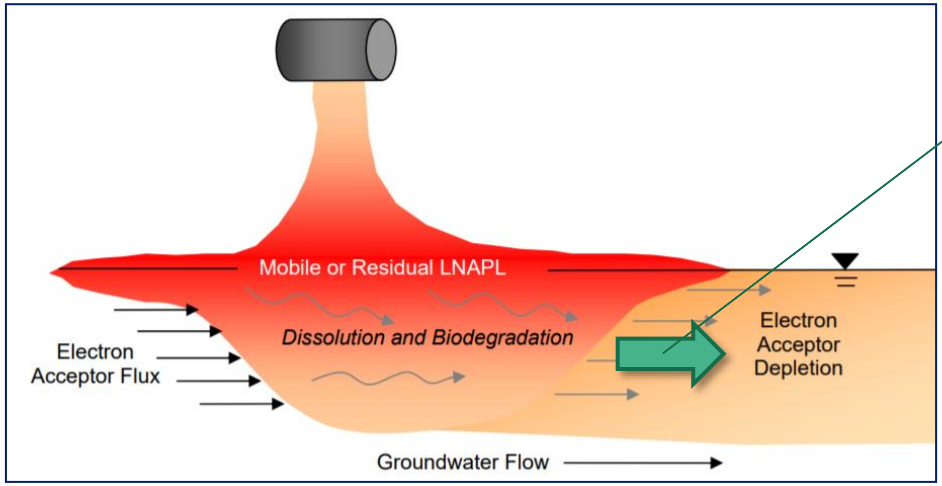
- **Volatilization pathway:**
  Methanogenis and volatilization

- **Groundwater pathway:**
  Dissolution and biodegradation

Monitored Natural Attenuation (MNA)

Natural source zone depletion (NSZD)

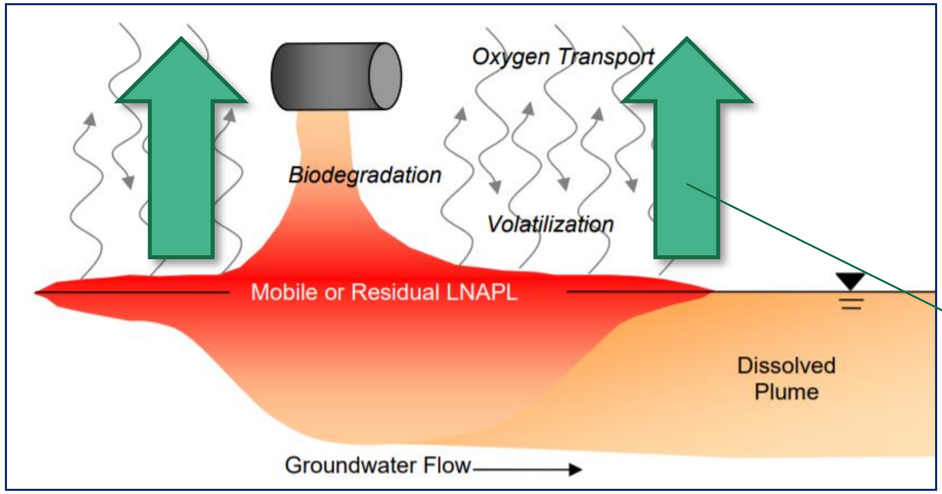
NSZD: Aqueous vs Volatilization expression



1-10%

NSZD due to dissolution in groundwater

The volatilization pathway contributes to 90-99% of the overall source depletion (ITRC, 2018)



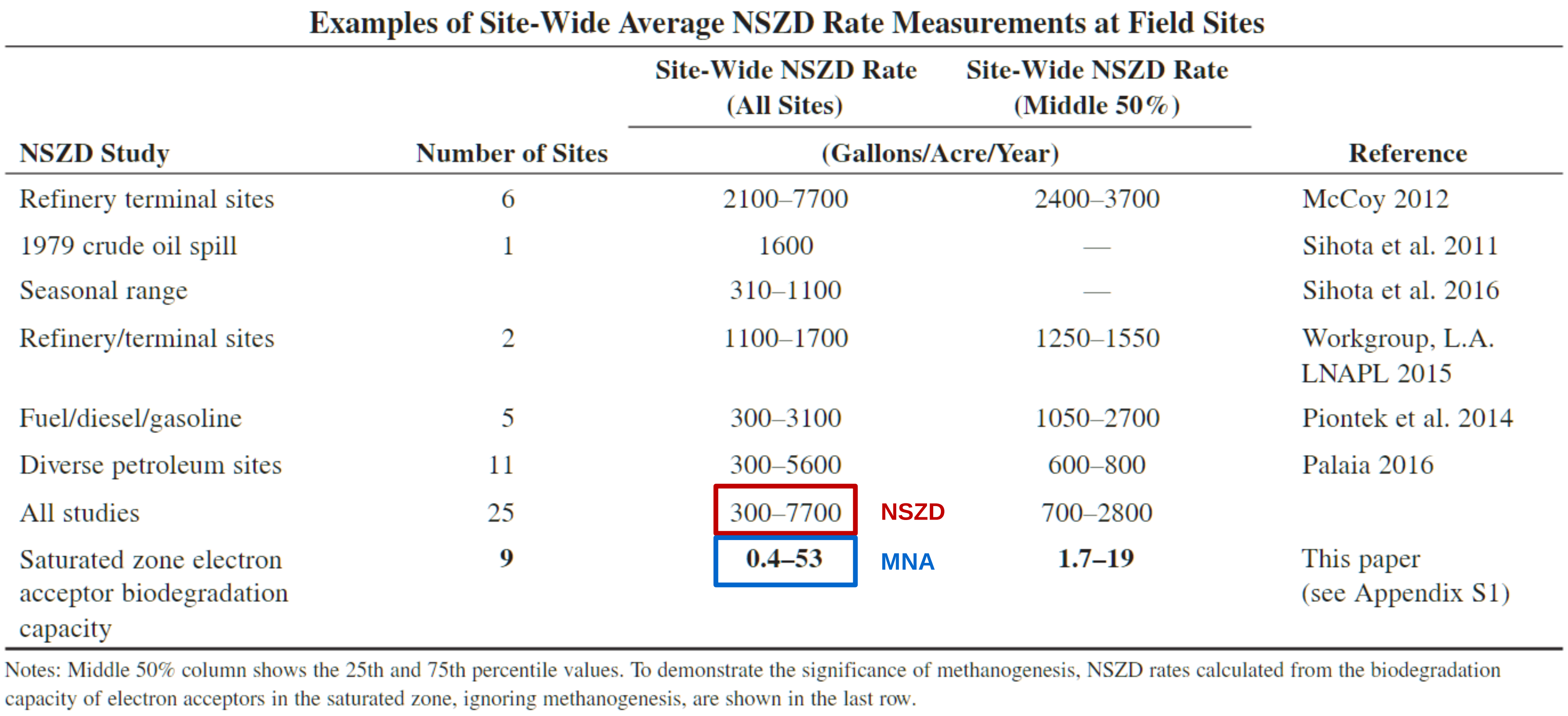
Source: Modified from ITRC (2009)

90-99%

NSZD due to NAPL degradation and volatilization

Examples of NSZD rates

Source: Garg et al. (2017)



Examples of Site-Wide Average NSZD Rate Measurements at Field Sites

		Site-Wide NSZD Rate (All Sites)	Site-Wide NSZD Rate (Middle 50%)	
NSZD Study	Number of Sites	(Gallons/Acre/Year)		Reference
Refinery terminal sites	6	2100–7700	2400–3700	McCoy 2012
1979 crude oil spill	1	1600	—	Sihota et al. 2011
Seasonal range		310–1100	—	Sihota et al. 2016
Refinery/terminal sites	2	1100–1700	1250–1550	Workgroup, L.A. LNAPL 2015
Fuel/diesel/gasoline	5	300–3100	1050–2700	Piontek et al. 2014
Diverse petroleum sites	11	300–5600	600–800	Palaia 2016
All studies	25	300–7700	700–2800	
Saturated zone electron acceptor biodegradation capacity	**9**	**0.4–53**	**1.7–19**	This paper (see Appendix S1)

NSZD

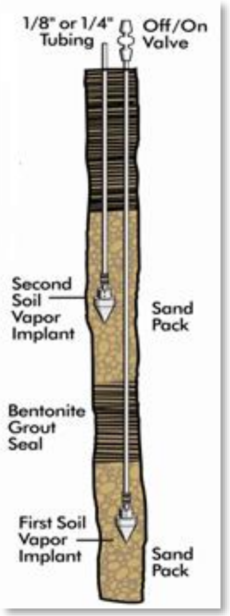
MNA

Notes: Middle 50% column shows the 25th and 75th percentile values. To demonstrate the significance of methanogenesis, NSZD rates calculated from the biodegradation capacity of electron acceptors in the saturated zone, ignoring methanogenesis, are shown in the last row.

NSZD rates in the order of 0.5-5 kg/m^2/year!

Main quantification methods for NSZD

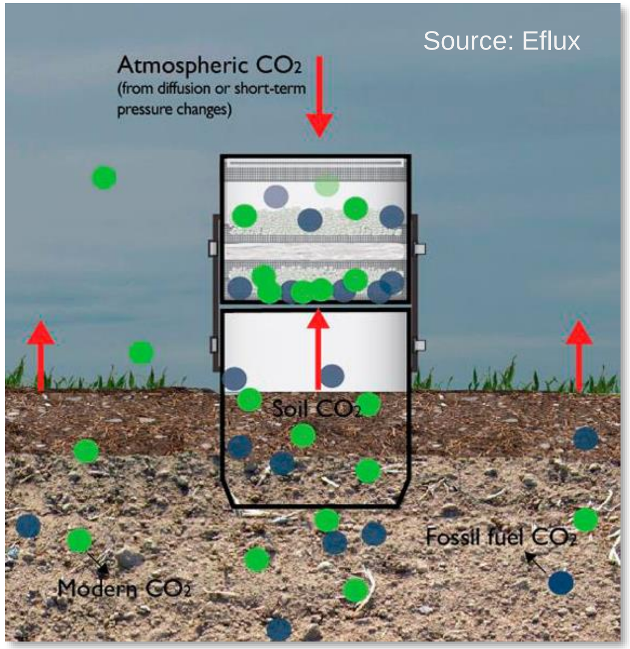
Soil gas sampling (Gradient method)



Source: H&P Mobile Geochemistry

NSZD rates from flux estimated from O_2 and CO_2 vertical profiles

CO_2 surface efflux (passive traps)


Source: Eflux

NSZD rates from measured CO_2 fluxes

CO_2 surface efflux (flux chambers)

NSZD rates from measured CO_2 fluxes

Focus of this presentation

Flux chambers types

Dynamic Closed Chambers (DCC)

In the closed chamber the concentration increase in the chamber (dC/dt) is continuously measured with a gas analyzer (e.g. PID or IR).

The flux of CO_2 or total VOCs is calculated as:

$J = (dC / t) \cdot H_{flux}$

- Fast measure (5-10 minutes)
- Economic (no lab costs)
- No VOC speciation

Open Flux Chambers (OFC)

In the open chamber an inert gas (N_2) is fluxed into the chamber to establish a steady state condition. The air of the chamber is then sampled (e.g. with a canister) and analyzed.

The flux of each VOC is estimated as:

$J = C_{flux} \cdot Q_{in} / A_{flux}$

- VOC speciation
- Sampling time (4-8 hours)
- Lab costs (e.g. canister)

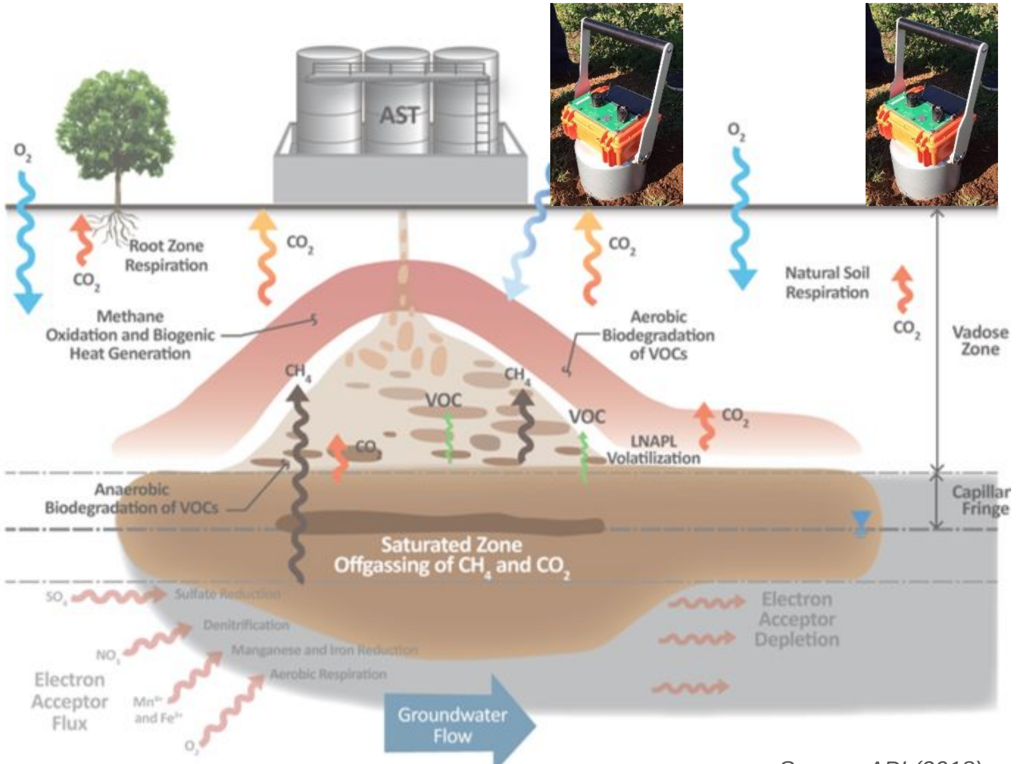
The flux chambers are inverted containers placed into the surface and in which the vapors emitted from the subsurface are accumulated over time.

Estimation of natural source zone attenuation using DCC data

DCC can be used to estimate the CO_2 efflux. CO_2 efflux measurements corrected for the background (soil natural respiration) can then be used to estimate a natural source attenuation rate

DCC above the source (J_{CO2})

DCC Blank sample ($J_{CO2,background}$)



Source: API (2018)

Natural attenuation rates

$$NSZD = \left(J_{CO_2} - J_{CO_2,background} \right) \cdot \gamma$$

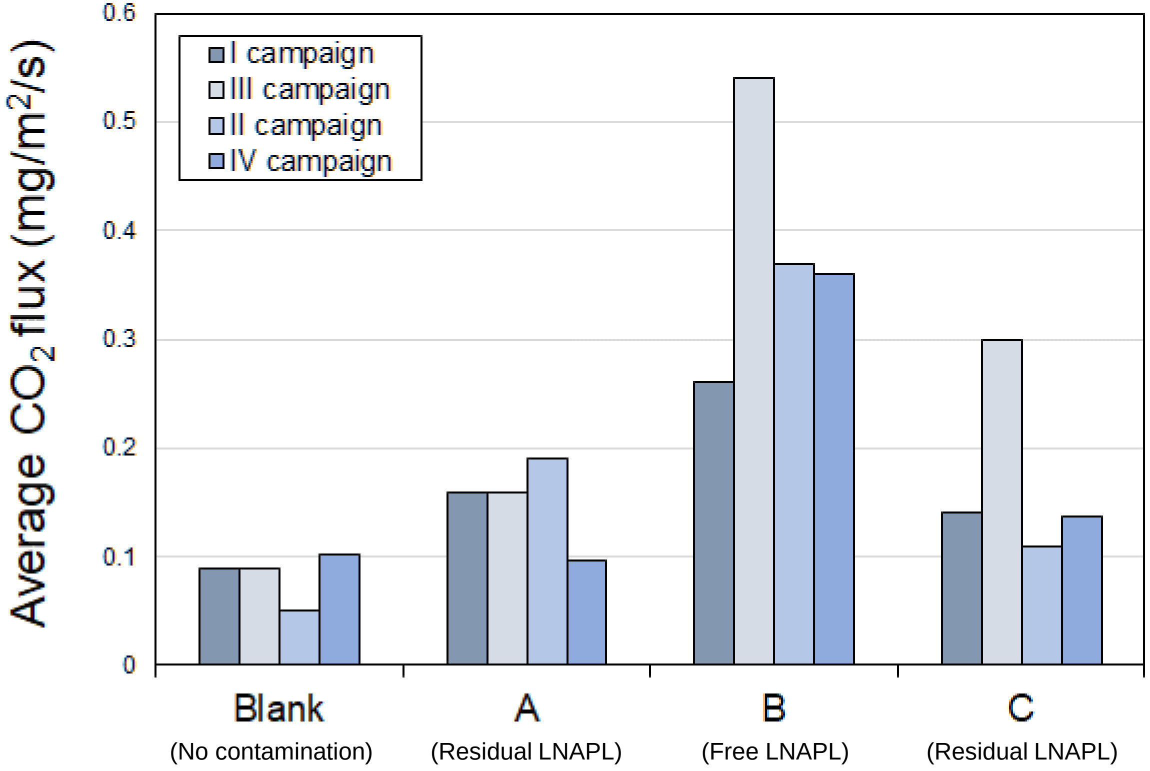
Representative mineralization reaction

$$C_{14}H_{30} + \frac{43}{2} O_2 \rightarrow 15 H_2O + 14 CO_2$$

Stoichiometric coefficient

$$\gamma = \frac{MW_{C_{14}H30}}{14 \cdot MW_{CO_2}} = \frac{198}{14 \cdot 44} = 0.32 \; \frac{g_{TPH}}{g_{CO_2}}$$

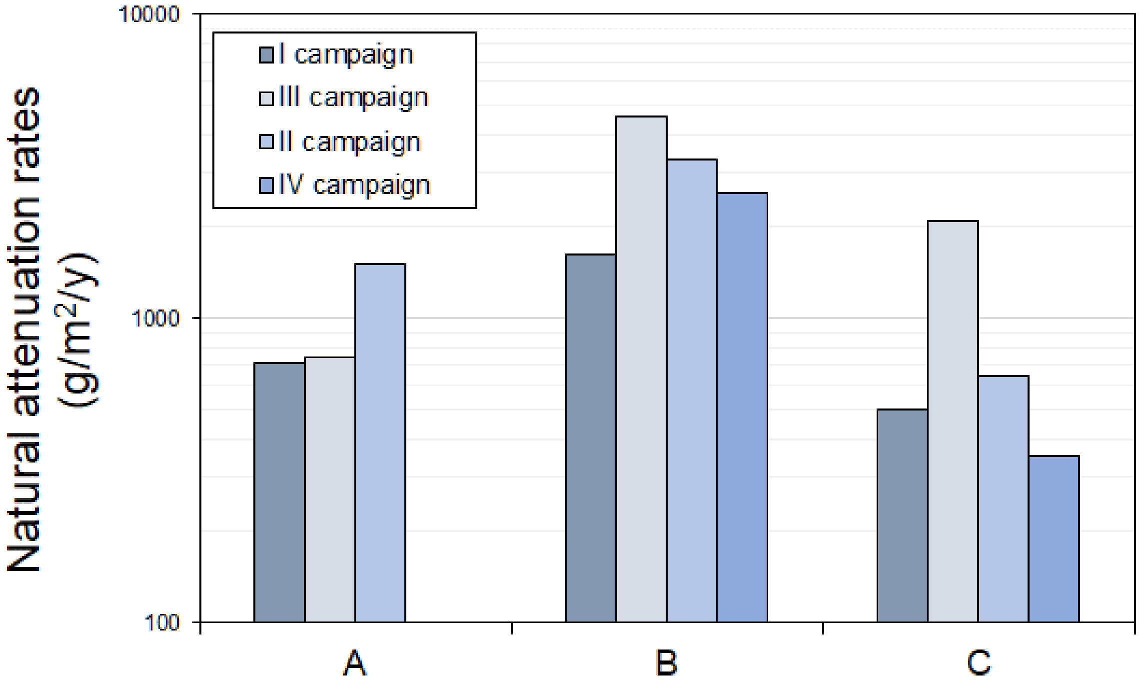
DCC case study: Total CO_2 flux



- **Relevant CO_2 fluxes in the non contaminated areas (soil natural respiration).**
- **Average values quite stable in the different campaigns.**
- **The highest CO_2 fluxes detected in the areas with the presence of free LNAPL.**

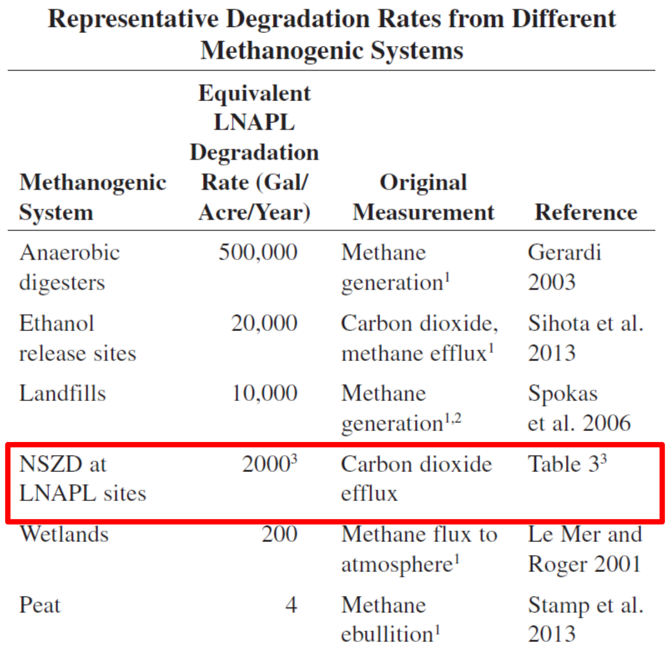
The higher the mass of TPH (LNAPL) the higher the CO_2 flux

DCC case study: Natural source attenuation rates



- **Average values quite stable in the different campaigns.**
- **The highest attenuation rates detected in the areas with the presence of free LNAPL.**

The estimated natural attenuation rates are not far from representative ones found for different investigated sites, i.e. LNAPL loss rate of 1500 $g/m^2/y$, i.e. 2000 gal/acre/y.



Representative Degradation Rates from Different Methanogenic Systems

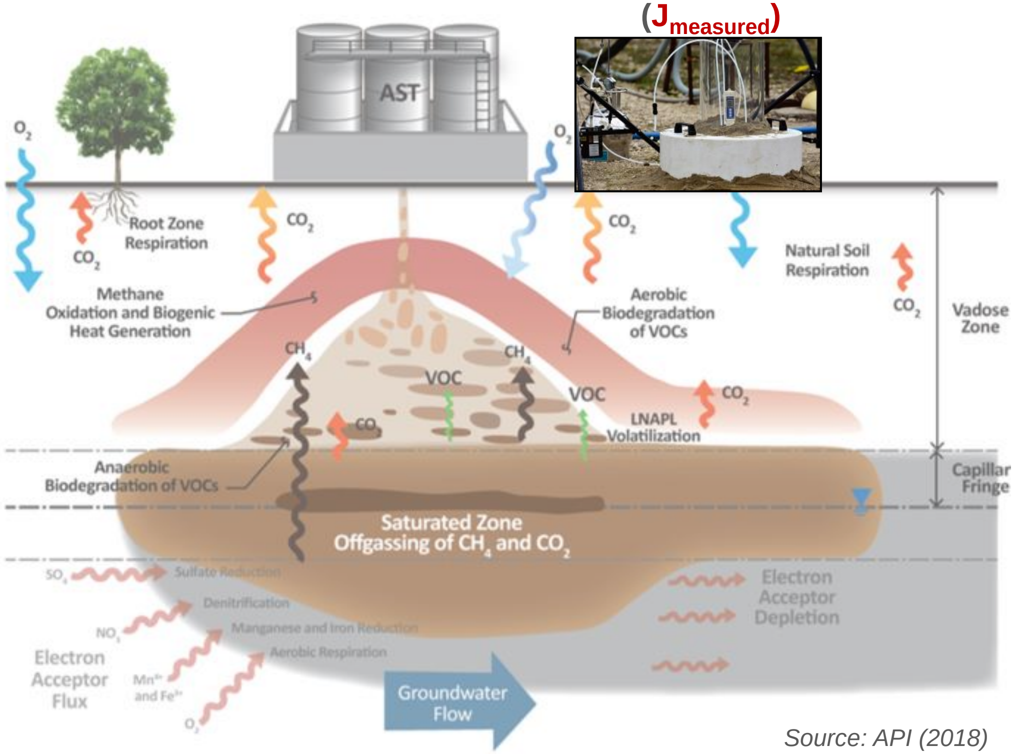
Methanogenic System	Equivalent LNAPL Degradation Rate (Gal/Acre/Year)	Original Measurement	Reference
Anaerobic digesters	500,000	Methane generation[1]	Gerardi 2003
Ethanol release sites	20,000	Carbon dioxide, methane efflux[1]	Sihota et al. 2013
Landfills	10,000	Methane generation[1,2]	Spokas et al. 2006
NSZD at LNAPL sites	2000[3]	Carbon dioxide efflux	Table 3[3]
Wetlands	200	Methane flux to atmosphere[1]	Le Mer and Roger 2001
Peat	4	Methane ebullition[1]	Stamp et al. 2013

Garg et al, (2017), Groundwater Monitoring and Remediation

Estimation of natural source attenuation rates using open chambers data

NSZD rates can be estimated by comparing the measured flux with one expected from diffusive model.

Open chamber above the source ($J_{measured}$)



Source: API (2018)

Natural attenuation rates

$$NSZD = J_{model} - J_{measured}$$

From the source concentration we can calculate the expected flux of VOCs emitted from soil considering no biodegradation (Fick's law):

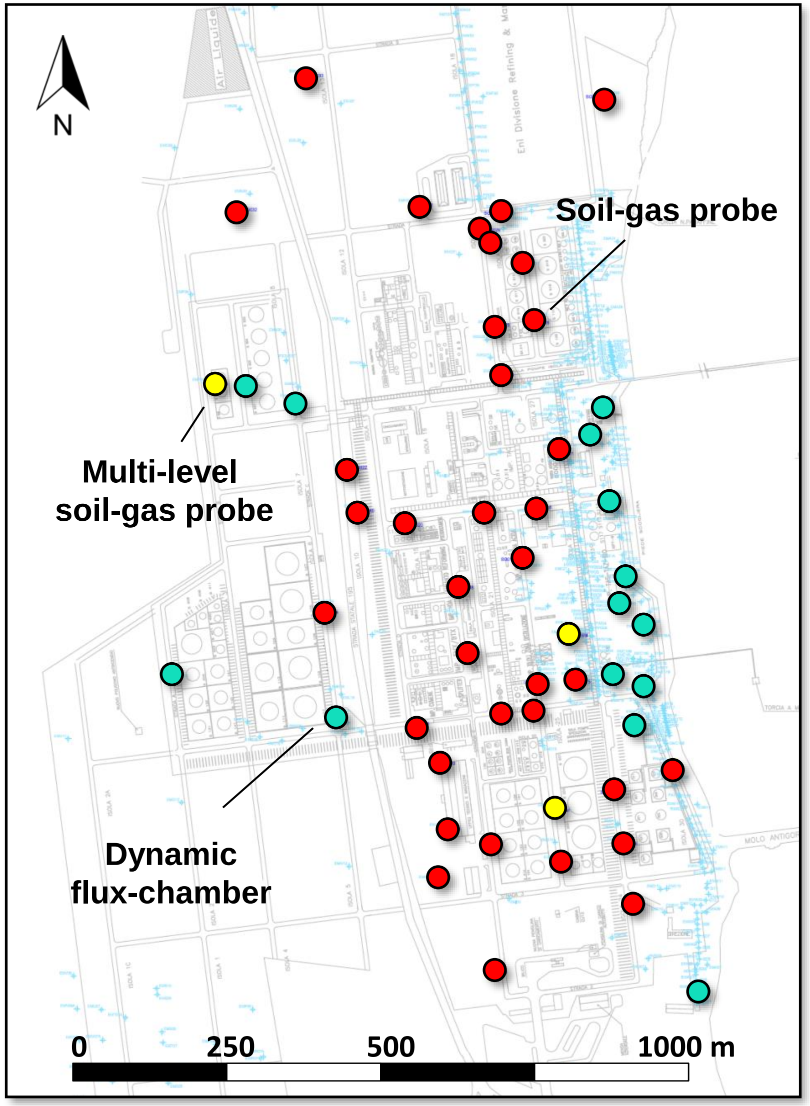
$$\mathbf{J_{model} = C_{source} \cdot H \cdot D_{eff} / L_{source}}$$

The effective diffusion coefficient can be estimated as:

$$\mathbf{D_{eff} = D_{air} \cdot \theta_a^{10/3} / \theta_e^{2}}$$

D_{air} = diffusion coefficient in air
θ_a = air-filled porosity
θ_e = soil porosity

Open flux chambers case study



CASE STUDY

Main source of contamination:
Groundwater

Constituents of concern:
BTEX, TPH

Groundwater depth:
1 - 5 m blg

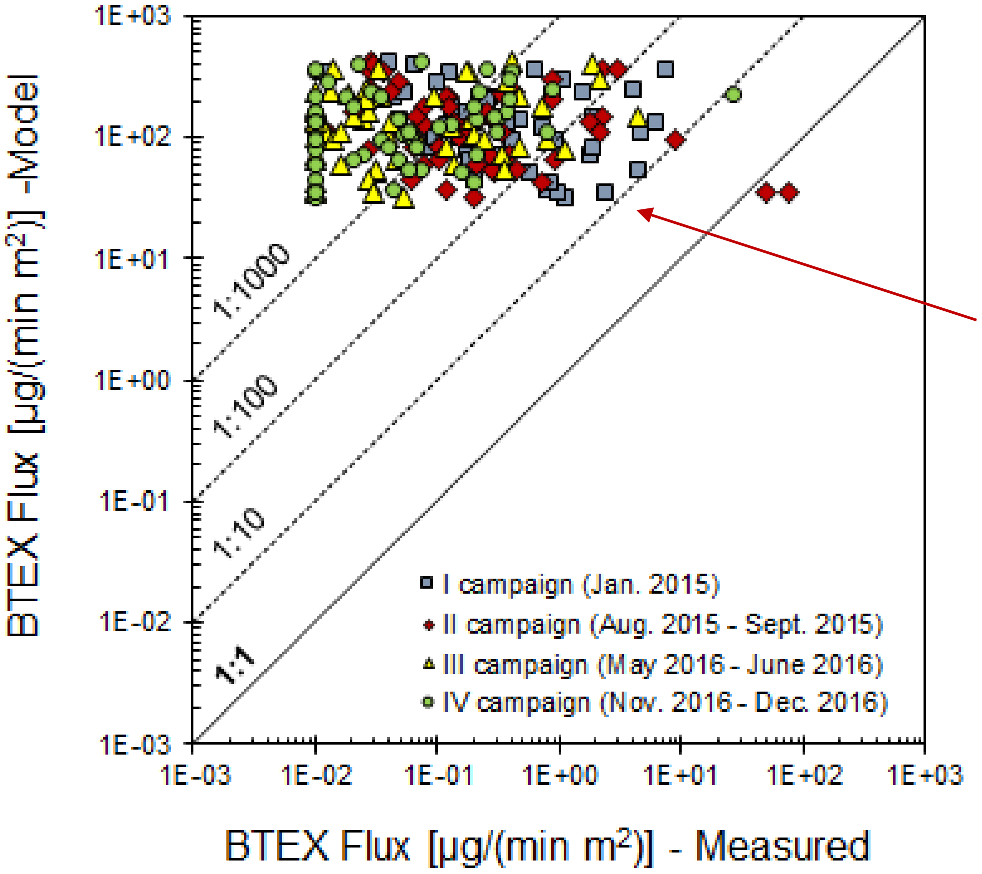
Soil Type:
Sand

Soil-gas monitoring points:
53 (4 seasonal campaigns)

Type of monitoring:
39 soil-gas probes
14 flux chambers

Source: Verginelli, I., Pecoraro, R., Baciocchi, R. (2018). Using dynamic flux chambers to estimate the natural attenuation rates in the subsurface at petroleum contaminated sites. Science of the total Environment, 619-620, 470-479.

Open flux chambers case study: Model vs Predictions (Flux chambers)



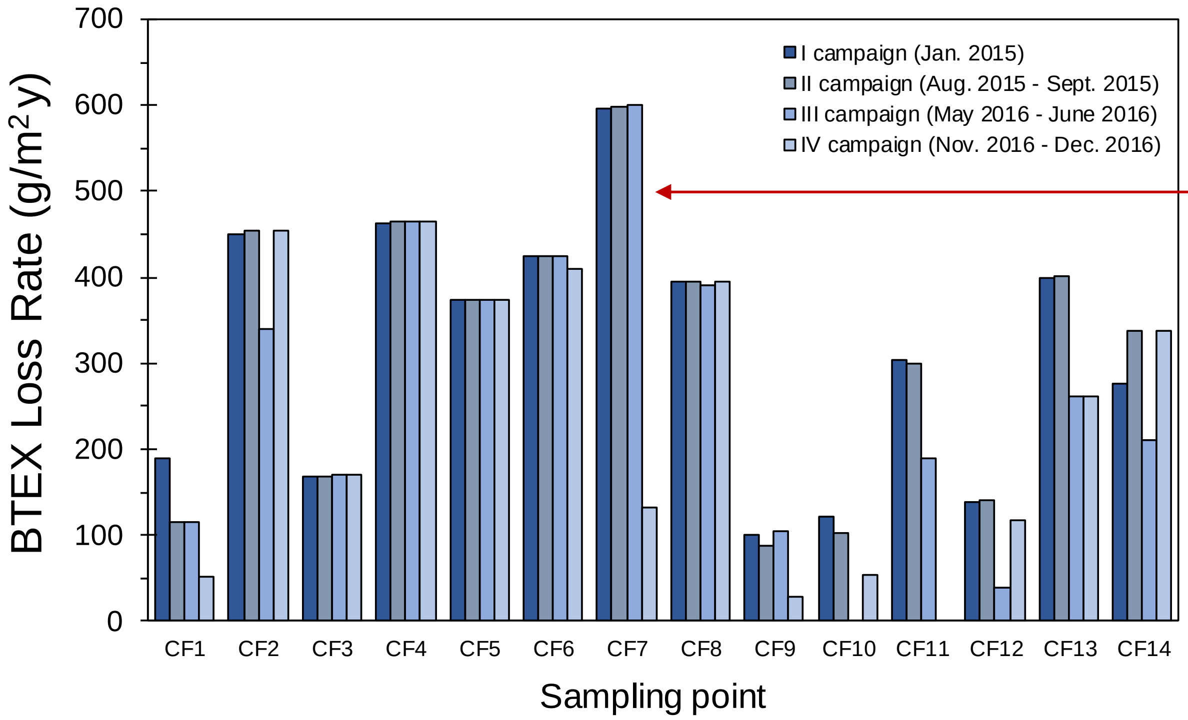
Non-reactive model overestimates the emitted flux of BTEX in some cases of over 3 orders of magnitude

Evidence of natural attenuation in the subsurface.

Similar results in all field campaigns → Low seasonable effects. These results are in line with what found by Hers *et al.* (2014) *“Evaluation of Seasonal Factors on Petroleum Hydrocarbon Vapor Biodegradation and Intrusion Potential in a Cold Climate”*

Source: Verginelli, I., Pecoraro, R., Baciocchi, R. (2018). Using dynamic flux chambers to estimate the natural attenuation rates in the subsurface at petroleum contaminated sites. Science of the total Environment, 619-620, 470-479.

Estimation of BTEX NSZD rates using the dynamic flux chambers

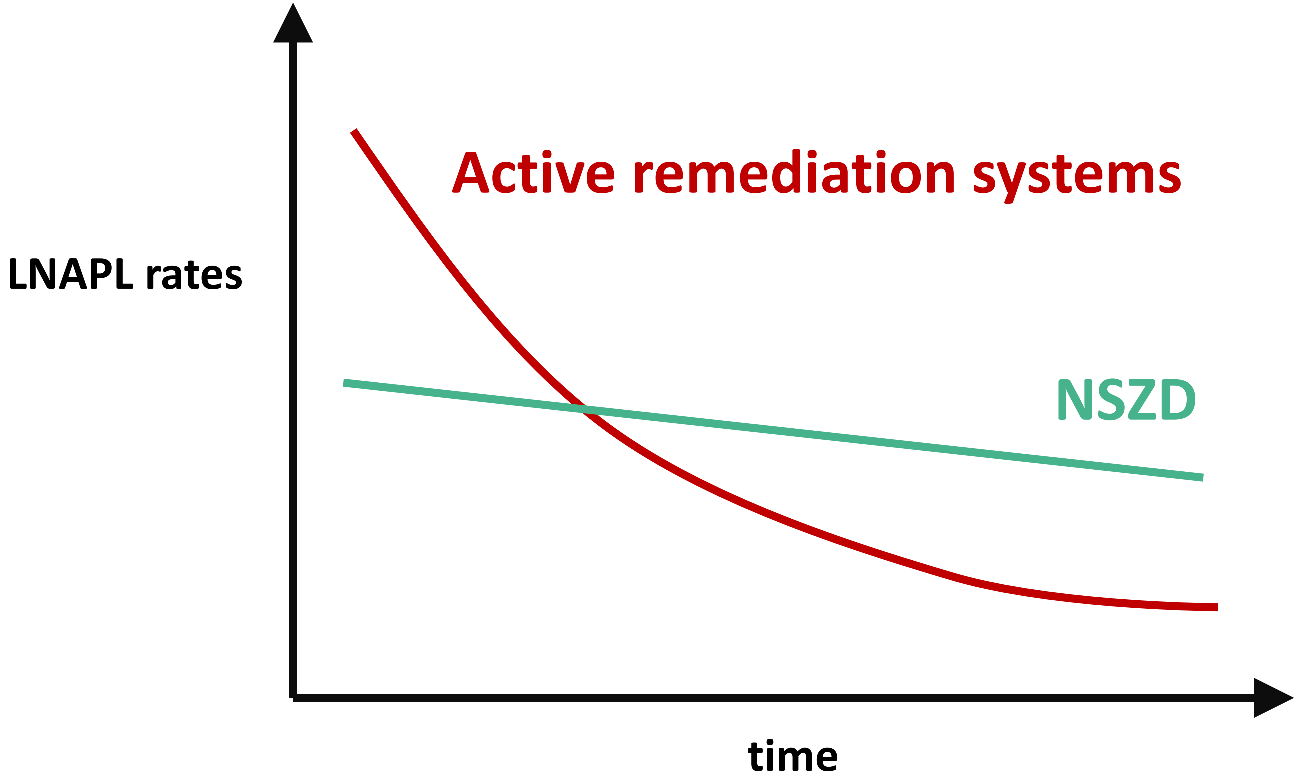


In some areas the estimated natural attenuation rates of BTEX are in the order of 0.4-0.6 kg/m^2/y (i.e. 500-800 gal/acre/y)

The estimated natural attenuation rates are not far from the ones reported in other literature studies (e.g. Garg et al. (2017) report for different investigated sites an average LNAPL loss rate of 1500 g/m^2/y, i.e. 2000 gal/acre/y)

Source: Verginelli, I., Pecoraro, R., Baciocchi, R. (2018). Using dynamic flux chambers to estimate the natural attenuation rates in the subsurface at petroleum contaminated sites. Science of the total Environment, 619-620, 470-479.

Final Remarks



Quantification of NSZD can be a key aspect for a proper management of petroleum hydrocarbon sites

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Thank you for your attention,

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