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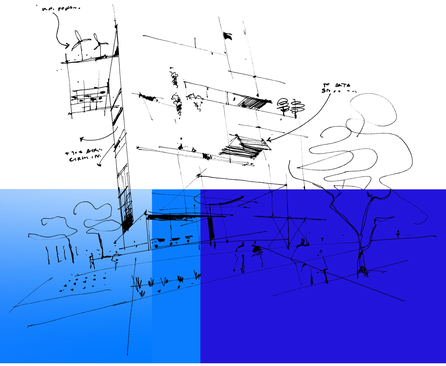
Quantification of the NSZD Rate for a Petroleum-based DNAPL Body through Biogas Efflux and Aqueous Indicators



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Objectives

- Evaluate total attenuation rate of petroleum-based DNAPL (petroDNAPL) body at former industrial facility in the Caribbean
- Quantify natural source zone depletion (NSZD) rate by measuring biogas efflux and quantify aqueous-phase attenuation rate using geochemical indicators

Background

- Peer-reviewed publications that quantify NSZD rates for petroDNAPL bodies largely absent from the literature although petroDNAPL and petroLNAPL degrade through similar processes (**Table 1**)
- C_{10-30} aromatic composition petroDNAPL, partially underlying capped landfill at depths ranging from 10 to 60+ feet below grade
- Site near coast with groundwater temperatures near 30°C
- CH_4 concentrations observed near saturation in the saturated zone

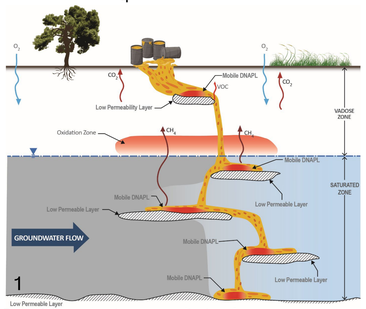
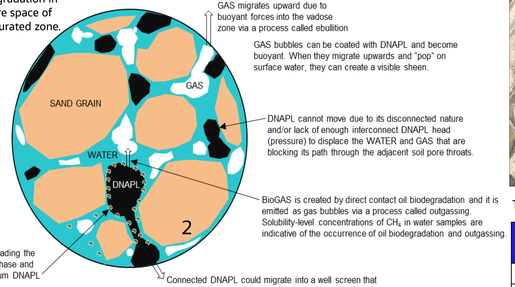


Figure 1. Comprehensive conceptualization of petroDNAPL NSZD processes.

Figure 2. Conceptualization of petroDNAPL degradation in pore space of saturated zone.

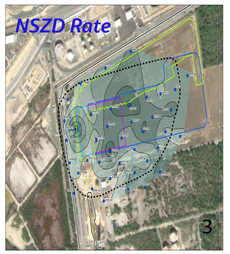


NSZD Approach

- NSZD rates measured at 40 locations across site, including 16 locations on earthen landfill cap
- Soil gas CO_2 efflux measured using dynamic closed chamber (DCC) equipped with infrared gas analyzer
- Soil gas samples collected at all locations to evaluate Carbon 14 (^{14}C) signature of CO_2 using the barium carbonate precipitation method
- DCC and ^{14}C results used to estimate location-specific NSZD rates
- Sitewide NSZD rate estimated by integrating across survey network

Table 1. PetroDNAPL and PetroLNAPL Comparison.

PetroDNAPL	PetroLNAPL
Sinks	Floats
Releases CH_4 into groundwater, a substantial portion of CH_4 reaches the vadose zone where it is converted to CO_2	Releases CH_4 directly into vadose zone where it is converted to CO_2
NSZD rates under-represented in literature	NSZD rates commonly quantified by measuring CO_2 efflux at ground surface



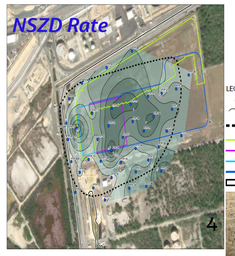
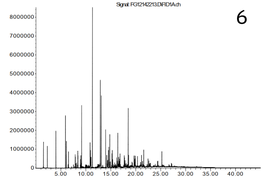


Table 2. NSZD Rates from Events 1 & 2.

Event	NSZD Rate (gal/year)	NSZD Rate per Area (gal/acre/year)
Event 1	3200	150
Event 2	3900	190

Figures 3 & 4. NSZD rates from Events 1 & 2, respectively. NSZD rates shown in g/m²/day.



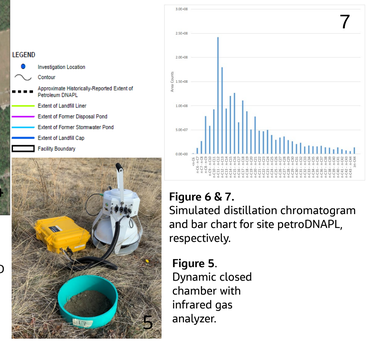
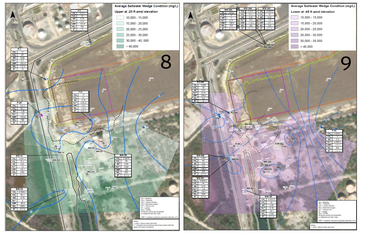


Figure 6 & 7. Simulated distillation chromatogram and bar chart for site petroDNAPL, respectively.

Figure 5. Dynamic closed chamber with infrared gas analyzer.

Aqueous Approach

- Aqueous attenuation rate estimated using geochemical indicators and industry-standard mass budgeting techniques (NRC, 2000) for the upper and lower aquifers
- Geochemical parameters included dissolved oxygen, nitrate, dissolved iron, sulfate, sulfide, carbon dioxide, and methane



Figures 8 & 9. Mass budgeting results from Event 1 for upper and lower aquifers, respectively. Salinity isocontours depict position of saltwater wedge.

Table 3. Aqueous attenuation rates for upper and lower aquifers from Events 1 & 2.

Event	Upper Aquifer (gal/year)	Lower Aquifer (gal/year)
Event 1	31	0.26
Event 2	21	0.31

Results

- NSZD and aqueous attenuation rates successfully quantified
- NSZD rate substantially higher than aqueous attenuation rate

Lessons Learned

- Total attenuation rate for petroDNAPL bodies may be underestimated by orders of magnitude without accounting for NSZD rates
- CO_2 efflux may be measured through an earthen landfill cap
- Similar methods may be applied to petroDNAPL sites (e.g. coal tar or creosote)
- Natural attenuation processes provide a robust containment strategy for petroDNAPL bodies, especially near coast due to presence of saltwater wedge

Reference: National Research Council 2000. Natural Attenuation for Groundwater. Remediation. Washington, DC: The National Academies Press.