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

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Background/Objectives. Peer-reviewed publications that quantify natural source zone depletion (NSZD) rates for petroleum-based DNAPL (petroDNAPL) bodies are largely absent from the literature even though petroDNAPL and petroleum-based LNAPL (petroLNAPL) degrade through similar processes. Unlike petroLNAPL, petroDNAPL sinks and the bulk of its mass resides below the capillary fringe. PetroLNAPL generally remains within the zone of water table fluctuation at the capillary fringe and releases methane (CH_4) directly into the vadose zone; there, CH_4 is converted to carbon dioxide (CO_2), allowing NSZD rates to be quantified by measuring CO_2 efflux at ground surface. PetroDNAPL sinks, becomes submerged, and loses direct contact with the vadose zone. A substantial fraction of the CH_4 it releases through ebullition reaches the vadose zone, where it follows a similar fate as petroLNAPL. Therefore, the extent to which NSZD rates may be quantified for petroDNAPL by measuring CO_2 efflux at ground surface is worth exploring.

The objective of this work is to quantify NSZD rates for a petroDNAPL body using methods typical for petroLNAPL at a former industrial facility in the Caribbean where CH_4 concentrations are near saturation in the saturated zone. The petroDNAPL is primarily aromatic in the C10 to C30 range and underlays a former industrial landfill impoundment that is covered by an earthen cap. The petroDNAPL depth ranges from 10 to 60+ feet below grade. The site is near the coast with average groundwater temperatures near 30 degrees Celsius. The results of this work support the transition from a groundwater recovery-based remedy that requires off-site disposal of hazardous waste to a more sustainable, resilient, nature-based remedy.

Approach/Activities. A survey network of 40 locations was used to measure the geospatial distribution of NSZD rates across the diverse topography and complex underlying soil conditions. Soil gas CO_2 efflux was measured using a dynamic closed chamber (DCC) equipped with an infrared gas analyzer (IRGA). The ^{14}C signature of CO_2 in soil gas was evaluated at all survey locations using the barium carbonate precipitation method. DCC and ^{14}C signature results were used to estimate location-specific and site-wide NSZD rates. Site-wide soil gas estimates were derived by integrating results across the survey network. The aqueous-phase NSZD rate was estimated using geochemical indicators and industry-standard mass budgeting techniques.

Results/Lessons Learned. The total NSZD rate (biogas plus aqueous-phase) was successfully quantified for this petroDNAPL body through measuring biogas efflux at ground surface and aqueous-phase geochemical indicators in groundwater. Biodegradation and biogas ebullition was affirmed, and CO_2 efflux was observed even through the earthen landfill cap. NSZD rates were consistent with values reported for petroLNAPL sites with a sitewide average value on the order of 200 gal/acre/year. These results suggest that similar methodologies may be used to quantify NSZD rates other petroDNAPL sites, such as coal tar or creosote.