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Quantifying Presence of Naturally-Occurring Methane Gas at Petroleum Hydrocarbon-Impacted Sites: Implications for Site Restoration Efforts

Julie Sueker (Julie.Sueker@arcadis.com) (Arcadis, Broomfield, CO, USA)
Allan Horneman (Allan.Horneman@arcadis.com) (Arcadis, Portland, ME, USA)
Monica Heintz (Monica.Heintz@arcadis.com) (Arcadis, Cherry Creek, CO, USA)
Mark Klemmer (Mark.Klemmer@arcadis.com) (Arcadis, Novi, MI, USA)
William Parry (William_Parry@csx.com) (CSX Transportation, Inc., Selkirk, NY, USA)

Background/Objectives. Petroleum hydrocarbon-impacted soils are encountered at many former railway and brownfields sites. The petroleum hydrocarbon concentrations may not be directly associated with significant risk or require remedial action. However, anaerobic biochemical transformation of the petroleum hydrocarbons can generate soil gas methane concentrations that exceed the lower explosive limit (LEL) of 5% by volume. Soil gas methane concentrations can be associated with both present and future risk, limitations to site development, and require costly remediation that may include soil excavation. In addition to petroleum hydrocarbons, elevated soil methane concentrations can have other sources, including stray gas (e.g., leaking natural gas pipelines) or biological transformation of naturally occurring organic rich soils. Therefore, excavation of petroleum impacted soils may not always be appropriate or successful in sufficiently lowering the soil gas methane concentrations.

Approach/Activities. Forensics analysis provides the toolbox to distinguish between methane gas sources and, if multiple methane sources are identified, assess the relative contribution from each source. These analyses can support decisions regarding potential soil removal efforts as well as understand potential risks associated with future site development. The investigation included fixed gas analysis, mercaptan analysis (stray gas), and methane gas stable isotope analysis, and radiogenic carbon (^{14}C) analysis of methane and organic soil. Methane gas sourced from naturally occurring Holocene soils will have appreciative ^{14}C content greater than 25 percent modern carbon (pMC – relative to an international standard), whereas methane gas singularly sourced from petroleum hydrocarbons will have a ^{14}C content of 0 pMC.

Results/Lessons Learned. The utility of methane gas forensics analysis is illustrated in a case study with soil gas methane concentrations up to approximately 30% by volume. The elevated methane concentrations were observed in an area with petroleum hydrocarbon concentrations up to 10,000 milligram per kg (mg/kg) in shallow urban fill materials that overlay organic-rich marsh deposits. Methane gas and organic rich soil ^{14}C analysis supported that 85% to 100% of the methane was generated from biochemical transformation of the naturally occurring organic rich soils whereas the total methane attributable to petroleum hydrocarbons were between 0 and 1.5% methane by volume; well below the LEL of 5%. Based on the results, no further remedial action associated with methane gas was required and an otherwise extensive, expensive, and not appropriate excavation and soil removal effort was avoided. Potential corrective actions for methane control can be more effectively designed based on appropriate methane source attribution.