

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

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Petroleum hydrocarbon impacted soils are encountered at many former railway and brownfields sites. The petroleum hydrocarbon concentrations may not be 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 for methane. Soil gas methane concentrations can be associated with both present and future safety concerns as well as limitations to future site development, and require costly remediation that may include soil excavation. However, in addition to petroleum hydrocarbons, elevated soil methane concentrations can have other sources, including stray gas (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.

Forensics analysis provides the toolbox to distinguish between methane gas sources and, if multiple methane sources are identified, assess the relative contribution from each methane source to support decisions regarding potential soil removal efforts as well as understand potential risks associated with future site development. The tools include mercaptan analysis (stray gas) and methane gas stable isotope and radiogenic carbon (^{14}C) analysis. 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 sourced from petroleum hydrocarbons will have a ^{14}C content of 0 pMC.

We will demonstrate the utility of methane gas forensics analysis 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 soils associated with old filled in marsh land. 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 and that the total methane attributable to petroleum hydrocarbons were between 0 and 1.5 percent methane by volume and well below the LEL of 5%. Based on the results, no further remedial action was required and an otherwise extensive, expensive, and not appropriate excavation and soil removal effort was avoided.