

Did My Remedial Amendment Produce All That Methane?

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Background/Objectives. Methanogens/Archaea are often the dominant microbes in reduced environments and methanogenesis is a requisite component of anaerobic bioremediation. If Archaea are not controlled, then in situ remedial actions employing conventional (i.e., no active control of Archaea) ERD amendments such as [emulsified] oils/lecithins, lactates/sugars, simple hydrogen release compounds or conventional ISCR reagents can generate excessive amounts of methane. However, methane in ecosystems can also originate thermogenically from regions of petroleum formation deep within the earth and/or via microbial fermentation of indigenous organic carbon and subsequent microbial reduction of carbon dioxide. Hence, the origin of methane is not always clear.

Such was the situation at a former remediation site where EHC® (a conventional ISCR reagent with no active methane control) was applied to treat chlorinated solvents in groundwater. The technology effectively reduced the concentration of contaminants in groundwater, but excessive methanogenesis (e.g., >800 mg/L yielding effervescent samples) was observed shortly after amendments were applied, and elevated methane concentrations >200 mg/L have been continuously observed, to date more than 5 years after reagent additions. However, it was not clear if the carbon originated from the ISCR reagent, natural organic matter in soil, and/or subsurface manufactured gas plant (MGP) residuals that were present at the site.

Approach/Activities. Carbon isotope analyses - radiocarbon ($D^{14}C$) and stable carbon ($d^{13}C$) – were coupled with methane (CH_4) and carbon dioxide (CO_2) data from groundwater samples to determine the origin of the respired carbon. For water CO_2 , dissolved inorganic carbon was converted to CO_2 and concentrations determined with a coulometer. This combination of both gasses provided an estimate of total degradation by assuming microbial degradation to CO_2 and, when there is active degradation, CO_2 is further reduced to CH_4 .

Results/Lessons Learned. The figure inset provides an overview of $d^{13}C$ and $D^{14}C$ values for CH_4 and CO_2 during degradation of coal-tar and wheat-based carbon. The $d^{13}C$ range for carbon sources respired in the process is approximately -26.5‰ to -33.0‰ for EHC/wheat and MGP/coal-tar, respectively. $D^{14}C$ is approximately 0‰ to -999‰ for EHC/wheat additions (young carbon) and MGP/coal-tar (old carbon), respectively. The large data range for $D^{14}C$ provides strong capability to confirm degradation. This approach coupled with microbial production and respiration rates can also predict contaminant degradation rates.

