Coupled Radiocarbon and Short-Term Incubations Measure In Situ Hydrocarbon Degradation Rates

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Background/Objectives. Chlorinated solvent contamination represents a significant environmental hazard, as well as, a challenging financial burden for those managing liability. A critical component in managing impacted sites is an understanding of contaminant attenuation rates - either pre-, during- or post-remediation effort. Methods that accurately assess contaminant conversion to end-products under natural or engineered conditions are particularly useful in site management. Recently, natural abundance radiocarbon analysis (carbon dating) has been applied to understand in situ contaminant conversion to CO_2. As fuels and industrial chemicals have traditionally been derived from petroleum feedstocks, they contain no ^{14}C which has a ~6,000 year half-life. This "tracer" is evenly distributed throughout the contaminant source providing a way to trace on-site CO_2 to background organic sources (soil organic matter) or to contaminant (^{14}C-free CO_2). A two component mixing model can be used to determine the proportion of a given CO_2 sample (dissolved in groundwater, soil gas, well casing gas, etc.) coming from contaminant(s). Combining the proportion (%) with a contemporaneously-measured CO_2 production rate (microbial respiration, for example) allows one to calculate the in situ contaminant conversion rate at the spatial scale used for measurement (ultimately per cubic meter). A model based on site hydrogeologic data can then be used to integrate spatially across a site to estimate total remediation over time.

Approach/Activities. We have used several means to collect CO_2 evolved on-site over the past 10 years. In this work, we report on a short-term incubation method which allows one to calculate an "instantaneous" estimate for contaminant conversion. The approach involves collecting adequate sample for radiocarbon analysis (~1 L) along with subsamples for short-term incubations. Groundwater is incubated in triplicate (with triplicate "killed" controls) at in situ temperature for several days. After incubation, live samples are preserved (in the same manner as controls). Samples are then analyzed by coulometry to determine CO_2 content. Respiration or CO_2 production rate is calculated by difference between live and killed samples. Concurrent samples are analyzed for CO_2 radiocarbon content. A two end-member mixing model created using a background well and CO_2 respiration/production (*e.g.* $\mu g\ L^{-1}\ d^{-1}$) is combined with amount derived from fossil source (%) to determine the contaminant conversion rate per unit volume. These values are modeled site-wide to determine a total site degradation rate.

Results/Lessons Learned. This "new" but related technique was applied at a gasoline spill site at Jackson Park, Bremerton, Wasdhington (not a chlorinated solvent site, but applicable studies underway at other locations will also be presented). CO_2 respiration rates ranged from non-detect up to ~7.5 mmol $L^{-1}\ h^{-1}$. Radiocarbon content ranged from modern (background well) to ~-600 ‰ (~40% modern). Coupling measurements, petroleum degradation ranged from 0 to ~140 $\mu g\ C\ L^{-1}\ d^{-1}$. Highest contaminant conversion rates were coincident with the higher petroleum concentrations with an area down-plume also showing increased rates. Site-wide model(s) along with methodological capabilities, ancillary analyses and limitations will be presented. Results from a CH site will be presented as available.