Development of Protocol for Carbon Dioxide Efflux Measurements Using Dynamic Closed Chamber for NSZD Estimates

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Background/Objectives. Natural source zone depletion (NSZD) is increasingly being considered in evaluation of remedial alternatives for management of sites impacted with petroleum hydrocarbons (PHCs). Aerobic and anaerobic biodegradation reactions produce CO_2 resulting in its accumulation in soil gas and efflux at the ground surface. The measurement of CO_2 efflux at ground surface using a dynamic closed chamber (DCC) is one common method where measurements are obtained using an infrared detector on the timescale of a few minutes. An important part of the DCC method involves differentiating contaminant soil respiration (CSR) from natural soil respiration (NSR) through radiocarbon analysis of collected air samples or background measurements.

The objectives of this research are to better understand how site factors and methods affect NSZD estimates using the DCC method with the goal of establishing a detailed protocol for conducting such measurements. The research builds upon multiple DCC monitoring campaigns conducted at a refinery site.

Approach/Activities. A detailed literature review was conducted to investigate processes and factors affecting DCC measurements. From this review an improved conceptual site model was developed identifying key factors affecting natural and contaminant soil respiration related to site biosphere (vegetation type), hydrosphere (soil moisture, depth to contamination), climatic and weather conditions (wind and temperature), and methodology (chamber collar location, size, and insertion depth). A matrix of factors and anticipated influence on CO_2 efflux and its spatial and temporal variability is developed. A detailed protocol is developed for collecting and analyzing samples for radiocarbon content (^{14}C fraction) including considerations relating to sample collection, integrity, volume and laboratory analyses.

Results/Lessons Learned. Respiration and photosynthesis are two competing processes that affect CO_2 generation, which is affected by vegetation and soil type and time of measurement. Consequently, high spatial and temporal variability in CO_2 fluxes from NSR may be observed. The implication is that if the background method is chosen for estimation of CSR, the planning of monitoring locations and times should address this variability. The data indicate a more robust method for estimation of CSR is a two-component mass balance approach that combines the CO_2 concentration and ^{14}C content at specific locations, where CO_2 efflux is measured. Soil moisture is demonstrated to have a significant effect on CO_2 efflux. Similar to protocols for soil gas sampling, it is recommended that efflux testing not be conducted during and shortly after rainfall events. The limited data available suggests that CO_2 effluxes at coarse-grained sites may be affected by wind and collar insertion depth, although this is a data gap warranting further study.