

## **Comparison of methods for estimating natural LNAPL loss rates at field sites based on CO<sub>2</sub> flux in soils**

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**Abstract.** Petroleum hydrocarbon liquids, referred to as light non-aqueous phase liquids (LNAPLs), are commonly found beneath petroleum facilities. It has been long recognized that the end product of petroleum biodegradation by soil microorganisms is CO<sub>2</sub> (and methane). Although quantification of petroleum biodegradation rates at field sites has been more challenging, recent research directly relates the rates of petroleum biodegradation to the measurement of soil gas CO<sub>2</sub> fluxes. These can be measured directly at grade using soil respiration methods, or by monitoring soil gas concentration profiles (coupled to soil gas transport models). Recent work at Colorado State University has focused on developing a novel method, using passive carbon dioxide sorbents (CO<sub>2</sub> Traps) at grade, which provide direct, time-integrated measurements. Other methods commonly used include the chamber method, which provides direct, instantaneous measurements at grade, and the gradient method, which uses soil-gas concentration profiles throughout the soil column to estimate surface flux. The objective of the study is to conduct a laboratory comparison of the available methods. Laboratory calibration of the methods against imposed fluxes will avoid the difficulties of field comparisons, where spatial variability can generate large differences in closely spaced measurements. A large column was filled with homogenous fine silt and fed at the bottom with known CO<sub>2</sub> flow rates equivalent to field-representative ranges of CO<sub>2</sub> fluxes. Methods for measuring CO<sub>2</sub> fluxes have been applied once steady state is achieved. The column includes instrumentation to monitor differential pressures (in order to identify any potential effects of short term ambient pressure changes, known as barometric pumping), as well as instantaneous values of soil temperature, soil moisture and CO<sub>2</sub> concentrations throughout the column. Real time data will enable calibration of different soil gas transport models. Models tested will include both diffusion and advection as transport mechanisms, and also steady state vs. transient conditions. The results of the study will help reconcile differences among the methods observed at field sites, and guide the selection of appropriate methods for field measurement of natural losses of LNAPL.