

SOIL-GAS IDENTIFICATION OF VADOSE-ZONE CARBON CYCLING: IMPLICATIONS FOR NEAR-SURFACE MONITORING AT CCS SITES

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Introduction: Strategies for identifying and interpreting the effects of environmental factors on soil-CO₂ concentrations are essential to developing accurate near-surface monitoring protocols at carbon storage sites. Because CO₂ exists naturally in the vadose zone and is spatially and temporally variable, it may be difficult to discern natural background fluctuations from a storage site leakage signal, especially in the early stages of leakage. This difficulty arises from abiotic and biotic cycling processes that may either produce and/or concentrate CO₂ yielding false positives in areas where leakage has not occurred, and processes that consume or disperse CO₂ and may yield false negatives in areas that would otherwise exhibit a distinguishable leakage signal. It is therefore important to have the capability to identify and ultimately quantify the natural processes that govern background CO₂ concentrations. Ideally this capability should be cost-effective and enhance the chances for correct and early leak detection in the near-surface without years of background soil-gas monitoring and should provide information on the source of an anomaly.

At a natural playa lake analogue site in west Texas, USA, we have successfully used simple soil-gas measurements of CO₂, CH₄, N₂, and O₂ to identify near-surface CO₂ cycling processes related to microbial CO₂ production and consumption, dissolution of CO₂ into recharging groundwater, and subsequent reaction of bicarbonate with soil carbonate. These observations have led to a framework for developing innovative monitoring protocols and a method for characterizing a site for its near-surface monitoring potential.

Playa Lake Processes: Playas exhibit extreme vadose-zone carbon cycling processes that vary in space and time, making them optimal places to study the effects of environmental variability on carbon cycling and CO₂ gas concentrations. Playas are broad, gently-sloping circular basins (~1 to 2 km in diameter) that accumulate surface runoff from the surrounding plains and subsequently transmit this runoff through 60 meters of vadose-zone sediments into the underlying aquifer. Organic matter that is transported into the vadose zone via water infiltrating through playa floors is oxidized by microbes at depths up to 15 meters, creating soil-CO₂ concentrations of up to 17%. This CO₂ soil-gas produced by microbes dissolves into infiltrating water and reacts with and dissolves soil carbonate.

Soil-gas Identification of Processes: Real-time field-based measurements of CO₂, CH₄, O₂, and N₂ were acquired at various depths up to 15 m within the vadose zone of a highly carbon-reactive playa lake. Soil-gas concentrations were compared to data on atmospheric conditions, organic and inorganic soil carbon, subsurface pressure, water flux, and surface water and

groundwater chemistry. Soil-gas methodology successfully identified major carbon cycling processes and gas transport gradients affecting background subsurface CO₂ and CO₂ surface flux. Molar relationships among CO₂ ≤ 17%, CH₄ ≤ 2%, and O₂ from 21-0% indicate microbial oxidation of organics and CH₄ oxidation is the source of CO₂ in playas. CO₂ production is regulated by water flux that supplies dissolved organics to microbes at depth and regulates oxygen supply by blocking vertical permeability and atmospheric gas exchange. Samples with CO₂+O₂ < 21 and N₂ > 78% indicate dissolution of CO₂ into recharging groundwater. Dissolution of CO₂ gas into recharging water is enhanced in the presence of soil carbonate according to the chemical reaction: CO_{2(g)}+H₂O+CaCO₃ ↔ 2HCO₃+Ca²⁺. This loss of CO₂ gas into the dissolved phase creates a pressure drop within the vadose-zone pore producing an advective gradient that forces air (with 78% N₂) into the pore, thereby increasing N₂ concentrations to above atmospheric in the soil-gas.

Results of the study indicate that relatively complex CO₂ cycling processes can be identified by simple soil gas measurements. The degree to which complex carbon cycling affects CO₂ concentrations is a function of the carbon reactivity of an environment which is governed by the amount and distribution of water flux, soil carbonate, and mobile organic carbon in the soils and sediments. When carbon reactivity is at a maximum, CO₂ cycling is complex, background CO₂ concentrations will fluctuate greatly, and input of exogenous CO₂ into the system will be difficult to constrain and quantify. When carbon cycling is low, near-surface monitoring is relatively simple. A summary of the factors that define carbon reactivity and their affects on near-surface soil-gas monitoring at geologic carbon storage sites is presented, along with recommendations for site evaluation with regard to near-surface monitoring potential.

PROCESS	COMBINATION OF EXISTING VADOSE-ZONE CONDITIONS				
	High Water Flux Only	High Water Flux + Organics	High Water Flux + Carbonate	Water Flux + Organics + Carbonate	Dry With Other Factors Variable
Organics → CO ₂	negligible	high	negligible	high	low
CO ₂ Dissolution	negligible	negligible	high	high	low
Gas Redistribution	high	high	high	high	low
Monitoring Difficulties	Soil breathing limited. Caution advised when interpreting surface flux measurements.	Surface flux measurements may underestimate subsurface CO ₂ Microbial CO ₂ input causes overestimation.	Carbonate dissolution is a CO ₂ sink Gas advection may cause mislocation of leak	Complex carbon cycling. Isotope data are necessary to constrain cycling.	Soil-gas monitoring is relatively straightforward and will accurately define CO ₂ leakage
Accuracy of anthropogenic CO ₂ estimation	Underestimate	Unknown	Underestimate	Unknown	Relatively Accurate

Figure 1. Framework currently being developed for near-surface monitoring site assessment.