INTEGRATED NEAR-SURFACE MONITORING AND ANALYSIS FOR CO_2 STORAGE VERIFICATION

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Introduction

Geologic carbon sequestration is the capture of anthropogenic CO_2 and its storage in deep geologic formations. To verify that this storage is effective and that CO_2 is not migrating to the near surface and seeping out of the ground, resulting in potential health, safety, and environmental risks, monitoring of storage sites will be necessary. Numerical simulations of leakage and seepage have shown that CO_2 concentrations in the shallow subsurface can reach relatively high levels even for modest leakage rates; however, once CO_2 seeps into the atmospheric surface layer, winds are effective at dispersing the CO_2[1,2]. Geologic CO_2 storage reservoirs will be chosen in large part for their low probability of CO_2 leakage away from the target formation within hundred to thousand year time scales. Therefore, CO_2 storage verification will involve searching for *potential* anomalies, likely of small magnitude, over tens of km^2 or more within a system with large spatial and temporal variation of CO_2 fluxes and concentrations arising from natural biological and hydrologic processes.

A range of technologies exists to measure CO_2 concentrations and fluxes in the shallow subsurface and the atmospheric surface layer. These technologies include (1) the infrared gas analyzer (IRGA) for measurement of point CO_2 concentrations, (2) the accumulation chamber (AC) technique[3] to measure point soil CO_2 fluxes, (3) the eddy covariance (EC) method[4] to measure net CO_2 flux over a given area, and (4) light distancing and ranging (LIDAR) to measure CO_2 concentrations over an integrated path. However, these technologies alone cannot solve the fundamental problem of discerning a small CO_2 leakage or seepage signal (LOSS) from the naturally varying background CO_2 fluxes and concentrations. Here, we describe the primary sources of background CO_2 in the near surface and the processes that control the natural variability of concentrations and fluxes of this CO_2. We then propose an integrated measurement, monitoring, and modeling strategy designed to meet the challenge of detecting a small CO_2 LOSS within this variability.

Controls on Background Fluxes and Concentrations. We define "background" CO_2 as CO_2 derived primarily from the atmosphere and biologically mediated oxidation of organic carbon. Background soil CO_2 fluxes and concentrations are dependent on CO_2 production in the soil, movement of CO_2 from sub-soil sources into the soil, and exchange of CO_2 with the atmosphere as controlled by concentration (diffusion) and pressure (advection) gradients. Table 1 shows generalized chemical and isotopic signatures related to different background sources of CO_2. Biologically produced CO_2 in soils (i.e., soil respiration) is derived from root respiration and decay of organic matter. While many factors may influence soil respiration rates, changes in atmospheric and soil temperature and soil moisture have been shown to strongly affect these rates and related concentrations and fluxes. CO_2 that enters soil from sub-soil sources can be derived from groundwater degassing of CO_2 derived from respiration, atmospheric, and carbonate mineral sources. Also, production of CO_2 at sub-soil depths can occur by oxidative decay of relatively young or ancient (e.g., peat, lignite, kerogen) organic matter in the vadose zone. Exchange of soil CO_2 from subsurface sources with the atmosphere can occur by diffusion and/or advection. Diffusive flow depends on the gas production rate and soil temperature, moisture and properties such as porosity, with each of these factors varying in both space and time. Advective flow can be driven by fluctuations in atmospheric pressure, wind, temperature, and rainfall.

Table 1. Chemical and Isotopic Signatures Related to CO_2 Derived from Different Sources

CO_2 source	$\delta^{13}C_{CO2}$ (‰)	$\Delta^{14}C_{CO2}$ (‰)	Near-surface CO_2 conc.	CO_2 conc. profile with depth	O_2 conc. profile with depth
Atmosphere	-7	-70	Low	-	-
Root respiration and decay of young soil organic matter	C_3plants: -24 to –38 C_4plants: -6 to -19	≥ -70	Low to moderate	Increasing through soil zone	Decreasing through soil zone
Decay of ancient organic matter	C_3plants: -24 to –38 C_4/aquatic plants: -6 to –19 Also age dependent	Highly depleted to absent, depending on age	Low	Increasing potentially through vadose zone	Decreasing potentially through vadose zone
Marine carbonate rocks	0 ± 4	Absent	Low	Increasing through vadose zone	No effect
Fossil fuel	Average: -27	Absent	Moderate to high	Increasing through vadose zone	No effect

Carbon-13 and 14 values are expressed relative to PDB and oxalic acid decay corrected to 1950, respectively.

Integrated Monitoring Plan. We assume that a given land area above the storage structure can be delineated as the area at risk from unintended leakage and seepage. This area, called the study area, will normally include the surface injection facilities and may extend for many kilometers away from surface facilities depending on the depth and areal extent of the storage reservoir and nature of subsurface structures and hydrologic systems.

Baseline Monitoring and Modeling. Prior to deep CO_2 injection, background spatial and temporal variability of subsurface and atmospheric CO_2 within the study area should be well understood. Figure 1 shows the general sampling frequencies of the range of background characterization measurements that should be made[5]. Particular attention should be paid to understanding natural variability in areas where CO_2 leakage and seepage would be most likely (e.g., close to the locations of injection and monitoring wells and geologic features such as faults and lithologic contacts). The study area should be characterized with respect to properties (e.g., soil type, soil and soil parent material organic carbon content, vegetation type and density, topography, and surface water hydrology) that could influence and cause important differences in background CO_2 concentrations and fluxes. Ecological modeling (e.g., LSM[6]) and flow and transport modeling (e.g., TOUGH2[1]) should be considered to develop a consistent conceptual model of the sources and sinks of carbon and water within the study area.

To capture both the overall spatial distribution and the small-scale spatial heterogeneity of soil CO_2 fluxes, concentrations, and isotopic compositions, fluxes and concentrations should be measured using the AC method and a portable IRGA, respectively, and soil

gases should be collected for chemical and isotopic determinations within the area along a large grid at widely spaced sampling intervals, and along a smaller grid at closely spaced sampling intervals. These measurements should also be made repeatedly over time at several sites to capture diurnal to seasonal variations. The carbon isotopic compositions of soil and sub-soil organic matter should be determined within the study area and measured repeatedly over time at several representative sites. In addition, pre-existing wells within the study area should be sampled to characterize background sub-soil gas chemistry and isotopic compositions (e.g., CO_2, O_2, $\delta^{13}C$, $\Delta^{14}C$) and their variability with depth.

Soil temperature and moisture and atmospheric temperature, pressure, and wind speed and direction should be monitored contemporaneously with soil CO_2 fluxes. Correlation analysis of CO_2 flux and environmental parameters should be performed. Using regression analysis, empirical relationships between correlated parameters could be established for the overall area, or each sub-region, if appropriate, and used to predict the background CO_2 fluxes expected under a given set of environmental conditions.

If the study area has relatively low slopes and horizontally uniform vegetation type and density as required by the EC method, then an EC station should be deployed during times of meteorologically stable conditions to characterize spatially averaged background CO_2 fluxes. The background temporal variability of these fluxes should be established by making measurements over diurnal to seasonal cycles. Eddy covariance CO_2 fluxes should be compared to average CO_2 fluxes measured by the AC method within the same footprint area to quantify the component of the background EC flux derived from soil and subsoil respiration.

Long-Term Monitoring. A range of measurements should be made within the study area during and after CO_2 injection into the storage reservoir at frequencies that will likely change with time following injection (Figure 1)[6]. The time over which it will be necessary to carry out such monitoring activities following injection is highly uncertain. Monitoring for CO_2 leakage and seepage should focus on rapid, economical, reliable measurements of soil CO_2 concentration and AC surface CO_2 fluxes along grids, supplemented by EC measurements. The objective here is to minimize the number of these measurements and then focus more time- and cost-intensive deep sampling (e.g., of wells, trenches) and isotopic measurements on "high-probability" anomalies. To this end, Bayesian statistical analysis of CO_2 flux and concentration measurements should be used to identify the presence (or absence) of CO_2 anomalies with high confidence. In addition, maps of sampling areas should be contoured for soil CO_2 concentration and flux magnitude and autocorrelation and cross-correlation coefficients of these parameters. Furthermore, measured CO_2 fluxes should be compared to the behavior of background CO_2 fluxes predicted by ecological models under a given set of atmospheric parameters and assessed for deviations from this behavior. Based on these combined analyses, the locations of further more costly and time-intensive sampling can be determined.

Where anomalously high soil CO_2 concentration and flux are located, gases should be sampled from the surface to the water table for chemical and carbon isotopic ($\delta^{13}C$, $\Delta^{14}C$) analyses. An increase in CO_2 concentration with depth would indicate CO_2 production at depth. Measured CO_2 and O_2 concentration-depth profiles should be compared to profiles generated by diffusion models of background CO_2 respiration and O_2 consumption to evaluate a biological respiration source of CO_2 at depth. Carbon-13 values at sub-soil depths should be compared to values for soil CO_2 and organic matter to look for differences indicative of a distinct source. Very low $\Delta^{14}C$ values would be expected at depth with a leaking fossil CO_2 source. The potential contribution of CO_2 derived from oxidation of ancient sedimentary organic matter should also be evaluated. Overall, the observations of CO_2 and O_2 concentration gradients, CO_2 production distribution, surface CO_2 fluxes, and carbon isotopic compositions must be consistent with the CO_2 source.

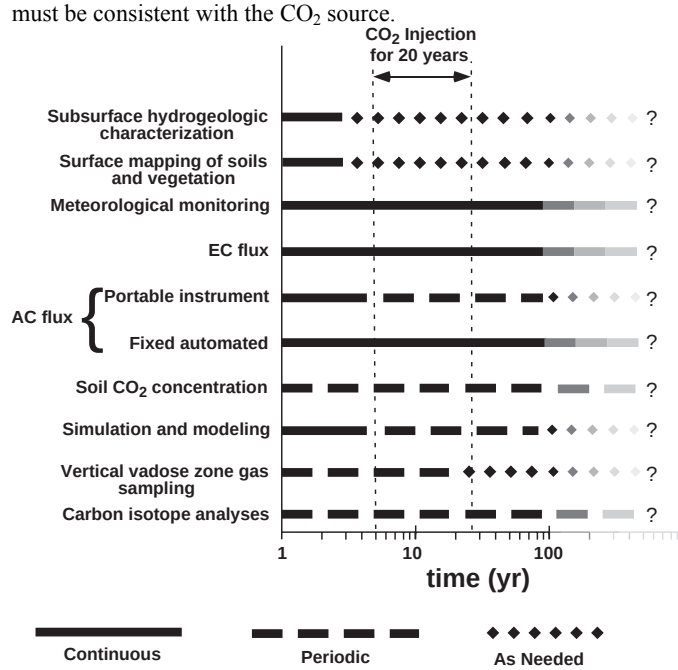

Figure 1. Example activity and schedule chart for CO_2 LOSS detection and monitoring showing generalized frequency of measurements (i.e., continuous, periodic, as needed) over time preceding, during, and following CO_2 injection. Lighter shading indicates increasing uncertainty in need for activities at long times following injection.

Conclusions

A great deal of knowledge and technology exists to detect and monitor CO_2. However, despite these resources, discerning a small CO_2 LOSS from natural variations will be challenging. The strategy that we propose involves comprehensive baseline monitoring and modeling to develop an understanding of and predictive capability for the natural system in the absence of CO_2 LOSS. Once this understanding is achieved and geologic CO_2 storage begins, a program of integrated measurement, monitoring, and modeling that emphasizes time and cost efficiency can be applied during and after the injection period. Measurements in conflict with expectations of the natural system should be thoroughly investigated by detailed vertical profile sampling and chemical and isotopic analyses, the results of which could definitively determine if an anomalous source of fossil CO_2 consistent with the geologic CO_2 storage site is present.

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