

**Carbon Dioxide Capture for Storage  
in Deep Geologic Formations –  
Results from the CO<sub>2</sub>  
Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

*Volume 2*

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# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

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## Chapter 21

# DETECTING LEAKS FROM BELOWGROUND CO<sub>2</sub> RESERVOIRS USING EDDY COVARIANCE

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### ABSTRACT

We describe the eddy covariance method of measuring earth–atmosphere CO<sub>2</sub> exchange, including past applications to measurements of volcanic venting of CO<sub>2</sub>. The technique involves continuous atmospheric measurements of both CO<sub>2</sub> mixing ratio and atmospheric winds from a tower platform. Equipment is robust and commercially available, and the methodology is well established.

The surface area covered by the measurement is described. The upwind coverage is typically  $(10-100)z_m$ , where  $z_m$  is the measurement height, and the cross-wind extent of this area is of the order of the upwind distance. Thus, a 10-m high tower detects fluxes from an upwind distance of 100–1000 m, and an area of order  $10^4-10^6$  m<sup>2</sup>. The eddy covariance method yields continuous measurements of earth–atmosphere exchange over such areas, typically expressed as averages over hourly or half-hourly time periods. The area measured depends on wind speed, wind direction, surface roughness, and stability of the atmospheric surface layer. The measurement works best under well-mixed atmospheric conditions which frequently occur on a daily basis, often for a majority of the day.

We assess the ability to detect leaks from geologic CO<sub>2</sub> reservoirs by comparing expected leakage rates to typical ecological flux rates. While the character and magnitude of ecological fluxes are well established, reservoir leakage rates and areas are uncertain. Fairly conservative estimates based on ensuring the economic viability of CO<sub>2</sub> storage are constructed. Our estimates of leakage rate and area yield leakage fluxes that range from 1 to  $10^4$  times the magnitude of typical ecological fluxes. The flux measurement areas readily encompass the assumed leakage areas ( $10-10^5$  m<sup>2</sup>). We conclude that this approach shows promise for the monitoring of belowground CO<sub>2</sub> storage. Leak detection is shown to be a simpler problem than leak quantification, but both can in principle be accomplished using eddy covariance under conditions favorable for the measurement.

### INTRODUCTION

Eddy covariance is a possible method to monitor for economically undesirable and potentially dangerous CO<sub>2</sub> leaks from CO<sub>2</sub> storage reservoirs. Although eddy covariance is relatively new to the geologic community, it has been used extensively in the meteorology and ecology communities to study CO<sub>2</sub> exchange between vegetation and the atmosphere [1–4]. The technique has recently been applied successfully to volcanic regions [5–8]. In this chapter, we describe the eddy-covariance method and evaluate its ability to detect leaks from deep aquifers.

### EXPERIMENTAL/STUDY METHODOLOGY

#### *Basic Principles of the Eddy-Covariance Technique*

The derivation presented here follows work previously published by Yi et al. [9]. The conservation equation for CO<sub>2</sub> in the atmospheric boundary layer can be written as

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} + w \frac{\partial c}{\partial z} = S_C, \quad (1)$$

where  $c$  is the  $\text{CO}_2$  mass density ( $\text{kg CO}_2 \text{ m}^{-3} \text{ air}$ ),  $S_C$  is a source or sink of  $\text{CO}_2$  in the atmosphere ( $\text{kg CO}_2 \text{ m}^{-3} \text{ s}^{-1}$ ),  $u$  and  $v$  are wind speeds ( $\text{m s}^{-1}$ ) in the horizontal ( $x, y$ ) plane,  $w$  is the wind speed in the vertical  $z$  direction, and  $t$  represents time. Molecular diffusion, insignificant for atmospheric transport at spatial scales greater than  $\sim 1 \text{ mm}$  [10] has been neglected. While oxidation of hydrocarbons and CO does lead to production of  $\text{CO}_2$  in the atmosphere [11] this has a characteristic time scale of weeks to months and can be ignored over the time scales of turbulent eddies in the atmosphere (seconds to minutes, Ref. [10]); thus, we set  $S_C = 0$ . Further, we apply Reynolds decomposition and averaging in combination with the turbulent continuity equation and align the  $x$ -coordinate along the mean horizontal wind to obtain

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \bar{w} \frac{\partial \bar{c}}{\partial z} + \frac{\partial \overline{u'c'}}{\partial x} + \frac{\partial \overline{v'c'}}{\partial y} + \frac{\partial \overline{w'c'}}{\partial z} = 0, \quad (2)$$

where the overbar represents the ensemble-averaged mean and the prime terms represent fluctuations about the mean. In practice, time-averages of point time-series data are used in place of ensemble averages. We integrate from the surface ( $z = z_0$ ) to the altitude of a sensor ( $z = z_m$ ) and obtain

$$\int_{z_0}^{z_m} \left( \frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \bar{w} \frac{\partial \bar{c}}{\partial z} + \frac{\partial \overline{u'c'}}{\partial x} + \frac{\partial \overline{v'c'}}{\partial y} \right) dz + \overline{w'c'}_{z_m} = \overline{w'c'}_{z_0}. \quad (3)$$

The term on the right-hand side of Eq. (3) is the flux of  $\text{CO}_2$  at the Earth's surface,  $F_0$ . The last term on the left-hand side, the covariance of turbulent fluctuations in the vertical wind and the  $\text{CO}_2$  density, is the turbulent flux of  $\text{CO}_2$  measured at some height above the surface. With negligible net longitudinal and lateral (mean and turbulent) transport, and negligible mean vertical velocity, Eq. (3) simplifies to

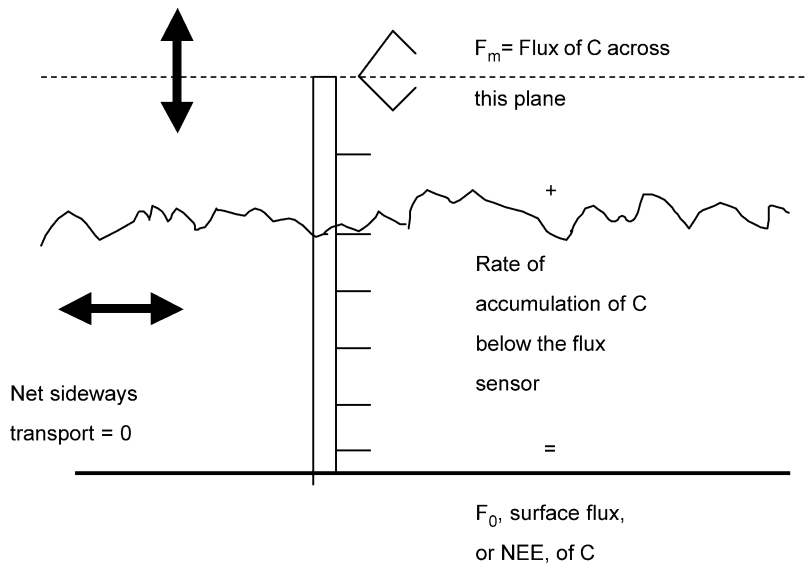
$$\int_{z_0}^{z_m} \frac{\partial \bar{c}}{\partial t} dz + \overline{w'c'}_{z_m} = F_0. \quad (4)$$

$F_0$  (the surface flux of  $\text{CO}_2$ ) is known as the net ecosystem–atmosphere exchange (NEE) in the ecological literature. It is the sum of the turbulent flux of  $\text{CO}_2$  across a horizontal plane above the plant canopy and the rate of accumulation of  $\text{CO}_2$  below the plane. This is illustrated in Figure 1. The assumption of zero net lateral transfer is generally satisfied when atmospheric turbulence is moderate to vigorous (e.g. sunny and/or windy days), but is often violated in very calm conditions (e.g. cold, clear, calm nights). Extensive evaluation of these assumptions exists in the micrometeorological literature [9, 12–17]. When the atmospheric surface layer is unstable, the accumulation of  $\text{CO}_2$  near the Earth's surface is negligible, and the surface–atmosphere exchange rate from Eq. (4) is

$$\overline{w'c'}_{z_m} = F_m = F_0, \quad (5)$$

where  $F_m$  is the flux of  $\text{CO}_2$  at the measurement height. This flux measurement method is commonly referred to as eddy covariance (hereafter EC).

An example of data used to compute the vertical flux of  $\text{CO}_2$  over the averaging time (typically 30 min or 1 h (e.g. Refs. [18,19]) is shown in Figure 2. The data were collected over a forest at midday in the summer. Both positive deviations in  $\text{CO}_2$  during downdrafts (e.g. at 17–18 min) and negative deviations in  $\text{CO}_2$  during updrafts (e.g. at 13–14 min) contribute to negative flux values. The hourly mean turbulent flux in the example is  $-0.21 \text{ ppm m s}^{-1}$  ( $-7.2 \text{ } \mu\text{mole C m}^{-2} \text{ s}^{-1}$  or  $3.1 \times 10^{-7} \text{ kg CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ). The negative sign means that, on average, turbulent eddies transport  $\text{CO}_2$  towards the Earth's surface, where  $\text{CO}_2$  is consumed by photosynthesis. This example also illustrates the variety of units used to describe  $\text{CO}_2$  fluxes. We present units of both mass and molar flux when possible, since both are fairly common.



**Figure 1:** Schematic diagram of the eddy-covariance method of measuring the surface flux  $F_0$  or net ecosystem–atmosphere exchange (NEE) of a scalar such as  $\text{CO}_2$ . An idealized instrumented tower and flux measurement sensor that rises a height  $z_m$  above the Earth’s surface is shown.

Molar flux units ( $\mu\text{mole C m}^{-2} \text{ s}^{-1}$ ) are most common in the ecological literature. Molar mixing ratios (moles  $\text{CO}_2$  per million moles dry air, ppm) are common units in studies of atmospheric composition and transport. Further eddy covariance examples can be found in Ref. [10].

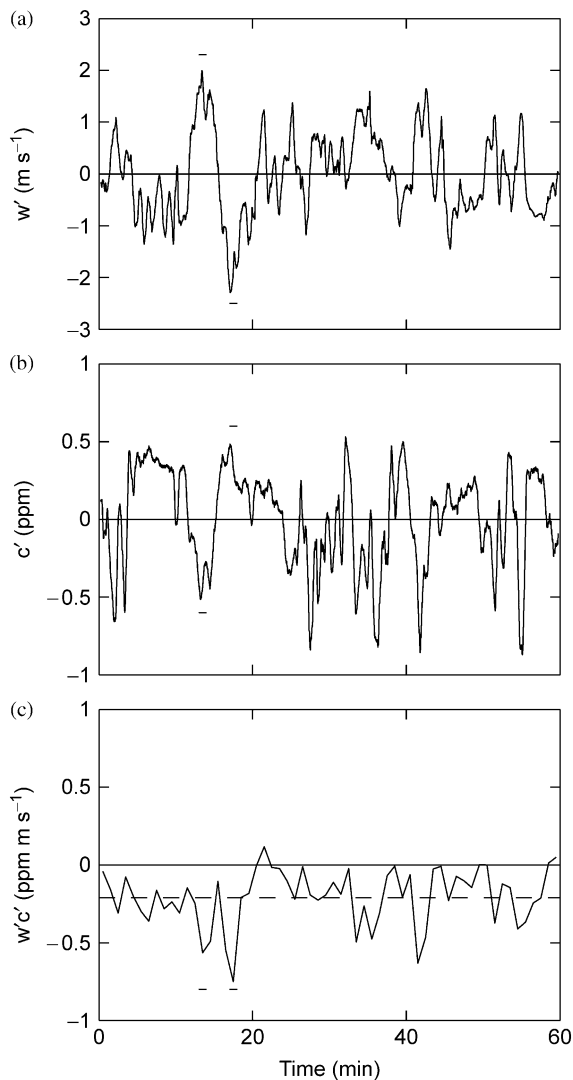
#### **Area Represented by EC Flux Measurements: The Flux Footprint**

An EC measurement captures fluxes corresponding to surface areas upwind of a tower, with areas closer to the tower being weighted more heavily. The per unit contribution to surface flux (either a positive or negative flux) and area of each element of upwind surface to the flux at a given point downwind is called the “flux footprint” [20–22].

The mass conservation equation of a diffusing material in the atmosphere is linear, which gives it the attractive mathematical property of superposable solutions. This allows multiple sources of  $\text{CO}_2$  to be treated by the superposition of the solutions for individual sources. It also enables a spatially distributed source on the surface to be treated as the superposition of a number of individual point sources. Horst and Weil [20] used this superposition property to rigorously define a flux footprint function  $f$  that through a convolution integral relates  $F_m(x_m, y_m, z_m)$ , the vertical turbulent flux of the diffusing material measured at position  $(x_m, y_m, z_m)$ , to  $F_0(x, y, 0)$ , the upwind spatial distribution of its surface flux:

$$F_m(x_m, y_m, z_m) = \int_{-\infty}^{\infty} \int_{-\infty}^{x_m} F_0(x', y', 0) f(x_m - x', y_m - y', z_m) dx' dy', \quad (6)$$

where  $x'$  and  $y'$  are dummy variables. This equation indicates that the measured flux at height  $z_m$  is the integral of contributions from all upwind surface elements; the flux footprint  $f$  gives the weighting of each elemental surface flux. In addition to environmental factors such as wind speed, wind direction, surface roughness, and stability,  $f$  depends on both the height  $z_m$  at which the downwind flux is measured and the upwind position on the surface. It is conventional to assume that the turbulent flow is horizontally homogeneous, so that the footprint function depends only on the separation between the measurement point



**Figure 2:** Example of 1 h of data measured at 122 m on a tower in northern Wisconsin during the afternoon on June 15, 1999. 30-s averages of (a) deviations from the mean vertical velocity and (b) deviations from the mean CO<sub>2</sub> concentration. (c) 1-min averages of the eddy covariance. In each panel, small horizontal lines indicate the times corresponding to the examples of an updraft and downdraft described in the text. The mean EC for the hour in this example is  $-0.21 \text{ ppm m s}^{-1}$  (shown as a dashed line in (c)).  $1 \text{ ppm CO}_2 = 1.5 \times 10^{-6} \text{ kg CO}_2$  at a typical air density for the Earth's surface ( $1 \text{ kg air m}^{-3}$ ).

and each elemental piece of upwind surface. With the mean wind in the  $x$ -direction, the streamwise separation is  $x_m - x'$  and cross-wind separation is  $y_m - y'$ , as indicated in Eq. (6). When  $z_m$  is in the surface or “constant-flux” layer, the integral of  $f$  over all upwind surface area is 1. For cases where the surface flux  $F_0$  is uniform in space, Eq. (6) simplifies to  $F_m = F_0$ .



Horst and Weil [20] showed that  $f$  can be interpreted as the solution to a point-source problem. If the upwind surface flux is produced by a point source of emission rate  $Q$  (mass/time) at position  $(x_s, y_s, 0)$ , so that

$$F_0(x', y', 0) = Q\delta(x' - x_s)\delta(y' - y_s), \quad (7)$$

then Eq. (6) becomes

$$F_m(x_m, y_m, z_m) = f(x_m - x_s, y_m - y_s, z_m)Q, \quad (8)$$

and

$$f(x_m - x_s, y_m - y_s, z_m) = \frac{F_m(x_m, y_m, z_m)}{Q}. \quad (9)$$

Thus, the footprint function  $f$  at a point  $(x_s, y_s)$  on the surface upwind can be interpreted as  $F_m(x_m, y_m, z_m)$ , and the flux at the downwind measurement point, divided by  $Q$ , the strength of the point source on the surface at the upwind point  $(x_s, y_s)$ .

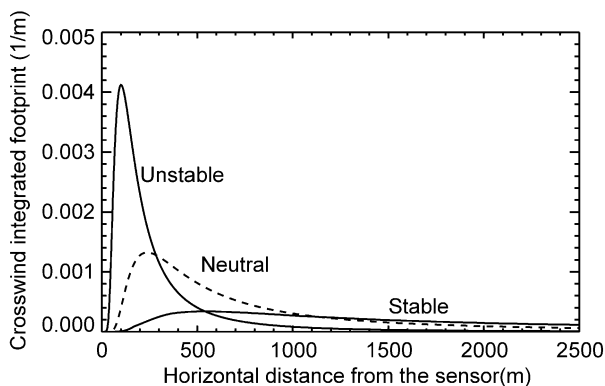
There is no known way to find solutions for statistical properties such as  $f$  from the equations governing turbulent flow; any such calculations require that the equations can be approximated in some way before they are solved [20]. Horst and Weil [20] have done such approximate calculations for the footprint function over a range of meteorological conditions in the surface layer. The evidence to date [7,23] suggests these calculations are reliable to at least within a factor of two in typical field conditions.

The lateral extent of the flux footprint  $f$ , the area monitored by an EC measurement, is approximately  $4\sigma_v x_u/U$ , where  $\sigma_v$  is the root mean square lateral wind velocity,  $x_u$  is the upwind extent of the footprint, and  $U$  is the mean wind speed [8,23]. This width is typically roughly equal to  $x_u$ , the upwind extent. The upwind extent is affected by both the measurement height above the surface  $z_m$  and the atmospheric stability; typical values of the upwind extent of the flux footprint range from  $(10-100)z_m$ , depending strongly upon atmospheric stability. A maximum upwind extent is of order 10 km for a very tall tower [4, 24]. Airborne EC can be used to estimate flux from very large regions [25,26], but only for a short time.

Examples of the upwind extent of the footprint for a 20-m tower as a function of atmospheric stability are shown in Figure 3. Unstable atmospheric conditions correspond to very convective conditions, i.e. strong sunlight and a large rate of buoyant production of atmospheric turbulence, and in general a well-mixed atmosphere. In unstable conditions the footprint function has a smaller spatial extent, meaning that fluctuations in mixing ratio are rapidly homogenized and the flux measured at the tower is influenced by areas closer to the tower. Neutral atmospheric stability corresponds to conditions when wind shear is a dominant source of atmospheric turbulence (e.g. an overcast day). Stable atmospheric conditions represent conditions governed by air near the Earth's surface that is colder than air aloft, as can occur through net radiative cooling of the Earth's surface. In neutral and stable conditions, vertical mixing is weak, and mixing-ratio fluctuations are transported long distances before becoming homogenized by turbulence. When cooling is very strong and winds weak, lateral flows can become strong and traditional application of the EC method becomes problematic. Atmospheric stability in the surface layer is quantified via a parameter known as the Monin-Obukhov length [10] and is readily estimated operationally by basic observations such as incoming solar radiation and wind speed [27].

#### ***Application of Eddy Covariance to Volcanic Regions***

Although EC has been used extensively in meteorological and ecological applications, recent work applying it to volcanic regions (e.g. Refs. [5-8]) is more relevant to detection of stored CO<sub>2</sub> leaks. In most ecological applications, the source or sink of CO<sub>2</sub> is assumed to be homogeneous across the Earth's surface. In volcanic applications, CO<sub>2</sub> fluxes are often spatially heterogeneous. The use of the method can be further complicated by significant topography and large surface heat fluxes. Nevertheless, EC measurements have compared well with chamber measurements under a broad range of atmospheric conditions (e.g. Refs. [5-8]). Emission of CO<sub>2</sub> from a volcanic area is analogous to a distribution of leaks from a belowground CO<sub>2</sub> reservoir. The measured EC flux is the convolution of the surface fluxes and the footprint function, Eq. (6), as shown in Figure 4 for a specific example [6]. Werner et al. [8] calculated that EC could be used



**Figure 3:** Cross-wind ( $y$ -direction) integrated footprint function  $f$  for a 20-m tower as a function of upwind distance ( $x$ ) for different atmospheric stabilities. The calculation is based on Horst and Weil, [20], and assumes a surface roughness of 0.1 m and a displacement height of 0 m. The upwind distance plotted here scales roughly linearly with the measurement height.

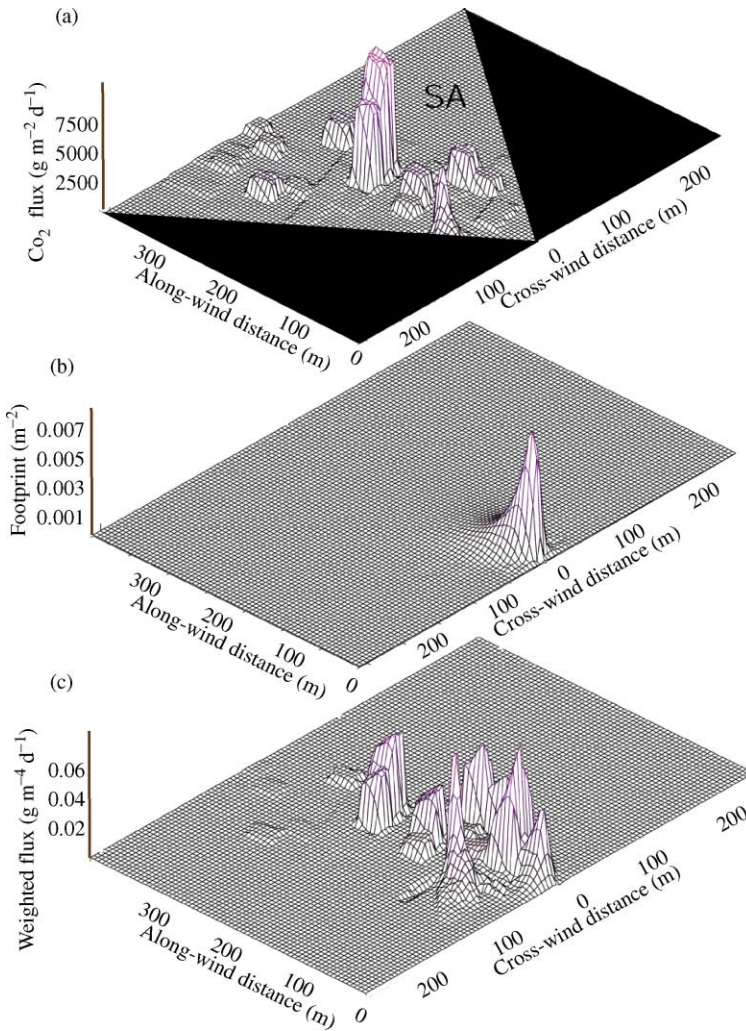
to detect even a small volcanic eruption or a slow volcanic leak. We shall extend this approach to detection of leaks from geologic storage after describing the instrumentation.

#### *Typical Instrument Setup*

EC flux measurements in the atmospheric surface layer require instruments with fast time-response (10-Hz measurement frequency is typically sufficient) and good precision. The most common sensors used for EC measurements of  $\text{CO}_2$  fluxes are infrared gas analyzers, such as those made by LI-COR, Inc., Lincoln, NE, USA. Both open-path (e.g. LI-COR 7500) and closed-path (e.g. LI-COR 7000) instruments have been used for EC measurements. The instruments are robust and stable for long periods of time (months to years) and relatively easy to deploy. Periodic calibration with gases of known  $\text{CO}_2$  mixing ratio is required, though this can be done quite infrequently (e.g. monthly) as absolute accuracy in the mixing ratio measurements is not required. For closed-path systems, a reference gas is required for leak detection. This can be either a gas with a known  $\text{CO}_2$  mixing ratio (differential mode) or a non-absorbing gas such as  $\text{N}_2$  (absolute mode). It is also necessary that air be pumped relatively rapidly through the cell to ensure sufficient time-response at the desired measurement frequency. Long-term application of closed-path infrared gas analyzers for flux measurements is described by several authors (e.g. Refs. [19,28]). Open-path measurements are also common in the  $\text{CO}_2$  flux literature (e.g. Ref. [8]).

Also required for EC flux measurements is a sonic anemometer (e.g. Campbell Scientific Inc., Model CSAT3, Logan, Utah) to measure the vertical velocity. This instrument measures orthogonal (component) wind speeds and sonic temperature which can be converted to virtual temperature by determining the time of flight of sound between pairs of ultrasonic signal transducers. Since the  $\text{CO}_2$  and wind sensors are not perfectly co-located, there is often a small lag in time between the two data streams. By maximizing the correlation coefficient of  $w'$  and  $c'$ , the lag between the signals can be determined [7,19] and EC fluxes can be computed.

A typical data recovery rate for a flux tower in the AmeriFlux network is 70%, including losses due to instrument failure and exclusion of data during periods in which vertical mixing is very weak (e.g. Ref. [29]). Data exclusion is more frequent at night when the atmosphere is typically stable (as a result of radiational cooling from the Earth's surface) and thus mixing is weak. Long data gaps can be avoided with periodic instrument maintenance.



**Figure 4:** An example of the sensitivity of EC measurements to heterogeneous sources distributed within the EC flux footprint, reprinted from Ref. [6] with the permission of the author. (a) CO<sub>2</sub> flux distribution as measured by chambers in volcanic area in Yellowstone National Park. The source area (SA) contributing to the flux measured at a 2-m tower located at  $x = 0$ ,  $y = 0$  is also shown.  $1 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1} = 0.26 \text{ } \mu\text{mole C m}^{-2} \text{ s}^{-1}$ . (b) Flux footprint for the 2-m tower for a moderately unstable atmosphere. (c) Weighted flux, a convolution of the flux footprint and the flux distribution. An integral of the weighted flux over the surface yields the observed EC flux at the 2-m tower (Eq. (6)).

## LEAK DETECTION

Leak detection can be accomplished by establishing background fluxes for a site, then continuously monitoring the site for significant deviations from these background fluxes. This is a significantly different problem than that of measuring long-term NEE of CO<sub>2</sub>, leading to differences in site selection criteria and

treatment of missing data. Quantification of the leak can be attempted with multiple flux measurements using one or more measurement systems. Details of this overall approach follow.

### **Site Selection**

Site selection for belowground CO<sub>2</sub> storage depends primarily on geology since a deep storage formation is required. Also, a remote location is preferable, allowing for time to react to a leak, as well as avoiding anthropogenic sources of CO<sub>2</sub> (such as those from power plants, nearby roads, etc.). While flat terrain and an extensive fetch of uniform vegetation are important in order to precisely measure the magnitude of fluxes [30], for leak detection we only need to detect changes and thus do not have such terrain and vegetation requirements. The characterization of background fluxes described below assumes a uniform fetch where most of the variance in background fluxes is described by parameters that influence ecological metabolism, such as temperature and sunlight. A highly heterogeneous site may require further segregation of background fluxes according to the flux footprint (e.g. in a simple case, dividing background flux data into a small number of distinct wind directions). Other than complicating the characterization of background fluxes, however, a non-ideal site in terms of terrain and vegetation cover does not prevent the application of EC to the problem of leak detection.

### **Background (Ecological) Fluxes**

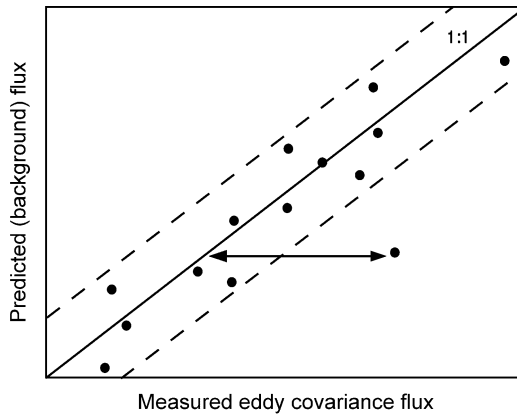
A first step in leak detection is the establishment of background (ecological) CO<sub>2</sub> fluxes for the area near a CO<sub>2</sub> belowground reservoir. Predicting the range of variability in ecological NEE of CO<sub>2</sub> is necessary if the area-integrated flux (Eq. (6), Figure 4) from a hypothesized leak is not significantly larger than the ecological background flux. In order to obtain continuous datasets of NEE for ecological studies, methods based on environmental conditions are currently employed to “gap fill” the missing data (e.g. Refs. [4,29]), and similar techniques can be used to predict environmental (background) fluxes for the purposes of leak detection. EC measurements at a potential leak site must be made before CO<sub>2</sub> injection, or at a second site with a similar flux footprint and vegetation. The measured ecological fluxes can then be characterized as a function of environmental conditions that describe a large fraction of the variance in ecosystem–atmosphere CO<sub>2</sub> exchange. The resulting parameterization can be used with measurements of radiation and temperature to create “modeled” fluxes which can then be compared to ongoing EC measurements at the site where leak detection is required. Measured fluxes that lie outside the range of natural variability, as described by the “gap-filling” functions, can be established as possible leaks (Figure 5). We shall now describe the details of establishing a parameterization for NEE.

In systems without underground sources of CO<sub>2</sub> (i.e. lacking both volcanic activity and leaky underground storage), the surface flux, or NEE of CO<sub>2</sub>, depends primarily on temperature, light, and the amount of green vegetation. Hourly ecological CO<sub>2</sub> fluxes are typically within the range of  $\pm 20 \mu\text{mole C m}^{-2} \text{ s}^{-1}$  during the growing season, with winter-season fluxes being much smaller ( $\pm 2 \mu\text{mole C m}^{-2} \text{ s}^{-1}$ ) in regions where snow and ice are common [4,30,31].

An established method [4] for predicting ecological fluxes is based on well-documented [32,33] soil and plant responses to soil or air temperature ( $T$ ) and photosynthetically active radiation (PAR). The equation

$$\text{NEE} = a_0 e^{a_1(T-a_2)} + b_2 - \frac{b_0 \text{PAR}}{(\text{PAR} + b_1)} \quad (10)$$

can be fitted to measurements of  $T$ , PAR, and NEE of CO<sub>2</sub> on data obtained without the possibility of leaks.  $a_0$ ,  $a_1$ ,  $a_2$ ,  $b_0$ ,  $b_1$ , and  $b_2$  are parameters describing characteristics of the ecosystem. Parameters include photosynthetic light response ( $b_0$ ), base respiration rate ( $a_0$ ), temperature sensitivity of respiration ( $a_1$ ), and photosynthetic light saturation level ( $b_1$ ). Another method, similar to the parameterization described above, is to produce a look-up table based on measurements of PAR and air temperature at a site [29]. Both parameterizations and look-up tables produce small errors when the amount of missing data is small [29]. The parameters obtained from fitting Eq. (10) to tower flux data are similar for similar ecosystems [34–36].



**Figure 5:** Schematic diagram of leak detection methodology. The  $x$ -axis represents ecological background fluxes predicted by characterizing the ecosystem fluxes as a function of environmental conditions (Eq. (10)).

The  $y$ -axis represents hypothesized hourly EC flux observations from a measurement system over a geologic sequestration site. The dashed line represents random variability in EC fluxes caused by limited sampling of a turbulent atmosphere [39]. Measurement fluxes that lie outside the range of neutral variability can be established as leaks or other anomalous fluxes.

The parameters (or lookup table values) vary slowly as a function of season, in concert with ecological processes such as leaf-out and leaf-fall [37]. A large fraction of the hour-to-hour variability in tower-based EC flux measurements over ecosystems can be explained by variations in environmental conditions, particularly PAR [29,38]. Most of the remaining variability can be explained by limited sampling of a turbulent field [39]. Hour-to-hour variability in ecological  $\text{CO}_2$  fluxes is typically similar to or less than the mean flux magnitude [19].

#### *Leak Detection Sensitivity*

A leak from an underground  $\text{CO}_2$  storage reservoir can be detected only if its flux increases the total flux significantly beyond the range of background (ecological) fluxes normally observed in the specific environment of the measurement. This concept is illustrated in Figure 5. A detection limit of about  $10 \mu\text{mole C m}^{-2} \text{s}^{-1}$  ( $4.4 \times 10^{-7} \text{ kg CO}_2 \text{ m}^{-2} \text{s}^{-1}$ ) is realistic for hourly measurements in a biologically active area. Longer sampling times reduce the detection limit since the variability due to turbulence is random and decreases with increased time-averaging [39], thus narrowing the range of random flux variability shown in Figure 5.

We turn to volcanic emissions of  $\text{CO}_2$  as an analogue to leaks from belowground  $\text{CO}_2$  reservoirs. Emissions from volcanic activity can be quite large: a flux of  $5 \times 10^{-5} \text{ kg m}^{-2} \text{s}^{-1}$  ( $\sim 1 \times 10^3 \mu\text{mole C m}^{-2} \text{s}^{-1}$ ) was measured in an area with significant tree kill [13] fluxes between  $10^{-6}$  and  $10^{-4} \text{ kg m}^{-2} \text{s}^{-1}$  ( $20\text{--}2 \times 10^3 \mu\text{mole C m}^{-2} \text{s}^{-1}$ ) were measured in Yellowstone [7], and the Lake Nyos 1986 disaster was associated with fluxes near  $10^{-2} \text{ kg m}^{-2} \text{s}^{-1}$  or  $2 \times 10^5 \mu\text{mole C m}^{-2} \text{s}^{-1}$  [40]. Emissions of this magnitude are readily detectable using EC [7, 8]. Saturation of the  $\text{CO}_2$  sensors (i.e.  $\text{CO}_2$  mixing ratios that exceed the range of sensitivity of the chosen gas analyzer) is possible, but did not occur in the geologic measurements by Werner [6–8], even though there were large variations in the  $\text{CO}_2$  flux. If sensor saturation does occur, this would provide the necessary leak detection, though the EC flux measurement would be rendered invalid.

We shall estimate leaks from geologic storage based on estimated reservoir size, and consider both slow and catastrophic reservoir failure. According to Herzog et al. [41],  $\text{CO}_2$  storage is economical as

long as the leak rate does not exceed 2.5% of the total CO<sub>2</sub> stored in 100 years. Assuming 100 million tonnes of stored CO<sub>2</sub> as a typical reservoir size [13], leakage of 1% of this total reservoir amount over an area of 10 m<sup>2</sup> spread evenly over a 100-year time period would result in a flux on the order of 10<sup>-2</sup> kg m<sup>-2</sup> s<sup>-1</sup> (2 × 10<sup>5</sup> μmole C m<sup>-2</sup> s<sup>-1</sup>), four orders of magnitude larger than typical growing season ecological fluxes. A diffuse leak of 1% of the entire reservoir (e.g. through faults) over an area of (300 m)<sup>2</sup> = 10<sup>5</sup> m<sup>2</sup>, and distributed over 100 years, would lead to a flux of order 10<sup>-6</sup> kg m<sup>-2</sup> s<sup>-1</sup> (20 μmole C m<sup>-2</sup> s<sup>-1</sup>), which is of the same magnitude as vigorous ecological fluxes. This would be detectable if background ecological fluxes are characterized in advance via typical sunlight and temperature relations (Eq. (10)). This crude analysis implies that eddy covariance is a promising technology for monitoring CO<sub>2</sub> reservoirs both for hazardous leaks and for leaks that would damage the economic viability of belowground storage.

Leak detection could fail in the case of a sudden, catastrophic leak during low-turbulence or unfavorable wind conditions. EC measurements might not promptly detect a sudden event if, at the time of the event, turbulent mixing was very weak or the flux footprint did not encompass the leak area. Relatively short gaps in the data are not necessarily problematic for detecting and quantifying slow leaks, but could prevent timely detection of such a catastrophic event. It seems prudent, therefore, to combine EC with chamber and/or mass balance [42] measurements near sites where leaks are possible.

### LEAK QUANTIFICATION

Leak detection differs from leak quantification. This is evident in Figure 4c, which shows the weighted contributions of spatially distributed surface fluxes to the EC flux measured at a tower site, the result of a convolution of the flux footprint  $f$  and the surface flux field  $F_0(x, y, 0)$ . As is clear from this figure, the location of a source of CO<sub>2</sub> has a strong impact on the flux measured at the sensor. The precise location and magnitude of a CO<sub>2</sub> source from geologic storage are not likely to be known. In this case a single observation, while likely to detect the leak if it falls within the main region of the flux footprint, will not allow the position and magnitude of the leak to be quantified. Therefore, (1) it is important that the potential source region for a leak be located within the tower flux footprint and further (2) quantification of leaks will either require independent verification of their location (e.g. chamber measurements once a leak has been detected via EC), or the application of multiple EC measurements with different flux footprints. Some combination of these approaches is possible. Multiple EC measurements with different flux footprints can be used to identify the magnitude and location of a leak because a large number of independent observations ( $F_m$ , Eq. (6)) can be satisfied by only a limited number of possible source distributions ( $F_0$ ). This could be accomplished with multiple flux towers. Alternatively, if the source is relatively steady over time, a single tower will provide measurements that are mathematically equivalent to multiple towers since the flux footprint changes over time because of changes in wind direction and stability. It is likely, therefore, that a small number of flux towers clustered around potential leak locations can provide accurate leak detection as well as leak quantification, though the latter will be more challenging.

### CONCLUSIONS

The eddy-covariance method for monitoring earth-atmosphere CO<sub>2</sub> exchange can be used to measure fluxes with hourly temporal resolution over areas of order 10<sup>4</sup>–10<sup>6</sup> m<sup>2</sup>. Instrumentation is robust and can be deployed in remote locations to collect data continuously. Suitable meteorological conditions exist on a daily basis at most locations and on average for roughly three-quarters of any given day. The method has been shown to be able to retrieve volcanic emissions in field tests [8].

We judge the method also as promising for the monitoring of leakage from geologic storage reservoirs. Our estimates are based on assumptions regarding reservoir size, area of leakage, and the total amount of CO<sub>2</sub> that escapes over an assumed time. These parameters are quite uncertain, but we have chosen what we believe characterize two important limits of the issue—catastrophic leakage and economically undesirable leakage. These leakage rates are compared to ecological fluxes which serve essentially as background noise for this application. We conclude that, using EC, CO<sub>2</sub> storage could be verified to be within the limits set by the economic viability of the storage. More careful assessment

of likely leakage rates and useful detection limits, and field test of this approach are warranted based on our findings.

## RECOMMENDATIONS

This work should be followed by a more accurate analysis of the likely magnitude, area and duration of potential leaks from geologic storage of CO<sub>2</sub>. This initial study has shown promise in utilizing EC to monitor storage sites, but is dependent upon rough estimates of leak rates and areas of emission.

Second, a discussion of the need for leak detection only, or leak quantification is needed. Both are possible using EC methods, but leak quantification is more technically demanding. The methodology should be evaluated in light of the cost of monitoring and the economic and environmental benefits of CO<sub>2</sub> storage. These discussions will guide future system design and testing.

Finally, field testing is warranted, particularly for the topic of leak quantification. Leak detection should be possible within the ranges of emissions and footprint areas described in this chapter. Leak detection experiments should be focused primarily on determining the operational costs and benefits of EC methods. Leak quantification, a more challenging technical problem, should be demonstrated in the field, followed by evaluation of the operational costs and benefits.

## NOMENCLATURE

$a_0, a_1, a_2, b_0, b_1, b_2$	NEE fit parameters
$c$	CO <sub>2</sub> mass density in air
$\bar{c}$	mean CO <sub>2</sub> mass density in air
$c'$	fluctuations in the CO <sub>2</sub> mass density in air about the mean
EC	eddy correlation
$f$	footprint function
$F_0, F_m$	vertical turbulent flux of CO <sub>2</sub> at heights $z_0, z_m$
$L$	Monin–Obukhov length
NEE	net ecosystem–atmosphere exchange of CO <sub>2</sub>
PAR	photosynthetically active radiation
$S_C$	source or sink of CO <sub>2</sub> in the atmosphere
$T_s$	soil temperature
$Q$	point source emission rate
$u, v, w$	wind speeds: along-wind, cross-wind and vertical
$\bar{u}, \bar{v}, \bar{w}$	mean wind speeds
$u', v', w'$	fluctuations in wind speed about the mean
$\overline{u'c'}, \overline{v'c'}, \overline{w'c'}$	turbulent fluxes of CO <sub>2</sub> in the along-wind, cross-wind and vertical directions
$\overline{w'c'}_{z_m}, \overline{w'c'}_{z_0}$	vertical turbulent flux of CO <sub>2</sub> at heights $z_m, z_0$
$x, y, z, t$	along-wind, cross-wind and vertical directions, and time
$x_m, y_m, z_m$	position of a measurement
$x_s, y_s$	position at the Earth's surface
$x_u$	upwind distance
$z_0$	surface of the Earth
$\delta$	Kronecker delta function
$\sigma_v$	root mean square lateral wind velocity
$x', y'$	dummy variables

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