

Measurement of advective soil gas flux: results of field and laboratory experiments with CO₂

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Abstract A multi-channel, steady-state flow-through (SSFT), soil-CO₂ flux monitoring system was modified to include a larger-diameter vent tube and an array of inexpensive pyroelectric non-dispersive infrared detectors for full-range (0–100 %) coverage of CO₂ concentrations without dilution. Field testing of this system was then conducted from late July to mid-September 2010 at the Zero Emissions Research and Technology project site located in Bozeman, Montana, USA. Subsequently, laboratory testing was conducted at the Pacific Northwest National Laboratory in Richland, WA, USA using a flux bucket filled with dry sand. In the field, an array of 25 SSFT and 3 non-steady-state (NSS) flux chambers was installed in a 10 × 4 m area, the long boundary of which

was directly above a shallow (2-m depth) horizontal injection well located 0.5 m below the water table. Two additional chambers (one SSFT and one NSS) were installed 10 m from the well for background measurements. Volumetric soil moisture sensors were installed at each SSFT chamber to measure mean moisture levels in the top 0.15 m of soil. A total flux of 52 kg CO₂ day⁻¹ was injected into the well for 27 days and the efflux from the soil was monitored by the chambers before, during, and for 27 days after the injection. Overall, the results were consistent with those from previous years, showing a radial efflux pattern centered on a known “hot spot”, rapid responses to changes in injection rate and wind power, evidence for movement of the CO₂ plume during the injection, and nominal flux levels from the SSFT chambers that were up to sevenfold higher than those measured by adjacent NSS chambers. Soil moisture levels varied during the experiment from moderate to near saturation with the highest levels occurring consistently at the hot spot. The effects of wind on measured flux were complex and decreased as soil moisture content increased. In the laboratory, flux-bucket testing with the SSFT chamber showed large measured-flux enhancement due to the Venturi effect on the chamber vent, but an overall decrease in measured flux when wind also reached the sand surface. Flux-bucket tests at a high flux (comparable to that at the hot spot) also showed that the measured flux levels increase linearly with the chamber-flushing rate until the actual level is reached. At the SSFT chamber-flushing rate used in the field experiment, the measured flux in the laboratory was only about a third of the actual flux. The ratio of measured to actual flux increased logarithmically as flux decreased, and reached parity at low levels typical of diffusive-flux systems. Taken together, the results suggest that values for advective CO₂ flux measured by SSFT and NSS chamber

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systems are likely to be significantly lower than the actual values due to back pressure developed in the chamber that diverts flux from entering the chamber. Chamber designs that counteract the back pressure and also avoid large Venturi effects associated with vent tubes, such as the SSFT with a narrow vent tube operated at a high chamber-flushing rate, are likely to yield flux measurements closer to the true values.

Keywords Geologic carbon sequestration · Soil gas flux · Continuous monitoring · Zero Emissions Research and Technology Program · ZERT · Venturi effect · Carbon dioxide · CO₂

Introduction

Geological sequestration has the potential capacity and longevity to significantly decrease the amount of anthropogenic CO₂ introduced into the atmosphere by combustion of fossil fuels such as coal (White et al. 2003, 2005; McGrail et al. 2006). Effective sequestration, however, requires the ability to verify the integrity of the reservoir and ensure that potential leakage rates are kept to a minimum. A critical part of this ability involves understanding the pathways by which CO₂ migrates to the surface, both in assessing the risks associated with siting a particular reservoir and in developing remediation approaches if the reservoir seal should fail. Field experiments to characterize these pathways, such as those conducted for the near-surface region at the Zero Emissions Research and Technology (ZERT) project test site in Bozeman, MT, USA require a flexible CO₂ monitoring system that can accurately and continuously measure soil-surface CO₂ fluxes for multiple sampling points at concentrations ranging from background levels to near 100 %. To meet this need, the authors have been developing and field-testing a steady-state flow-through (SSFT), multi-chamber, off-grid, remotely controlled system capable of both spatial and temporal monitoring of CO₂ fluxes for extended periods (Amonette and Barr 2009; Amonette et al. 2010).

In a field test of the previous measurement system during the summer of 2008 (Amonette et al. 2010), results were limited to flux levels below 500 $\mu\text{mol m}^{-2} \text{day}^{-1}$, well below levels observed by co-located commercial non-steady-state (NSS) chambers, and were considered to be biased by the inducement of an 8 Pa vacuum inside the chamber stemming from use of a narrow vent tube. Consequently, the system was modified to allow measurement across the full CO₂ concentration range and to decrease the vent-induced vacuum to <1 Pa. This modified system was tested during an intentional release of CO₂ at the ZERT site during the summer of 2010. In addition to the SSFT

chambers, the site was instrumented with volumetric moisture sensors in the top 15 cm of soil, a multi-level wind tower that monitored velocities at distances of 0.35–2 m above the surface, and four commercial NSS chambers. To help explain the complex effects of wind, soil moisture, and chamber operating parameters on fluxes measured during the field experiment, a series of flux-calibration tests was also conducted in the laboratory using the flux-bucket design of Evans et al. (2001). Here, the results of the field and laboratory experiments with the modified SSFT system are reported. These results show that chamber-based flux measurement systems significantly underestimate advective CO₂ fluxes unless steps are taken to decrease backpressure inside the chamber.

Materials and methods

Flux measurement

Details of the SSFT flux chamber design prior to modification and of the flux calculations have been reported elsewhere (Amonette et al. 2010; Amonette and Barr 2009). Two modifications were made for this study. The CO₂/H₂O gas analyzer was replaced by an array of four nondispersive infrared pyroelectric detectors (IRC-A1 Carbon Dioxide Infrared Sensor, Alphasense, Ltd., Great Notley, UK, <http://www.alphasense.com>) having different ranges of sensitivity to CO₂ (i.e., maximum CO₂ concentrations of 0.5, 5, 20, and 100 % by volume). These were mounted serially to measure CO₂ concentrations in air flowing through a narrow channel (Fig. 1, ESM only). The second modification was to replace the narrow (1.59 mm) chamber vent by a tube having a diameter of 3.6 mm and length of 5.8 cm, based on calculations of Hutchinson and Mosier (1981) for diffusion flux measurements by SSFT systems. This modification decreased the pressure drop across the vent to well below 1 Pa at the chamber flushing rate used in the field experiment.

The signal from the pyroelectric detectors was quite sensitive to temperature and required correction before being used to calculate the flux. The detector temperature was not recorded during the field experiment, and thus had to be estimated. This process involved a laboratory calibration of the temperature of the detector inside the measurement and control system with the ambient temperature. Ambient temperature data collected continuously at 5-min intervals at the ZERT site were then used to estimate the detector temperature and thereby the size of the signal correction.

In addition to the steady-state flux measurement system, an array of four NSS flux chambers (Licor LI-8100-104 Long-Term Chambers, LI-COR Biosciences, Lincoln, NE, USA) was also deployed. These were mounted on 10-cm

collars that extended 7.5 cm into the soil. The NSS chamber vents had a tapered cross-section as described in Xu et al. (2006) to minimize Venturi effects.

Field experiment

Locations of the flux chambers, central measurement and control system, N₂ supply used for purging, and the horizontal injection well at the ZERT field site are shown in Fig. 1. Twenty-five SSFT chambers were deployed in five rows spaced 2.5 m apart and oriented perpendicularly to the horizontal well. Spacing between chambers in each row was 1 m. An additional SSFT chamber was located 10 m from the injection well to provide a background measurement. The four NSS chambers were paired with SSFT chambers along the middle row at distances of 0, 1, 3, and 10 m from the injection well and deployed 0.5 m south-west of the steady-state chambers.

As discussed by Spangler et al. (2010) and Oldenburg et al. (2010), the water table at the ZERT site varies during the year but typically is on the order of 1.5 m below the surface during mid-summer. Because the injection well is about 2 m below the surface, CO₂ is injected below the water table, and the pressure differences resulting from small changes in injection-well pipe elevation lead to localized emissions or “hot spots” at the higher end of each injection zone isolated by packers. The chamber in the middle row positioned directly above the injection well marks the boundary between two such zones, and is in the center of a known high-flux region.

The test injection was started at 12:35 PM MST on 19 July 2010 (ordinal day 200.523), and continued for exactly 27 days (672 h), ending at 12:35 PM on 15 August 2010

(ordinal day 227.524). The injection rate into the two packer zones encompassed by the monitoring array was maintained at 52.1 (±0.7) kg day⁻¹ except for a 260-min period on 31 July 2010 (starting at ordinal day 212.79) when main power was lost and the injection paused.

Concentrations of CO₂ in the SSFT flux chambers were monitored at 4.8-h intervals starting 3 days before the injection, continuing during the 27 days of the injection (672 h) and for 27 days after the injection. Flux data from the NSS chambers were collected at 30-min intervals starting a few h before the injection and continuing until 31 days after the injection. For better comparison with the SSFT data, the NSS data were plotted as a 5-h running average.

Meteorological data for the experiment, including barometric pressure, air temperature, relative humidity, and precipitation were collected at the ZERT-site weather station in the same manner as described in Spangler et al. (2010). Wind speed and direction data were collected by sonic anemometers mounted at 0.35, 0.85, and 1.5 m elevation above grade on a tower located 2 m southeast of the injection well (Fig. 1).

Laboratory experiments

At PNNL, a series of experiments was performed using a flux bucket identical to that described by Evans et al. (2001) (Fig. 2, ESM only). For most of these experiments, CO₂ (99.8 % purity) was metered into the bottom of the bucket at a nominal 2.0 l min⁻¹ using a N₂-calibrated mass flow controller (Omega FMA5516, <http://www.omega.com>). Calculations using this flow rate, the bucket geometry, and a correction factor of 0.74 for the heat capacity of the 99.8 % CO₂ yielded a known applied flux of 4,250 μmol m⁻² s⁻¹. The CO₂ then flowed through 25.4 cm of 20–30-mesh Ottawa sand (ASTM C778, US Silica Company, Ottawa, IL, USA) before entering the atmosphere at the top of the bucket. An SSFT flux chamber configured as in the field experiment (15-cm collar that extended 11.4 cm into the sand, 3.6-mm inside-diameter vent tube) was positioned in the center of the flux bucket (Fig. 2, ESM only). An aquarium pump was used to pump air from inside the chamber through the pyroelectric detector array and then into the atmosphere at a nominal flushing rate of 40 ml min⁻¹ (N₂ calibration) metered by a 0–50 ml min⁻¹ N₂ mass flow controller (Aalborg Instruments, <http://www.aalborg.com>). The actual chamber flushing rate was then calculated by correcting for measured CO₂ concentration. Variations on this basic flux-bucket experiment involved different values of CO₂ influx (0.021 and 0.178 l min⁻¹), different chamber flushing rates (17–460 ml min⁻¹) and collar depths (3.8, 6.4, and 8.9 cm sand depth), and the application of wind across either the vent tube only (using a 10.2-cm diameter improvised wind tunnel fabricated from

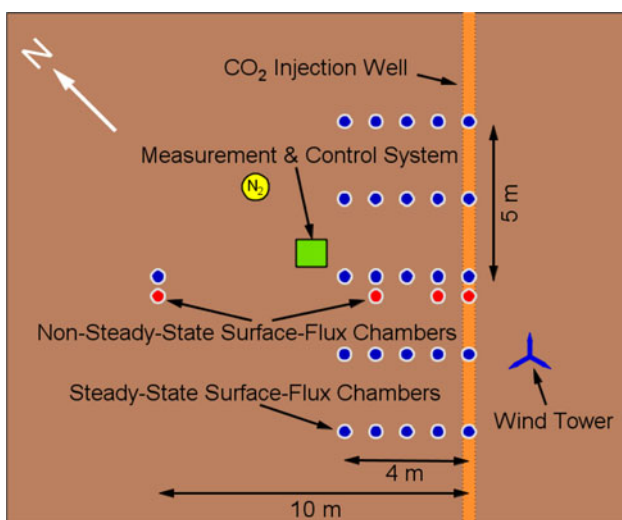


Fig. 1 Plan view of Summer 2010 field experiment at ZERT site in Bozeman, MT

plastic pipe) or the entire chamber/sand surface. Wind was applied horizontally using fans of different capacity and wind velocities at specific points were measured using a hand-held anemometer (Model 45118, Extech Instrument Corporation, Waltham, MA, USA, <http://www.extech.com>).

Results and discussion

Field experiment

Spatial patterns

The pattern of CO₂ efflux within the 4 × 10 m zone sampled by the SSFT-chamber array was highly localized (Fig. 2a) in agreement with previous observations (Amonette et al. 2010). On ordinal day 218.7, after 18 days of injection, five chambers accounted for 84 % of the total flux, with a single chamber located directly over the hot spot accounting for 35 % of the total flux from the 25 chambers in the array (Fig. 3, ESM only). Eight days later (i.e., ordinal day 226.3), the total flux measured in the array was about 30 % higher and the same five chambers accounted for 76 % of the flux. Relatively more flux was emitted from the northern portion of the array (Fig. 2b) suggesting that much of the increase was from degassing of CO₂-saturated groundwater that generally flows in that direction (Amonette et al. 2010; Spangler et al. 2010).

The volumetric H₂O content of the soil also formed a highly localized pattern centered on the hot spot after 26 days of injection (Fig. 2c). The singular enhancement of H₂O content at the hot spot continued until the injection ceased, whereupon it returned slowly to the levels measured for nearby chambers with much lower flux levels. Given the passage of CO₂ through about 0.5 m of water before encountering the vadose zone, it is likely that the CO₂ was saturated with H₂O and this, coupled with extremely high flux values, maintained a high soil-moisture content at the hot spot during the injection.

Temporal patterns

Unfortunately, a data logger programming error prevented storage of SSFT chamber flux data greater than about 45 μmol m⁻² s⁻¹ during the first 2 weeks of the injection. The mean of the CO₂ fluxes from seven “peripheral” chambers that maintained fluxes below 45 μmol m⁻² s⁻¹ during that period is plotted in Fig. 3. A distinctive diurnal signature is seen in these data, with amplitudes generally in the 5–8 μmol m⁻² s⁻¹ range. During the fourth week of the injection, however, flux levels roughly twice as high were measured, and these suggest the eventual diffusion of CO₂ into the peripheral regions.

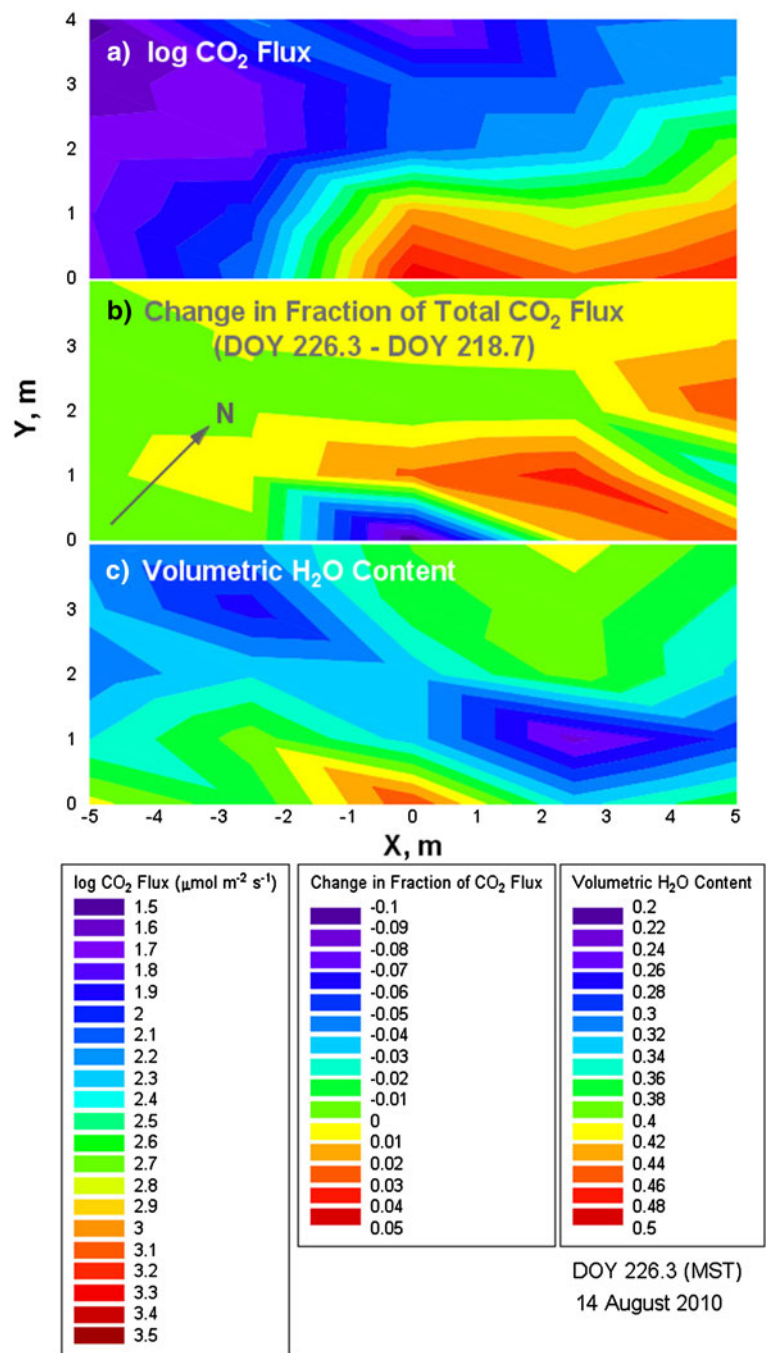
Additional variability, not on a diurnal cycle, is also present in the temporal data. Major anomalous decreases in CO₂ flux rates are present at about ordinal days 215, 217, 240, 251 and lesser decreases at days 202, 220 and 235, as indicated by dashed lines in Fig. 3. As in Amonette et al. (2010) wind power densities were calculated from the velocity data collected at 0.35 m (the height of the fresh air inlet to our flux chambers) assuming an altitude-adjusted constant air density of 1.0625 kg m⁻³. The non-diurnal flux anomalies are well-correlated to major wind events, as shown by the 12-h mean wind power density data (Fig. 3).

Further examination of the flux data suggests that the overall response to the wind events is muted during the last 2 weeks of the monitoring period (i.e., after ordinal day 240). For example, a wind event nearly as large as that at day 215–217, occurred at day 251 yet a much smaller response was seen in the flux data. Moreover, even the diurnal fluxes seem to be smaller than seen earlier. One possible explanation for this is a change in the air-filled porosity of the soil surface. According to this hypothesis, as the air-filled porosity decreases, the impact of wind on gaseous flux would also tend to decrease due to a loss of pore connectivity and shrinkage in air-filled pore diameter. To test this hypothesis, we used volumetric moisture data and values of 1.4 and 2.65 g cm⁻³ for bulk and particle densities, respectively, to calculate the air-filled porosity during the monitoring period. These data show fluctuations between about 30 and 40 % porosity during most of the experiment (inversely correlated with rain events), followed by a significant decrease to less than 10 % air-filled porosity by the end of the period as the soil neared saturation (Fig. 3). Wind events followed by significant rain events (as at day 251) thus significantly decrease the impact of the wind on soil gas flux. In contrast, the major wind event at day 215–217 had little or no precipitation associated with it, and the flux anomaly was much greater.

Comparison with NSS chambers

Time-resolved data for the paired SSFT and NSS chambers located 1 and 10 m from the injection well are shown in Fig. 4a, d. The chambers located 1 m from the well, represent a high advective-flux situation during the injection (ordinal days 200–227), but rapidly transition to a low diffusive-flux situation a few days after the injection ceases. The chambers located 10 m from the well represent a low, natural, diffusive-flux situation at all times and exhibit strong diurnal flux patterns. The pattern for the NSS chamber at 1 m, however, is weak during the first 2 weeks of the injection and not evident at all during the next 2 weeks. No diurnal pattern is evident in the SSFT flux data collected at 1 m distance from the injection well.

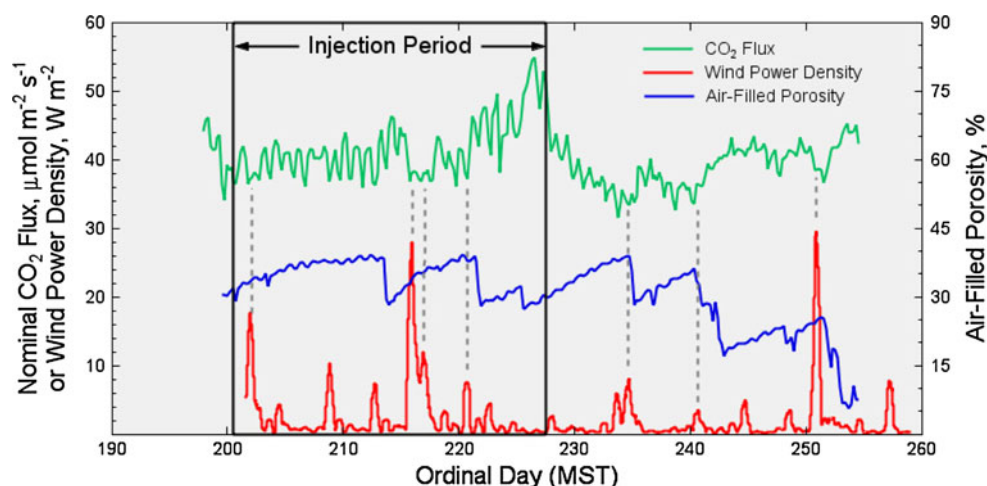
Fig. 2 Contour maps of **a** the log of the nominal CO₂ flux measured on ordinal day 226.3, **b** the change in the fraction of total CO₂ flux measured for the entire array on ordinal day 226.3 relative to that during the first day of the injection (DOY 218.7), and **c** the volumetric H₂O content of soil outside the SSFT flux chambers on ordinal day 226.3



An idea of the response of the two types of chambers to wind can be gauged from the wind power density data (12-h running mean) plotted in Fig. 4e. The response of the SSFT chambers is consistent with that shown in Fig. 3, i.e., a general decrease with prolonged strong wind events when air-filled porosity is above 20 %. The NSS chambers, however, show opposite responses to these events depending on whether the flux is advective or diffusive in nature. For example, during the major wind event on ordinal days 216–218, an *increase* in measured flux is seen

under advective conditions (Fig. 4b), whereas a *decrease* is observed under diffusive conditions (Fig. 4d). The increase in flux was surprising, given that the wind velocity (5-min mean) at 0.35 m above the ground surface, which is the approximate height of the vent, never exceeded 5.2 m s⁻¹ and thus stayed well below the 7 m s⁻¹ level at which the Venturi effect was expected (Xu et al. 2006). This result suggests that under advective flux conditions, the NSS chamber is much more susceptible to the Venturi effect than when only diffusive flux is being measured.

Fig. 3 Averaged temporal data (7 SSFT chambers with low flux rates) for nominal CO₂ flux, soil air-filled porosity (outside the chambers), and wind power density (measured at 0.35 m above the ground surface). Dashed lines link anomalous decreases in flux with the wind events to which they are attributed



A direct comparison of the nominal flux values measured by the two types of chambers was made by calculating the mean flux for each paired chamber during the injection (ordinal days 218–227) and after the injection (ordinal days 241–250). These values were then plotted as a function of the distance from the injection well (Fig. 5). Regardless of the level of flux or whether it was advective (during injection) or diffusive (after injection) in nature, the SSFT value was consistently several times larger than the NSS value for flux. The SSFT/NSS flux ratios generally clustered around a value of about 6.7, although smaller values (4.2–4.4) were obtained directly above the injection well. We attribute this anomaly to spatial heterogeneity in flux for that pair of chambers, which would likely be maximized under high advective flux conditions.

A likely explanation for the relationship between SSFT and NSS fluxes relies on fundamental differences in how the two methods respond to advective flux. The SSFT approach nominally measures a steady-state concentration based on advective dilution with fresh air drawn into the chamber through the vent tube. It is thus a more open system that operates at a lower internal pressure due to constant pumping of air out of the chamber. This tendency to create a vacuum inside the chamber was a concern in the previous study by Amonette et al. (2010) and has been noted previously by others (Kanemasu et al. 1974; Welles et al. 2001). In contrast, the NSS approach attempts to measure the rate of increase in concentration with no induced pressure change and minimal back-diffusion. Under advective-flux conditions, however, it can only equalize pressure by passive venting. Further complicating matters, the geometry of the venting in the two systems differs, in that the NSS system has approximately the same diameter vent tube to equalize pressure for a four-fold larger chamber cross section. As a result, a higher internal chamber pressure would likely be maintained inside the NSS chamber than the SSFT chamber under advective conditions, and this would tend to further suppress the flux estimate

relative to the SSFT system. Thus, while both SSFT and NSS systems yield low flux estimates under advective conditions, the NSS chamber used in this study responds more strongly to advection than the SSFT chamber. The NSS chamber is not designed for advective flux measurements (Rod Madsen, personal communication). However, the manufacturer has suggested a modification to the chamber that makes such measurements more accurate (LI-COR 2012).

Laboratory experiments

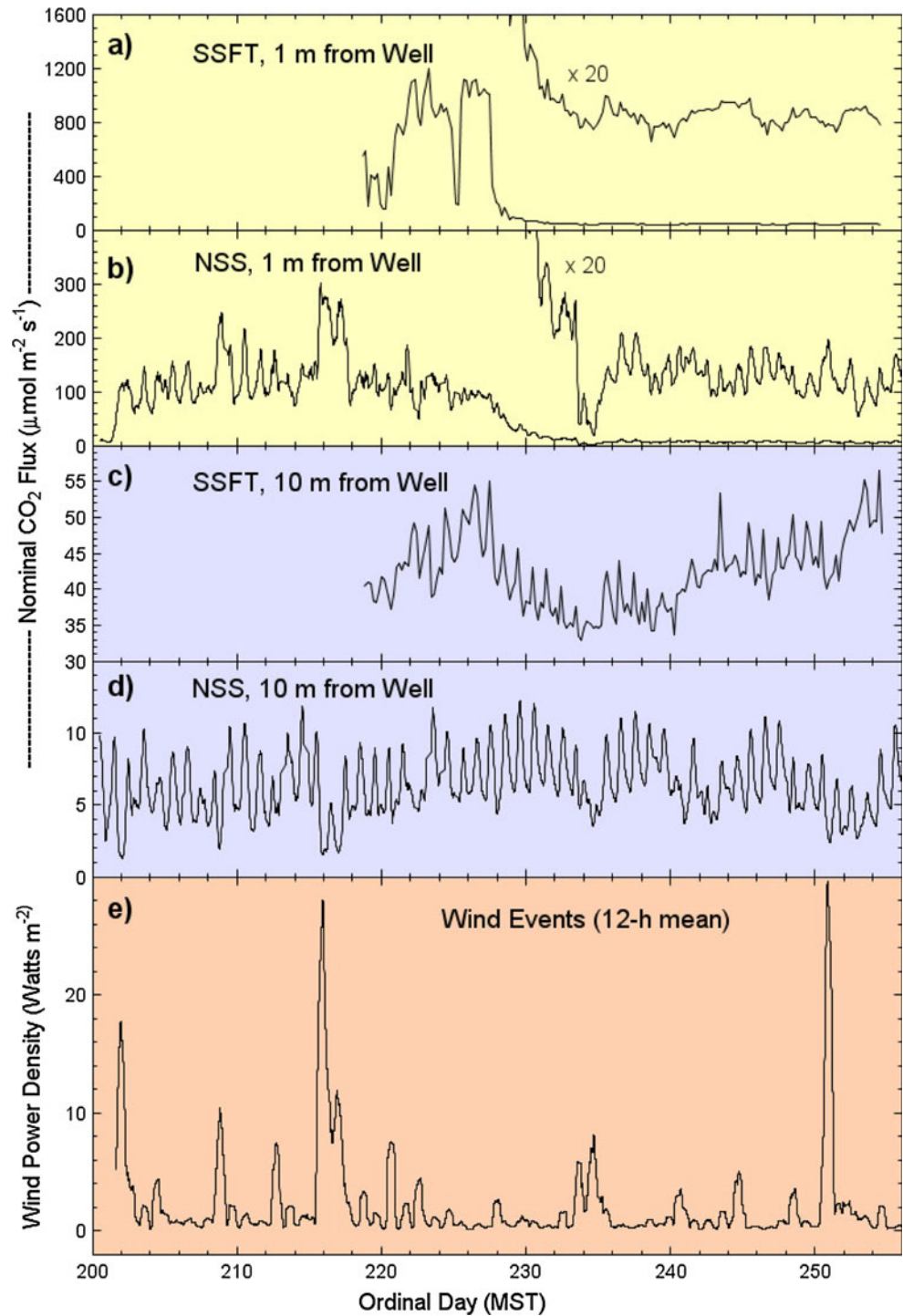
A number of experiments were performed in the laboratory with an SSFT chamber installed in a flux bucket filled with a 25.4-cm thick layer of sand and receiving a known influx of 99.8 % CO₂. This approach allowed calibration of the accuracy of the SSFT chamber, as well as determination of the effects of wind, advective-flux level, collar depth, and chamber flushing rate on the flux data collected.

Wind power density

The effect of wind on the nominal flux measured by the SSFT chamber was tested in two configurations. In the first, wind at a power density of 12 W m⁻² (corresponding to a velocity of about 2.7 m s⁻¹) was applied only to the vent tube, using a long 10.2-cm-diameter pipe as a wind tunnel to prevent any impact on the rest of the system. The result with this configuration showed a very strong increase in flux within 10 min of application of the wind (Fig. 6, blue data). Peak values that were about 75 % higher than those obtained under calm conditions were reached within 30 min. Upon cessation of the wind, the measured flux returned to the initial level within an hour.

For the second test, wind at the same power density was applied to the entire system so that the vent as well as the top surface of the sand was affected. The fluxes measured during the first 10 min were identical to those measured

Fig. 4 Changes in nominal CO₂ flux measured by co-located SSFT and NSS chambers positioned 1 m (a, b) and 10 m (c, d) from the injection well. Also shown (e), is the mean (12-h) wind power density at 0.35 m above the ground



when only the vent tube received wind, but then dropped rapidly during the next 30 min to a level about 10 % lower than that obtained under calm conditions (Fig. 6, red data). Ten minutes after cessation of the wind, the flux dipped slightly and then returned to the original “calm” level within an hour.

The results of these two experiments clearly show that both the chamber vent and the soil surface are affected by

the Venturi effect. The response to wind by the chamber vent is quite rapid, whereas the effect of wind on the soil surface requires about twice as long to manifest itself in the measured flux values. Whether the observed flux increases or decreases will depend on the relative magnitude of the pressure drops induced by the wind on the vent and on the soil surrounding the chamber collar. The decreases in fluxes seen in the field experiment during wind events

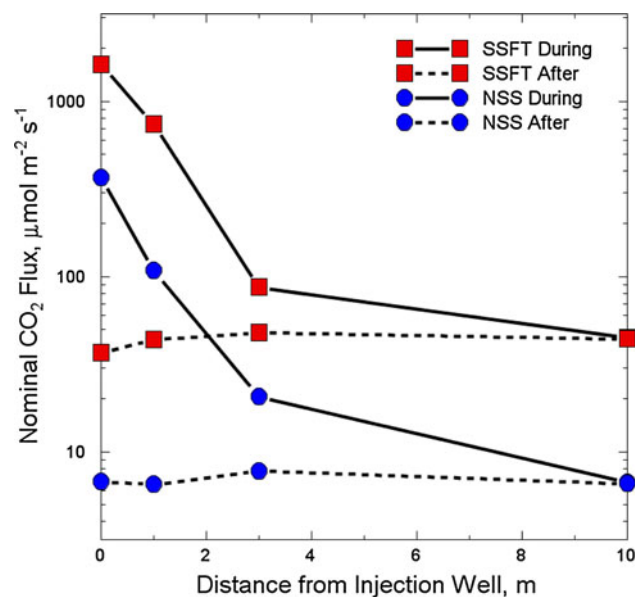


Fig. 5 Mean nominal CO₂ flux measured by the SSFT and NSS approaches during the injection (ordinal days 218.7–227.0) and after the injection (ordinal days 241.0–250.0) for co-located chambers positioned 0, 1, 3, and 10 m from the injection well

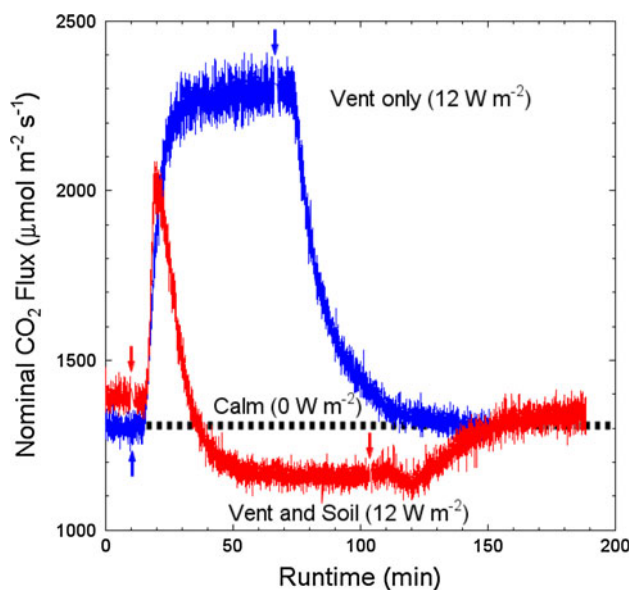


Fig. 6 Effect of wind on nominal CO₂ fluxes measured by the SSFT chamber under laboratory conditions using the flux bucket. Wind at a power density of 12 W m⁻² was applied to the vent only or to the entire system (*vent and soil*) using a fan. Fan start and stop times are indicated by *vertical arrows*

(Figs. 3, 4) can thus be explained as real phenomena, rather than artifacts of chamber measurements. Determination of the true magnitude of the flux during these events, however, will depend on the development of a better understanding of the relative forces involved. Flux decreases reported by Amonette et al. (2010) for similar wind events

were much larger than those seen in the current 2010 data, and this difference is probably due to the use of smaller diameter vent tubes in 2008 that were much less susceptible to the Venturi effect than the vent tubes used in the present work. Indeed, a repetition of the flux bucket experiment using a chamber fitted with the 2008 vent tube resulted in a 37 % decrease in flux when a 2.2 m s⁻¹ wind was applied to both vent and sand surface and only a 2 % increase in measured flux over 30 min when applied to the vent tube only (data not shown).

Advective flux level

The field results showed that the relative performance of the SSFT and NSS chambers was related to the flux level. Several experiments were conducted with the SSFT chamber in the flux bucket to determine how the flux level impacted the measured flux relative to the known flux maintained by the flux bucket. Three advective fluxes were tested: 4,250, 510, and 59 μmol m⁻² s⁻¹. These fluxes, which are for CO₂ introduced into the bottom of the flux bucket, represented nearly the entire range of fluxes measured in the field. The ratio of the measured flux to the known flux was calculated and plotted against the log of the known (predicted) flux (Fig. 7). The ratio of measured to predicted flux dropped from about 90 % of the predicted value at the lowest flux to about 30 % of the predicted value at the highest flux. A strong linear relationship ($r^2 = 0.995$) was obtained between the ratio of measured to predicted flux and the log of the flux. Extrapolation of this relationship predicts that, for this system, flux would be measured accurately only when it was at a level of about 25 μmol m⁻² s⁻¹.

Taken with the data from the field presented in Fig. 5, these results suggest that measured values of flux by both the SSFT and NSS approaches are likely to be significantly lower than the true values, particularly at the high fluxes encountered in the ZERT experiment. However, if a measure of total advective flux is available, the strong logarithmic relationship seen between measured flux level and actual flux level offers a potential way of deriving the true CO₂-flux value.

Chamber parameters

The effect of collar depth on measured flux was investigated in identical experiments with a series of collars ranging in depth from 11.4 to 3.8 cm. These tests (Fig. 4, ESM only) showed a highly significant ($r^2 = 0.9997$) linear increase in nominal flux with collar depth for experiments conducted at the highest influx (4,250 μmol m⁻² s⁻¹). The flux measured with the deepest collar, which was used in the field experiment also, was about 25 % larger

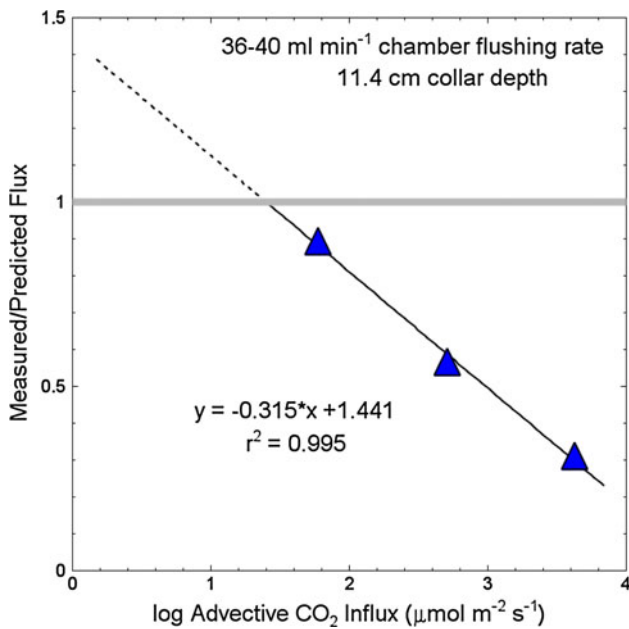


Fig. 7 Effect of advective-flux level on the ratio of the nominal CO₂ flux measured by the SSFT flux chamber to the actual CO₂ flux entering the *bottom* of the flux bucket

than that measured with the shallowest collar. This result is consistent with expectations because, near the sand surface, significant back-diffusion of air occurs and results in a dilution of the CO₂ concentration. Advection would continue at the same flux, but the ability to measure it based solely on CO₂ concentration decreases the nearer to the surface that samples are taken.

Lastly, the effect of SSFT chamber flushing rate on the measured flux was investigated. Flushing rates from 20 ml min⁻¹, roughly half the value used in the field experiment, to about 460 ml min⁻¹, more than an order of magnitude higher, were tested. The results of these experiments (Fig. 8) showed a continued increase of nominal flux values across the entire range, yielding unrealistic values at the higher end of flushing rates. The response to flushing rate was linear until the nominal flux reached a level that was about 85 % of the known flux into the bottom of the bucket. At this level, the response dropped off slightly but continued to increase to yield unrealistic values.

Some dilution of the CO₂ would occur near the surface of the sand and thus the ability to measure net flux is limited by the degree of back-diffusion that occurs. Evans et al. (2001, Fig. 6) determined CO₂ depth profiles for a lower flux (3,260 μmol m⁻² s⁻¹) using 30-mesh sand and a comparable flux-bucket geometry without a chamber in place. Their data showed that at a depth of 5.7 cm the CO₂ would be diluted by about 35 %, and at 11.4 cm the dilution would be about 12 %. At the higher flux rate used in

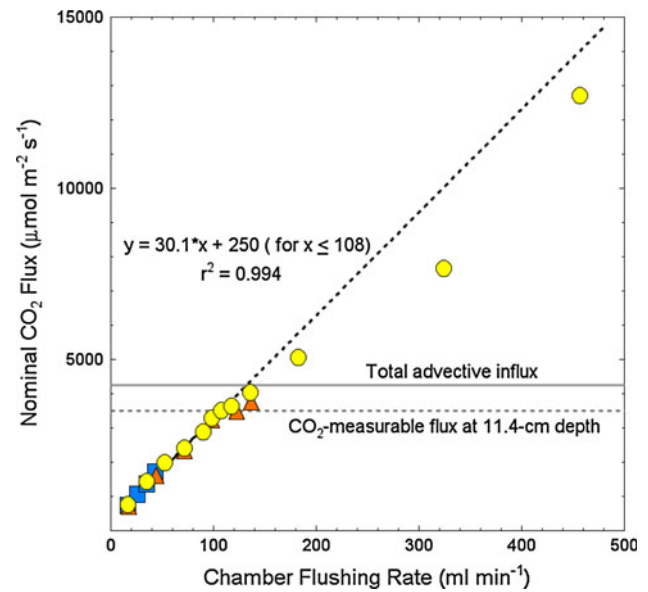


Fig. 8 Effect of chamber flushing rate on nominal CO₂ flux measured by the SSFT chamber in the laboratory. The three mass flow controller (MFC) arrangements used were 2.0 L min⁻¹ (circles), 50 mL min⁻¹ (squares), and three 50 ml min⁻¹ MFCs in parallel (triangles)

the present experiment (4,250 μmol m⁻² s⁻¹), one would expect the dilution factors to be smaller at comparable depth. Further, one would expect that the relevant depth in our chamber for comparison with the data of Evans et al. (2001) would not be the bottom of the collar but somewhere near the middle of the collar depth because some back diffusion from the sand surface inside the chamber would still occur. An estimate of about 15 % dilution at 5.7 cm depth (center of the soil inside the collar) and 4,250 μmol m⁻² s⁻¹ coincides well with the break in nominal flux response to increased chamber flushing rate in the present data, and this level has been identified in Fig. 8 as the CO₂-measurable value of advective flux in the SSFT system.

A physical explanation of these observations can be based on the relative pressures inside the chamber and in the soil. As noted by Evans et al. (2001) and confirmed by the present data, placement of a chamber into the surface layer of a soil has a profound effect on the flux pathways. Backpressure from the enclosed volume in the chamber redirects flux away from the chamber collar and results in lower values measured for flux by the chamber. Our data suggest that this backpressure can be overcome by application of a significant vacuum inside the chamber (e.g., by increasing the chamber flushing rate and decreasing the vent-tube diameter). As the backpressure inside the chamber decreases, measurable flux increases linearly and the original flux pathways in the soil inside the collar are restored. Once the point of flux parity is reached a change

in the system occurs and now flux must be drawn from pathways outside the original volume enclosed by the chamber collar with further decreases in chamber pressure. Capture of additional flux units by the chamber requires a progressively larger vacuum (i.e., higher chamber-flushing rate) and the response drops accordingly.

Conclusions

The results of the field and laboratory experiments reported here show that accurate measurement of gaseous flux by the chamber method (whether SSFT or NSS) is very difficult, particularly when advective flux is involved. Under stable environmental conditions (calm, constant soil moisture content, small temperature range, diffusive flux only), reasonable values can be obtained. With advective flux, however, back pressure within the chamber as well as back diffusion must be accounted for, and this requires the ability to frequently measure and control the pressure inside the chamber at a level that allows flux to continue at the same rate as when the chamber is not present. Either a highly sensitive pressure-measurement system to determine the pressure gradients inside and adjacent to the chamber or a flushing-rate type of calibration is likely required for the most accurate results.

The present results show that, in the absence of an adequate pressure balance, chamber measurements of advective fluxes are likely to be substantially lower than the actual values and that this error increases logarithmically with the level of advective flux. The measurements reported in this study confirm earlier observations of highly localized dynamic advective-flux patterns in soils and lend new insight into the impact of wind on soil-gas fluxes. Most importantly, these results show that a strong Venturi-type effect operates both on the chamber vents and the soil, and is muted as gaseous pore interconnectivity in the soil is eliminated by moisture-filled pore space.

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