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Observed response of soil O_2 concentration to leaked CO_2 from an engineered CO_2 leakage experiment

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ABSTRACT

The response of soil O_2 concentration to artificially released CO_2 was investigated during an engineered surface CO_2 leakage experiment at a research facility at Bozeman, Montana, USA in the summer of 2010. Results show that (1) when there is no CO_2 leakage, generation of CO_2 at the research site was primarily due to oxidation of organic matter, soil O_2 concentration is correlated negatively with soil CO_2 concentration and soil moisture and positively with soil temperature. This represents the site's intrinsic relationship of soil O_2 concentration with other soil environmental factors under natural conditions. (2) When there is CO_2 leakage, soil O_2 concentration is negatively associated with soil CO_2 concentration, and positively associated with soil moisture and soil temperature. The observation that the dependence of soil O_2 concentration on soil moisture is reversed from negative to positive when there is a CO_2 leakage should be useful for CO_2 leakage verification. Anomalous changes of soil gas composition at a CO_2 sequestration site may provide important and direct signatures of CO_2 leakage and important information of its impact on the environment, especially O_2 dependent soil respiration processes, which may be compromised with elevated CO_2 and reduced O_2 concentrations.

1. Introduction

Long-term geological CO_2 storage (GCS) in geological formations such as depleted oil and gas reservoirs, deep saline aquifers, and unmineable coal seams has been proposed as one of the most promising remedy options to mitigate global anthropogenic CO_2 emission to the atmosphere (Bachu, 2000; IPCC, 2005; Van der Zwaan and Smekens, 2009). Because fossil fuel (gas, oil, coal) burning is still at the heart of the present world's energy economy, implementation of GCS technology can help sustain the present economic development without sacrificing the environment. Since CO_2 gas can be absorbed onto coal, the unmineable coal seams, which are too deep for economical mining, can be used to store CO_2. The experience learned from existing commercial CO_2 injection projects (acid-gas injection, CO_2 injection in Sleipner, In Salah, Snøhvit, etc.) and CO_2 injection at pilot projects (Nagaoka, Frio, Ketzin, Otway, US Regional Partnerships) demonstrates that geological CO_2 storage in gas reservoirs and saline aquifers is technologically feasible (Michael et al., 2010). However, there are potential risks of failure of containment of stored CO_2. These include (1) structural discontinuities and weak points such as fractures, faults; (2) wells drilled for oil and gas exploration and production; (3) gas permeable channels/faults in the caprocks (Annunziatellis et al., 2008); (4) geomechanical disruptions due to increased pressure in the reservoir (Gasda et al., 2004; IPCC, 2005; Pruess, 2005; Celia et al., 2009; Grimstad et al., 2009); or (5) failure of injection wells and transportation pipelines, etc. (Heinrich et al., 2003). If a leaking event happens, all possible impacts on the environment should be assessed for the purpose of long-term safety and control measures (Heinrich et al., 2003; Wei et al., 2011). This will contribute to gaining public confidence and acceptance of the GCS technology.

Under normal conditions, the gaseous composition of soil air bears the imprint of a variety of complex microbiological, biophysical, and biochemical processes, dynamics of plants, organic content and humidity condition of the soil systems (Amundson and Davidson, 1990). For instance, the CO_2 and O_2 concentrations in soil are usually linked to the biological processes of soil biota respiration and the decomposition of organic matter. In a compilation of soil CO_2 data under various normal conditions, soil types, and ecosystem classifications, soil CO_2 concentrations varies from 0.04% to up to 13.0% by volume in the upper horizons of soil (Amundson and Davidson, 1990). In most cases, tropical forest soils have

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relatively high soil CO_2 concentration, while soils in arid and semi-arid regions have relatively low soil CO_2 concentration (Brook et al., 1983). A number of studies have been carried out in natural analogs with CO_2 releasing into the atmosphere (e.g. Annunziatellis et al., 2008; Beaubien et al., 2008; Pettinelli et al., 2008; Arts et al., 2009; Battani et al., 2010) and non-leaking natural deep CO_2 reservoirs (e.g. Pauwels et al., 2007; Gal et al., 2010, 2011) to characterize the distribution of anomalous gas (e.g. CO_2) distribution and its association with properties of surface and subsurface geology. At geological CO_2 storage sites, if there is any leakage from CO_2 reservoirs, the soil CO_2 concentration on the leaking paths should be well over the upper-bound limit at normal conditions.

Soil O_2 concentration variation is a consequence of soil respiration (root and soil microbial respiration) in the vadose zone under natural conditions. While on the other hand, its availability has a profound impact on O_2-dependent processes such as microbial transformations of organic C and N in the soil (Topp et al., 2000). Soil O_2 concentration is one of the main factors regulating nitrification, denitrification, and the release of nitrous oxide (N_2O). Oxygen in soil is consumed during nitrification by nitrifying bacteria (Goreau et al., 1980) and in turn its concentration can influence nitrification and denitrification rates and N_2O production (Khalil et al., 2004). Both CO_2 toxicity and O_2 deficiency can cause respiration inhibition in the soil. For a specific soil, as air-filled porosity declines with increasing soil moisture, diffusion becomes increasingly restricted. Thus, soil moisture content should also be an important factor affecting O_2 concentration in the soil, followed by the soil temperature and availability of organic carbon that determines the consumption of O_2 (Ryden, 1983; Rolston et al., 1984).

When there is leakage of CO_2 from a geological CO_2 storage site, soil CO_2 gas partial pressure will increase, well above the limit under normal conditions. Accordingly, O_2 and other gas partial pressure will decrease. Therefore, gas composition changes in the soil atmosphere may be a direct indicator for monitoring a possible leakage. On the other hand, leaked CO_2 will change the soil gas composition and subsequently result in a change in soil chemistry (Beaubien et al., 2008; Wei et al., 2011). Elevated soil CO_2 concentration impacts the soil geophysical properties (Zhou et al., 2012), soil microorganism ecosystems and plant ecosystems (Macek et al., 2005; Jossi et al., 2006; Vodnik et al., 2006; Beaubien et al., 2008; Krüger et al., 2009; Pierce and Sjögersten, 2009; Patil et al., 2010; Lakkaraju et al., 2010). Observation in *karst* regions demonstrated that a higher level of soil CO_2 concentration will change the limestone denuation rates, and subsequently the geomorphologic change in the long run (Brook et al., 1983). Adamse et al. (1972) suggested that for the proper functioning of a healthy root system, a minimum soil O_2 concentration of 12–14% is required. Studies carried out at sites of naturally occurring CO_2 and volcanic sites, and studies on leaking CH_4 gas on plants have shown that elevated soil CO_2 and/or CH_4 concentrations reduce plant growth, disrupt plant photosynthesis, inhibit root respiration and even kill the vegetation (Hoeks, 1972; Arthur et al., 1985; Vartapetian and Jackson, 1997; Cook et al., 1998; Miglietta et al., 1998; Smith et al., 2005a; Macek et al., 2005; Vodnik et al., 2006; Pfanz et al., 2007). For the volcanic sites such as Latera caldera of Italy where deep geothermal CO_2 and other trace gases such as CH_4 and H_2S in the soil horizon are released to the atmosphere from a venting structure, the trace gas species may also have strong impacts on vegetation (Beaubien et al., 2008). These studies attributed the adverse effects of gassing to the displacement of soil O_2 by the CO_2 and CH_4 gases which deprive the plant roots and their associated microbiota of O_2 for respiration (Patil, 2012). In turn, other plant functions such as water and nutrient uptake, transpiration, photosynthesis, and ultimately plant health are thus affected. Decreased soil O_2 concentration due to CO_2 gassing is thus a key parameter in assessing the impact of gassing on plants when CO_2 leakage events occur.

To investigate monitoring and detecting technologies of CO_2 leakage and assess the environmental impact due to possible leakage events, (even though the possibility is small) (Heinrich et al., 2003), facilities such as the Artificial Soil Gassing And Response Detection (ASGARD) (Smith et al., 2005b; West et al., 2009), the Zero Emission Research and Technology Center (ZERT) (Spangler et al., 2010), and CO_2 Field Lab project (http://www.sintef.no/Projectweb/co2fieldlab) were engineered to take on these tasks. Most field studies of soil gases have focused more on the flux at the soil–atmosphere interface than on the concentrations within the soil. Simultaneous measurement of CO_2 and O_2 concentrations and two-variable regression analysis of the data show a negative linear relationship between O_2 and CO_2 concentrations as O_2 gas was displaced by naturally migrated (Vodnik et al., 2006; Beaubien et al., 2008; Annunziatellis et al., 2008; Gal et al., 2012; Romanak et al., 2012) or injected CO_2 gas (Patil et al., 2010; Al-Traboulsi et al., 2012). The observed reduction of soil O_2 concentration is usually attributed to the displacement by the exogenous CO_2. However, other factors such as water vapor and temperature may contribute as well. The relationships between soil gases (e.g. CO_2 and O_2) and soil environmental factors such as soil moisture and soil temperature under normal or during CO_2 leakage conditions have not yet well investigated. The objective of this paper is to investigate the subsurface soil CO_2 and O_2 dynamics during and after soil CO_2 release, and the relationship of soil O_2 concentration with the soil CO_2 concentration, soil moisture, and soil temperature under normal and leaking scenarios using the ZERT CO_2 release facility.

2. Field experiment

The simulated leakage of sequestrated CO_2 was carried out in the summer of 2010 (from July 19 to August 15) at a field facility engineered by the Zero Emission Research and Technology Center (ZERT), in an agricultural plot in Bozeman, Montana, USA (Spangler et al., 2010; Lewicki et al., 2010). This research site was developed to allow controlled studies on near-surface CO_2 transport, detection technologies, and possible environmental impacts due to leaking CO_2. As shown in Fig. 1(a), a 100 m long horizontal well trending toward the north-east direction was installed at the site for the controlled release of CO_2. The horizontal well casing was installed through horizontal directional drilling, leaving the overlying layers intact. The pipeline has a 70-m long central slotted (perforated) section, and 12- and 15-m long unslotted sections on its sloping NE and SW ends, respectively. The slotted section was divided into six zones separated by seven 0.4-m long inflatable packers, with five zones (each 12 m long) and one zone (Zone 6, about 9 m long). The pipeline was buried at a depth of approximately 2.0–2.3 m in Zone 5, about 0.5 m below the groundwater table, within a layer of alluvial sandy gravel, overlaid by a clayey silt layer of about 0.20 m and a layer of topsoil of approximately 0.30 m. The topsoil of the field site consists primarily of fine-grained organic silts and clays over a layer of cobblestones. A plot of about 10 m × 10 m was cordoned off in Zone 5 for soil and plant study. The plot was kept unmowed and under natural conditions through the whole period of measurement from July 18 to September 15, 2010. Soil CO_2 and O_2 concentrations, soil moisture, and soil temperature were measured at two sites along a traverse perpendicular to the pipeline (Fig. 1(b)). Fig. 1(b) shows the positions of two study sites in Zone 5 relative to the pipeline: one site (hotspot site) was at the edge of a high CO_2 concentration spot during CO_2 release and was about 1 m away from the pipeline. The other site was about 10 m away from the pipeline. CO_2 and O_2 concentrations 10 m away from the

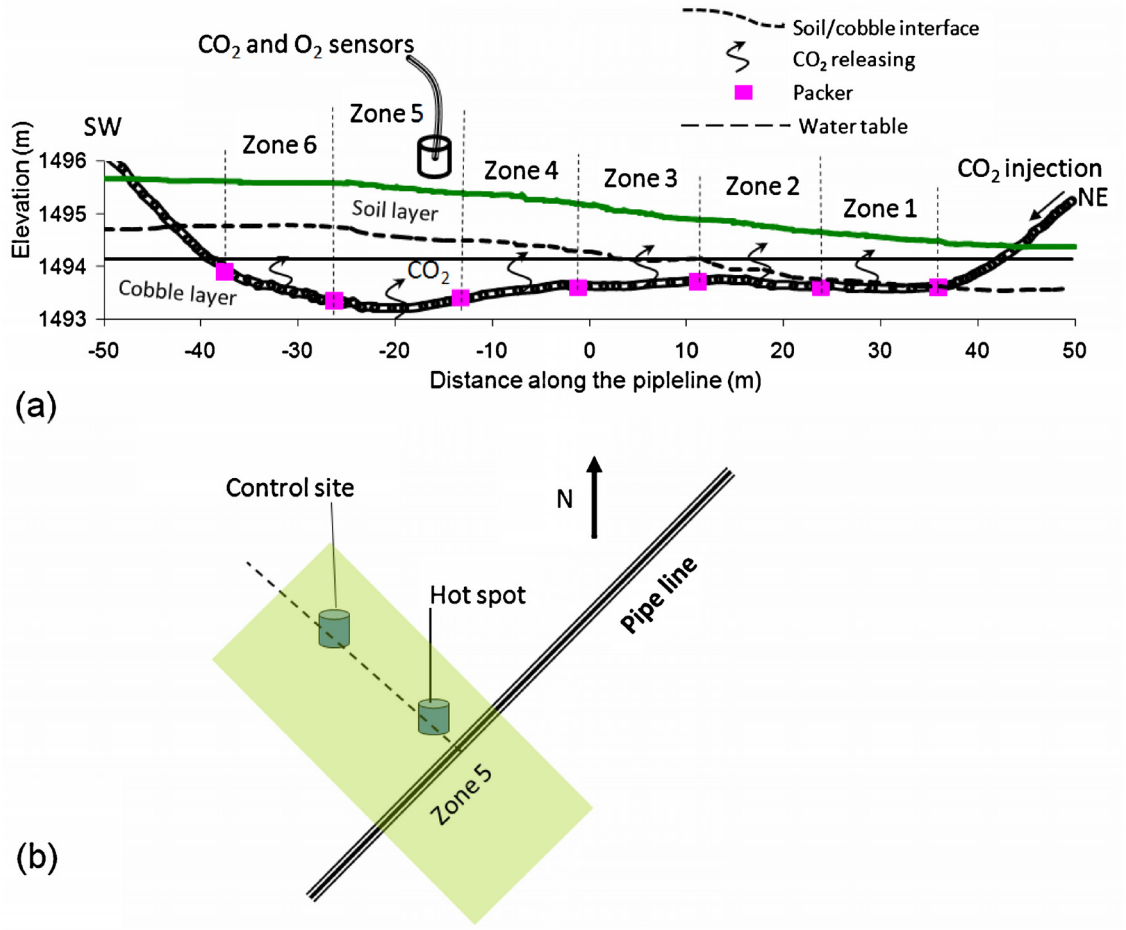

Fig. 1. (a) A cross-section view that runs through the pipeline with CO_2 releasing in 6 zones controlled by 7 packers. The positions of packers, soil–cobble interface, land surface, and the horizontal well in were estimated from Oldenburg et al. (2010) and Lewicki et al. (2010). (b) The two sites at which CO_2, O_2, soil moisture, and soil temperature sensors were deployed – one at the hotspot site (high CO_2 concentration) but 2 m away from the pipeline and the other is 10 m away from the pipeline taken as the control site.

pipeline are basically not impacted by the CO_2 release (see Section 3). Thus it is taken as the control site for reference. At each site, a sensor for soil CO_2 concentration measurement was collocated with an O_2 sensor, a soil moisture sensor, and soil thermistor. The positions of these sensors in Zone 5 were also shown in Fig. 1(a).

The vegetation cover at the hotspot site and the control site is shown in Fig. 2. The pictures of the top row were taken on July 18, 2010, one day before the start of the experiment. The top-left is of the hotspot site and the top-right is of the control site. The vegetation consisted of a mixture of naturally occurring plants dominated by grass (Orchard grass, *Dactylis glomerata*; Kentucky bluegrass, *Poa pratensis*) and dandelion (*Taraxacum officinale*). The canopy at the control site was thicker than that of the hotspot site. The photos of the bottom row were taken on August 16, one day after the termination of CO_2 release. At the end of the CO_2 release experiment, the vegetation canopy at the hotspot site was thinner and more stressed than that of the control site.

A shallow CO_2 release experiment was conducted at a pre-set release rate of about 0.15 tons per day from 12:35 pm on July 19 to 12:35 pm on August 15, 2010. The CO_2 release rate at each zone was controlled and recorded by a mass flow controller at the zone. Logging of the flow rates for all the six mass flow controllers started well before the beginning of the CO_2 release experiment and lasted a couple more days after the release so that the background noise of the flow meters could be estimated.

The soil CO_2 volume concentration was measured using Vaisala CARBOCAP® GMT221 infra-red (IR) CO_2 probes with in-soil adapters. The accuracy (including repeatability, non-linearity and calibration uncertainty) at 25 °C and one atmospheric pressure is ±(1.5% of range + 2% of reading). This type of fast-response sensor can provide continuous measurements of soil CO_2 concentration and enable dynamic observation of soil CO_2 evolution with and without CO_2 leakage. The sensors were calibrated and linearized up to 20.00% in volume. These CO_2 sensors were deployed at a depth of 15 cm, within the root zone of grass and dandelion. Selection of 15 cm depth was a result of three purposes: soil gas dynamics study, minimizing disturbance of gassing routines, and providing root-zone gas data for surface vegetation monitoring. Soil CO_2 measurement was started one and half days before the start of CO_2 release so that the background soil CO_2 concentration could be estimated. The atmospheric pressure and temperature compensations due to deviation of measurement conditions from the calibration conditions (1013 hPa and 25 °C) were made following Tang et al. (2003) for the CO_2 measurement that was taken every 5 min.

We used two O_2 sensors (SO-1110, Apogee Instruments, Inc.), one at a hotspot and the other at a control site in Zone 5, co-located with the CO_2 sensors, to monitor the change of the soil O_2 concentration in the soil atmosphere. Field calibration in the open air at the ZERT site was carried out at about 2pm on July 12, 2010. Several readings were taken for each O_2 sensor and then the average was taken as the calibrated reading. For the O_2 sensor deployed at the hotspot site, the reading is 48.267 ± 0.167 mV. For the O_2 sensor deployed at the control site, the reading is 48.600 ± 0.100 mV. The zero offset is approximated as 2.5 mV. These result in a calibration

Fig. 2. The vegetation canopy at the hotspot and control sites. Generally the vegetation canopy at the control site was thicker and healthier than that at the hotspot site. By August, grasses became less green at both sites due to normal, seasonal dieback. (For the color version of this figure, the reader is referred to the web version of the article.)

factor of 0.458% O_2 per mV for the sensor deployed at the hotspot and 0.454% O_2 per mV for the O_2 sensor at the control site. Temperature effects on the sensors were corrected using the following equation:

$$O_2 = O_{2M}\left[1 + \left(\frac{T_M - T_C}{T_C}\right)\right] \quad (1)$$

where O_{2M} is the measured O_2 concentration, T_M is the soil air temperature [K] at the time of the measurement, and T_C is the air temperature [K] at calibration. The O_2 sensor was placed inside the diffusion head with the sensor opening facing down to facilitate the best contact of the electrolyte and the electronics with the soil air. The O_2 sensor voltage output is recorded by a data logger with a 0–100 mV range and an accuracy of 5 microvolts (μV). The data logger was programmed at an interval of 30 min. We ignore the change in the amount of O_2 available to the sensor due to the small change in the surface atmosphere. Compared with soil CO_2 measurement, there are less abiotic factors to account for in O_2 concentration measurement because soil O_2 concentration is not subject to pH-driven dissolution chemistry, and O_2 is much less soluble in water compared to CO_2. For instance, under one atmosphere at 20 °C, the mole fraction solubility of CO_2 in water is 7.07×10^{-4}, while that of O_2 is only 2.50×10^{-5} (Gevantman, 2005). The sensor chemistry is not influenced by humidity, but its output is expected to decrease because O_2 is displaced by water vapor molecules in the air. We did not measure the water vapor in the soil atmosphere, but the soil moisture content and soil temperature at both the hotspot and control sites were measured using two 5TE sensor suits (Decagon Devices, Inc.), each being co-located with the CO_2 and O_2 sensors at the hotspot and control sites.

A 5TE suite is a multi-function three-pronged probe that consists of a thermistor and three thin metal electrodes that are 1.0 cm apart. Soil temperature was measured by the surface-mounted thermistor with a resolution of 0.1 °C. Volumetric soil moisture was measured up to 50.00% in total soil volume with a resolution of 0.08% by supplying a 70 MHz oscillating electromagnetic wave to a pair of electrodes.

3. Observed results

3.1. Release rate

Fig. 3 shows the time series of the total flow rate and flow rate at Zone 5 as recorded by the mass flow controllers at all zones. We focus on the flow rate of Zone 5 where the co-located O_2, CO_2, and 5TE sensors were deployed. The average noise level of the mass flow controller in Zone 5 after the termination of CO_2 release is −1.633 kg/day. The average of the recorded release rate by the controller during the releasing period is 25.735 kg/day. Considering the negative noise bias of the mass flow controller, the actual mean release rate at Zone 5 is estimated to be about 27.368 kg/day. Subtracting this value from the time series of the flow rate recorded by the controller in Zone 5 during release, the noise levels of during release along with those of pre-release and post-release are shown in Fig. 3 (bottom curve). We can see that the noise levels of the three different periods of time have the same level (peak-peak values). This suggests that the estimated mean release rate at Zone 5 of about 27.368 kg/day is reasonable.

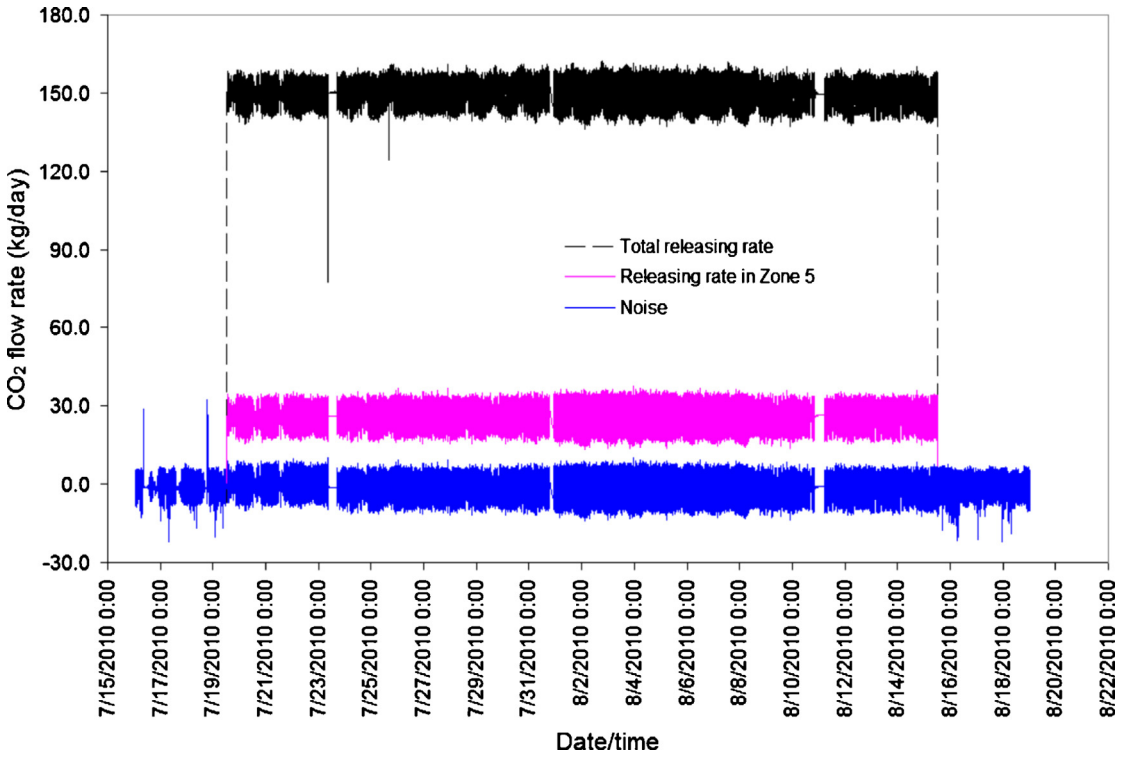

Fig. 3. The time series of the total CO_2 releasing rate of all zones and that of Zone 5 for the 2010 summer experiment.

3.2. Soil CO_2 and soil O_2 concentrations

The dynamic evolution of the soil CO_2 and O_2 volume concentrations (in units of %) in the soil air were shown in Fig. 4(a) for the hotspot site and in Fig. 4(b) for the control site.

At the hotspot site, the soil CO_2 concentration generally increased from the start to 10 am on July 31, 2010, then varied between 12.00% and 18.00% during the rest of the release experiment. After the CO_2 injection was turned off at 12:35 pm on August 15, 2010, the soil residual CO_2 concentration decayed quickly until August 23, 2010. Then the soil residual CO_2 concentration decreased at a slower rate until reaching the background level of about 0.81% (see Section 3.2). The decrease of soil CO_2 concentration from the maximum 18.00% to the background level represents the upward diffusion of soil residual CO_2 and eventual entrance to the surface atmosphere after the release. The soil O_2 concentration dropped down from 20.710% at the start of the CO_2 release to a minimum of 18.190%. The temporal variation of soil CO_2 and O_2 concentrations manifests as two opposite traces during the CO_2 release. The pre-release soil O_2 concentration varied between 20.400% and 20.710% (average: 20.570%), while soil CO_2 concentration varied between 1.02% and 1.13% (average: 1.09%), representing the background O_2 and CO_2 levels just before the CO_2 release experiment.

After the CO_2 injection was turned off at 12:35 pm on August 15, 2010, the soil O_2 concentration increased due to the downward infusion of atmospheric oxygen, reaching the background level of about 20.570% on August 23, 2010. After that, soil O_2 concentration decreased with time at a slower rate. Within the three weeks following the termination of CO_2 release, the soil CO_2 concentration varied between 1.30% and 2.70%, while the soil O_2 concentration varied between 20.200% and 18.800%, showing a decreasing trend with time. However, during the first week after the termination of the CO_2 release (August 15–23, 2010), the soil CO_2 concentration generally decreased from about 15.00% to 2.50%, still well above the background CO_2 level, while the soil O_2 concentration increased from 18.500% to 20.300%, indicating the recovering process of soil O_2 to the background level from the re-infusion of the surface air.

At the hotspot during the 27-day's CO_2 release, the soil O_2 concentration varied between 18.220% and 20.690%. The small-amplitude see-saws of the O_2 concentration curve indicate the diurnal changes of O_2 affected by diurnal variation of soil temperature and to a lesser degree by O_2 related soil microbial activities. The spectral densities from a spectral analysis of the time series O_2 data for the hotspot and control sites are shown in Fig. 5. Since the measurement interval was half an hour, the unit for the period is thus half an hour in the spectral density charts. The peaks at both charts correspond to the same period of 48.119 units or 24 h and 3.57 min. The 3.57 min were due to measurement error, resulting in a relative error of 0.25%. This confirms the existence of the small diurnal (24 h) see-saw component. The atmospheric pressure is dependent on elevation and changes with time on a long run, while the time series of the O_2 measurements were carried out at the same site, impact of variation in atmospheric pressure on soil O_2 concentration during the short period of measurement in summer is thus neglected. However, since the temperature fluctuates between day and night, the absolute O_2 concentration, and thus O_2 sensor output, fluctuates. When the temperature effect is not corrected, it produces an apparent change in the relative gas concentration.

Fig. 4(b) shows that the soil CO_2 concentration at the control site varied with time between 0.49% and 1.50% (net change: 1.01%; average: 0.81%) during the whole measurement period. The average 0.81% is taken as the site's mean background level of soil CO_2 concentration. At the control site, the soil CO_2 concentration varied between 0.81% and 0.92% (average: 0.86%) for the pre-release, between 0.49% and 0.93% (average: 0.64%) for the during-release, and between 0.58% and 1.50% (average: 0.95%) for the post-release. The soil O_2 concentration at the control site varied between 20.740% and 21.040% for the pre-release, between 20.220% and 21.180% during the release, and between 19.060% and 20.640% for the post-release. During the observation, the soil O_2 concentration varied between 19.060% and 21.180% (net change: 2.110%). The similar

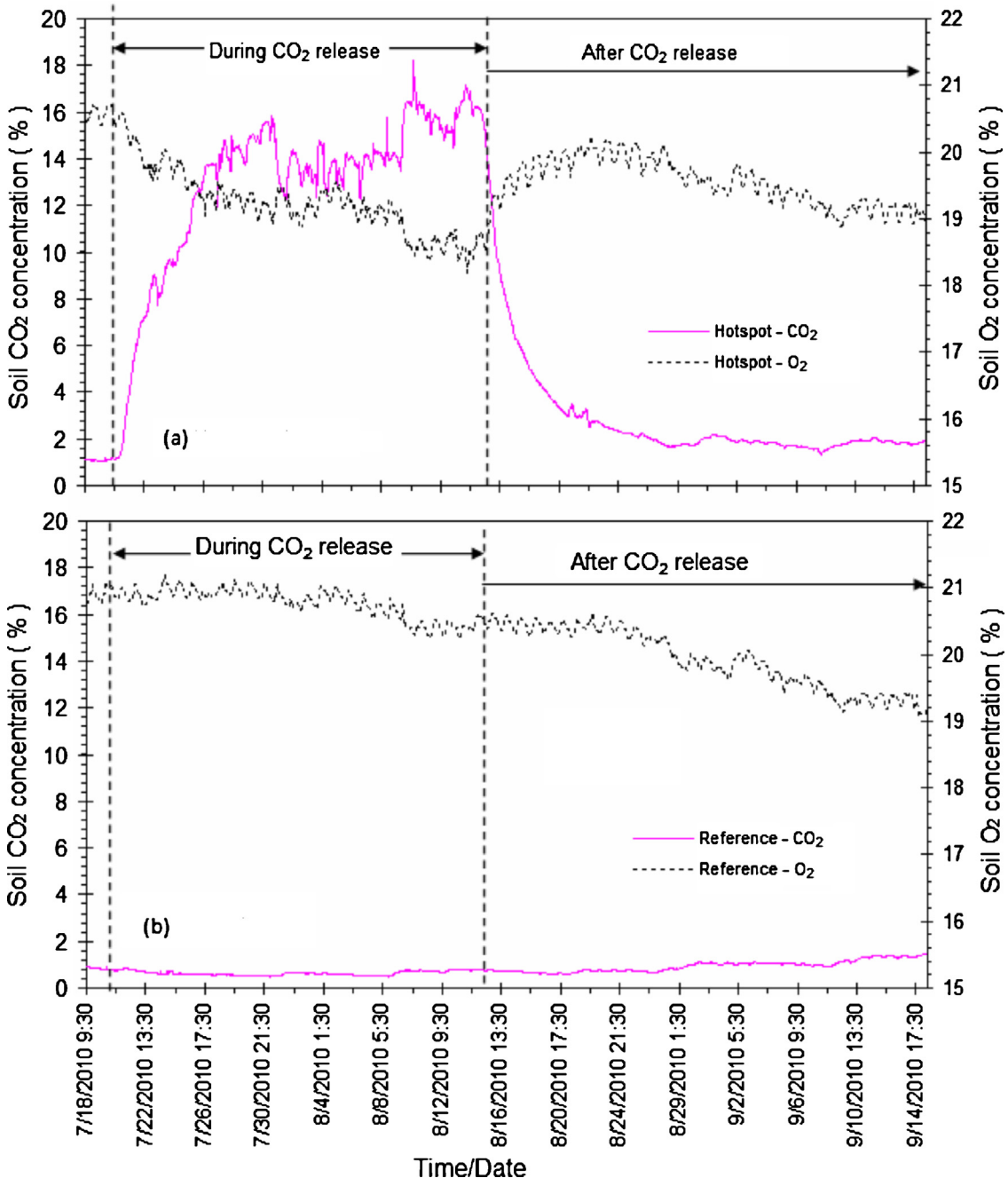

Fig. 4. The temporal variation of the soil CO_2 and O_2 concentrations at the hotspot (a) and the control (b) sites for the whole period of observation (7/18–9/15, 2010). Unit: % volume.

ranges of variation of soil CO_2 and O_2 concentrations during the three periods of time indicate that the soil CO_2 and O_2 concentrations at the site are basically the background concentration levels. After August 23, 2010, soil O_2 concentration was also observed to decrease with time as at the hotspot site, representing the impact of soil temperature on the soil O_2 level (see Section 3.3).

3.3. Soil temperature and soil moisture

The soil temperature and soil moisture curves measured by the 5TE suite of sensors at each site with the same depth as CO_2 and O_2 sensors are shown in Fig. 6. At the control site, the soil temperature varied between 9.2 °C and 18.5 °C (net change: 9.3 °C) during the whole observation. Spectral analysis shows that the fluctuation of the soil temperature curves at an hourly scale is due to the diurnal changes. The larger diurnal change at the hotspot site than at the control site might be caused by the difference in vegetation cover (see Fig. 2) and the differences in root biomass and respiration. The two sites were only about 10 m away in a generally uniform and flat pasture land. Soil texture was visually observed to be very similar, though no quantitative quantification of soil composition/texture was performed. Changes in soil matrix caused by the leaked CO_2 at the hotspot site may also lead to its higher sensitivity to external changes than at the control site, but we speculate the impact on the soil gas and soil water transportation due to such changes is small and thus neglected.

During the release, no rainfall occurred, and soil moisture was observed to decrease generally with time at both sites. At the hotspot, the soil moisture varied between 0.154 and 0.197 m^3/m^3. Sudden changes of soil moisture after CO_2 release at either site

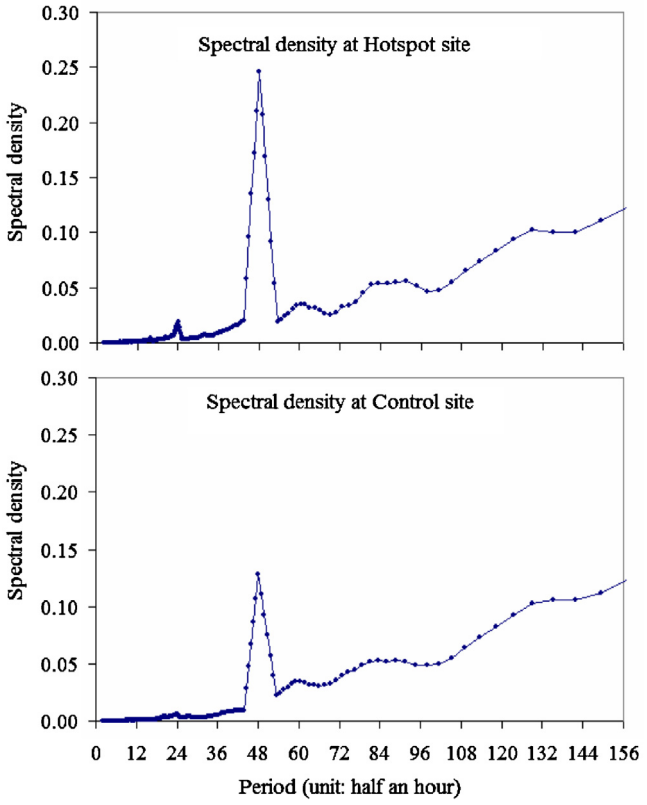

Fig. 5. The temporal variation of spectral density resulted from a spectral analysis of the time series of soil O_2 concentration data at the hotspot (top panel) and the control (bottom panel) sites.

were due to the arrival of infiltrated rainfall water at the soil moisture sensors. From the termination of CO_2 release to the end of the measurement, there were a few rainfall events, some of these events were intense enough to penetrate into the depth where the 5TE sensors were deployed.

4. Data analyses and discussion

4.1. Relationship between soil O_2 and soil CO_2 concentration

To isolate the impact of the released CO_2 from effects due to possible difference in site-dependent factors such as soil moisture, vegetation, and soil temperature, analysis was performed on the time series data only from the same site. In reference to Fig. 4, the whole observation at the hotspot site is divided into three periods: pre-, during-, and post-release, for data analyses. Two-variable regression analysis shows that there is no statistically significant correlation between the soil O_2 volumetric concentration and soil CO_2 volumetric concentration for the pre-release period of time. This might be because the data collected was only from one and one half days and the number of data samples may not be enough for the regression analysis to be conclusive.

Fig. 7 shows the relations between the soil O_2 and soil CO_2 concentrations for the during-release and the first week (August 15–23) of post-release at the hotspot site. A strongly negative correlation was found between the soil O_2 and CO_2 concentrations with a slope value being −0.124, a correlation coefficient $R = -0.917$ and a low p-value ($p < 0.0001$). The linear trend equation of soil O_2 concentration versus soil CO_2 concentration for the during-release is

$$\theta_{O_2} = -0.124\theta_{CO_2} + 20.843 \quad (2)$$

where θ is the volume concentration in units of % of a gas indicated by the subscript. For instance, θ_{CO_2} stands for the soil CO_2 concentration. The intercept of the trend line with the soil O_2 concentration axis corresponds to the atmospheric O_2 concentration value of 20.843%. The decrease of O_2 concentration is well associated with increasing soil CO_2 concentration, indicating the replacement of soil O_2 by the injected CO_2.

During the first week after the termination of the CO_2 release (August 15–23, 2010), the soil CO_2 concentration and the soil O_2 concentration are strongly correlated with a correlation coefficient $R = -0.914$, indicating the depletion of soil O_2 by the residual CO_2 from the release. The linear trend equation takes the form

$$\theta_{O_2} = -0.102\theta_{CO_2} + 20.271 \quad (\%) \quad (3)$$

The slope variation from −0.124 for the during-release to −0.102 for the post-release indicates that the dependence of soil O_2 concentration on the soil CO_2 concentration is stronger during the CO_2 release than the post-release. From both cases we can infer that the soil O_2 concentration was diluted by the released CO_2.

In the three weeks that followed (August 23 to September 15, 2010), soil O_2 continued to be replenished from the surface air, while the residual soil CO_2 continued to decrease by diffusion to the surface atmosphere (data not shown). The soil O_2 concentration is positively correlated with the soil CO_2 concentration with $R = 0.531$, $n = 1104$, $p < 0.0001$:

$$\theta_{O_2} = 0.774\theta_{CO_2} + 18.005 \quad (\%) \quad (4)$$

The reverse of the relation between soil O_2 concentration and the soil CO_2 concentration may be caused by the role of replenishment of O_2 from surface air.

At the hotspot site, since the change of the soil CO_2 concentration due to the release was much larger than the background CO_2 concentration fluctuations, the effect of pumping of soil air through pressure fluctuations during CO_2 release may not be neglected any longer. The change of O_2 concentration during the release can be reasonably assumed to be just diluted or depleted by the released CO_2. The maximum depletion efficiency of O_2 by CO_2 is estimated to be $(20.710 - 18.190\%)/(18.50 - 1.06\%) = 0.14$. The slope in the linear relationship between the soil O_2 and CO_2 concentrations discussed above represents the average displacement while the maximum depletion efficiency represents the maximum possibility of displacement. Based on the results of a similar experiment on a pasture grass plot at 15 cm depth at the ASGARD facility, in which the soil CO_2 varied between 19.50% and 76.25%, the soil O_2 concentration varied between 4.93% and 16.20% (Patil et al., 2010), the maximum depletion efficiency of O_2 by CO_2 is estimated to be 0.20. Relative to the reference case of one-by-one mole displacement, it is 6% larger than the present case.

For CO_2 leaking situations, measurements at natural analogs such as Latera caldera, Italy and Sainte-Marguerite, France (Beaubien et al., 2008; Annunziatellis et al., 2008; Gal et al., 2012) and artificially induced CO_2 sites such as ASGARD, UK (Patil et al., 2010; Al-Traboulsi et al., 2012) and ZERT, USA (the present study) showed that a negative linear relationship between the soil O_2 and CO_2 concentrations exits: $\theta_{O_2} = a + b\theta_{CO_2}$ where a and b are site-dependent constants. All these studies showed that the value of slope b is smaller than 1, indicating more than one mole of CO_2 is required to displace one mole of O_2 rather than on the commonly conceived one-by-one mole basis. Physically, exogenous CO_2 is usually released from a pressurized system (either natural reservoir or artificial release from supply pipe or tank). Once CO_2 is released into soil air, it experiences an isobaric expansion, considering the soil air is an isobaric open system. The exogenous CO_2 mixes with other soil gas components through convection (advection plus diffusion). This forced convection is dependent on soil gas diffusivity

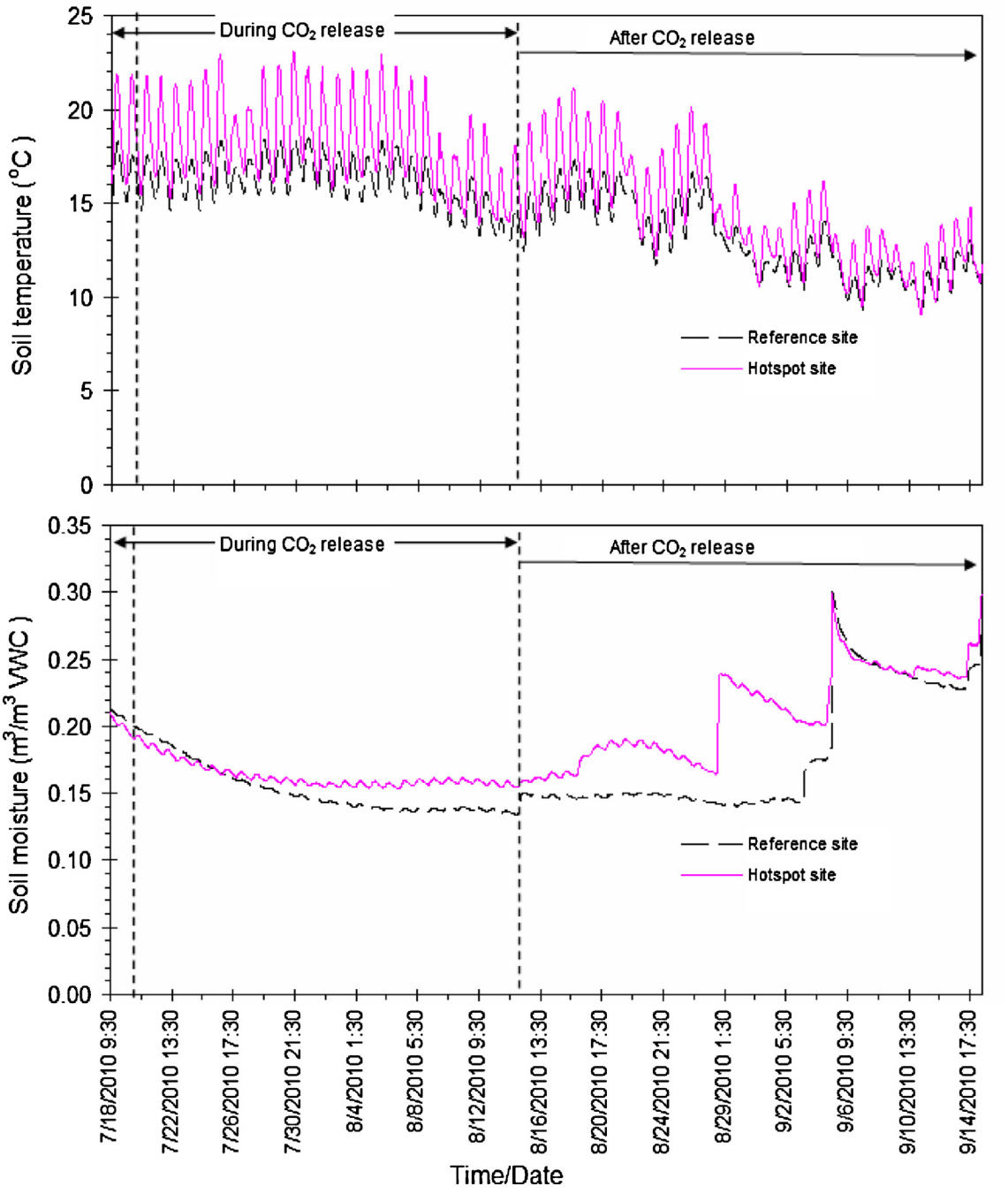

Fig. 6. The temporal variation of the soil temperature and soil moisture at the hotspot and the control sites for the whole period of observation (7/18–9/15, 2010). VWC = volumetric water content, in unit of m^3/m^3.

and the pressure difference between the CO_2 reservoir or tank and local soil air pressure where CO_2 and O_2 concentrations are measured. The concentration of other gases (O_2, N_2, etc.) is reduced or diluted due to the expansion process and addition of CO_2. Therefore, we speculate that the slope b in the linear relationship between the soil O_2 and CO_2 concentrations depends on the pressure difference and CO_2 generation processes (e.g. soil respiration, Romanak et al., 2012).

For the control site, since the soil CO_2 concentration during the release was not significantly different from the pre- and post-release, analysis is thus performed for the whole observation. Fig. 8 shows the relationship between the soil O_2 and CO_2 concentrations. Though the variation ranges for both parameters were small, soil O_2 concentration was observed to decrease linearly with increasing soil CO_2 concentration, with slope being −2.076:

$$\theta_{O_2} = -2.076\theta_{CO_2} + 21.999 \quad (\%) \tag{5}$$

This relationship is statistically significant with a correlation coefficient $R = -0.886$ and p-value <0.0001. It shows that an increase in soil O_2 concentration was associated with a decrease in soil CO_2 concentration, representing the intrinsic relationship between the soil O_2 and CO_2 at the site under natural conditions. At the control site, diffusion along concentration gradients is the primary mechanism for gaseous transport in soils. In most soils under natural conditions, pressure gradients are negligible means of gaseous transport (Hillel, 1998; Turcu et al., 2005). Thus, the effect of pumping of soil air through pressure fluctuations is thus usually

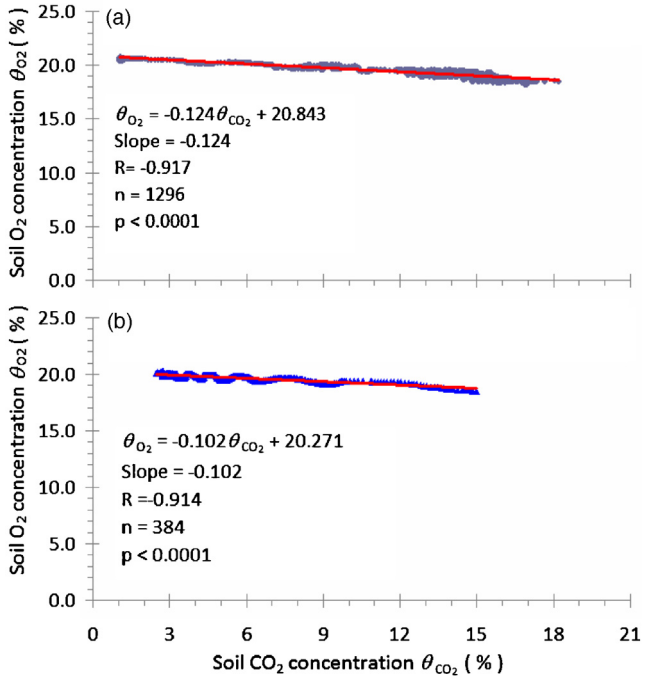

Fig. 7. The soil O_2 volumetric concentration versus the soil CO_2 concentration at the hotspot site for (a) during-release (July 19 to August 15, 2010); and (b) the first week after the release (August 15–23, 2010). *R* is the correlation coefficient, *n* is the number of data points, and *p* is the *p*-value.

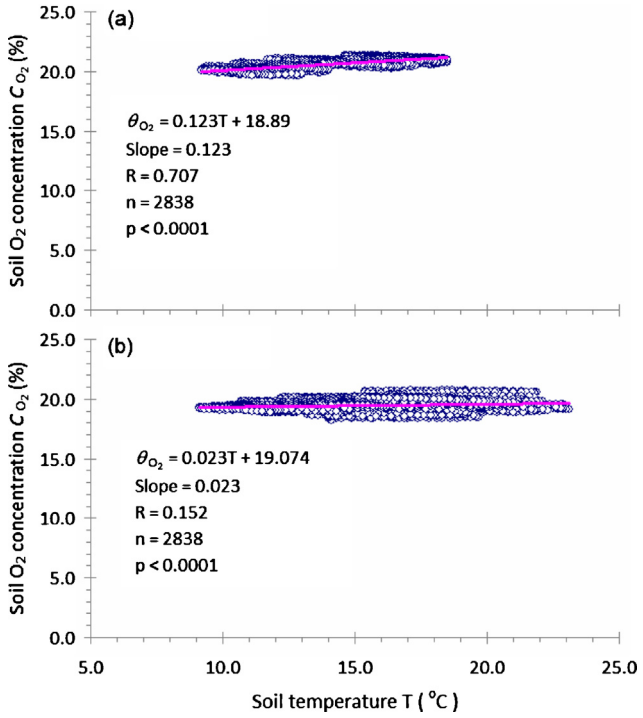

Fig. 9. The soil O_2 concentration versus the soil temperature at (a) the control site; and (b) the hotspot site for the whole period of observation (7/18–9/15, 2010).

neglected (Tans, 1998). Romanak et al. (2012) discussed two basic soil CO_2 generation processes: oxidation of organic matter due to aerobic microbial respiration: $CH_2O + O_2 \rightarrow CO_2 + H_2O$ and methane oxidation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. If any of these two reactions occurs in a closed system where measurement is carried out (formations in deep subsurface may be a good approximation) and the product H_2O is in vapor, then the relationship of concentration of O_2 versus that of CO_2 should have a slope of −1 and −0.5, respectively for the two cases. Given that an actual system may be composed of two or more oxidation reactions occurring simultaneously, plus other diffusion processes within soil, the slope is expected to be more complex than a system of a single reaction. For instance, dilution of O_2 concentration due to water vapor that depends on soil moisture and the dependence of soil O_2 concentration on soil temperature should be also important. Without considering these factors and just attributing the variation of O_2 concentration to CO_2, we got a slope of −2.076 from the single variable analysis. However, further multivariate analysis showed that the slope is −1.084 (see Eq. (12)), very close to −1. It is this slope value that actually represents the contribution of CO_2 to the variation of soil O_2 concentration. This also indicates that at our control site, generation of CO_2 was primarily due to oxidation of organic matter, agreeing well with Romanak et al.'s process case of aerobic microbial respiration; other processes involving oxidation of methane may not be as important.

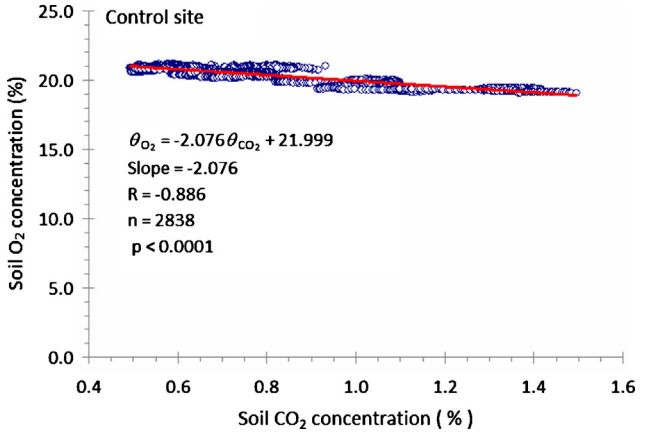

Fig. 8. The soil O_2 concentration versus the soil CO_2 concentration at the control site for the whole period of observation (7/18–9/15, 2010).

Comparison of the O_2–CO_2 relations (Eq. (5) versus Eq. (2)) at the control and hotspot sites during CO_2 release demonstrated the decrease of magnitude of slope due to CO_2 release (from 2.076 to 0.124) and the reduction of the sensitivity of soil O_2 concentration to soil CO_2. Compared to the hotspot site, the sensitivity of soil O_2 concentration to the soil CO_2 concentration at the control site is even stronger (larger magnitude of slope value). The situation at the control site represents the relationship of soil O_2 and soil CO_2 under normal conditions, where gas change is due to slow soil respiration processes, soil gases are in equilibrium and diffusion is thus the dominant if not the sole transport process. However, in the forced systems such as CO_2 leakage from a geological storage or engineered artificial CO_2 release experiment due to pressure difference, diffusion may not be the only transport mechanism in soil gas dynamics. The isobaric expansion of the injected CO_2 results in forced convection that reduces the sensitivity of soil O_2 to CO_2 for the CO_2 releasing case.

4.2. Relationship between soil O_2 concentration and soil temperature

The dependence of soil O_2 concentration on soil temperature at the control and hotspot sites is shown in Fig. 9. At the control site, the soil O_2 concentration was observed to increase with the soil temperature. A linear trend is found between the soil O_2 concentration and soil temperature T (°C):

$$\theta_{O_2} = 0.123T + 21.999 \quad (\%) \tag{6}$$

with a correlation coefficient $R = 0.707$ and a p-value <0.0001. Soil temperature contributes positively to the soil O_2 concentration. This relationship is a result of the temperature impact on gas thermal process under isobaric condition and soil and root respirations.

At the hotspot site for the whole period of observation, the temperature dependence of the soil O_2 concentration becomes:

$$\theta_{O_2} = 0.023T + 19.074 \quad (\%) \tag{7}$$

with a correlation coefficient $R = 0.152$. Here we did not analyze the data based on the during- or post-release periods of time because the soil temperature was assumed to be independent of the CO_2 release, i.e., heating or cooling of soil by the heat content in the released CO_2 was ignored. The correlation coefficient is small, but the calculated statistical significance level is still high (p-value <0.0001) because the number of samples ($n = 2838$) is large. Observation at both sites showed that soil O_2 increased with increasing soil temperature T (°C), or vice versa. However, small slopes show that the dependence of soil O_2 concentration on soil temperature is weak. Weak relationship is prone to disturbances due to other processes such as soil respiration. The correlation coefficient is higher at the control site than that of the hotspot site. The relationship between soil O_2 concentration and soil temperature at the control site represents the base relationship of the background. Simultaneous measurements of soil O_2 concentration and soil temperature at the same depth provide useful information about the relation between soil respiration and soil temperature under normal conditions. However, CO_2 leakage may disturb such a relationship, reducing the correlation coefficient and slope value. In fact, slope value decreased from 0.123 for the control site to 0.023 for the hotspot site. Weaker dependence of soil O_2 concentration on the soil CO_2 concentration (see Figs. 7(a) and 8) and less dependence on soil temperature at the hotspot site than at the control site (decrease of slope value from 0.123 to 0.023 and decrease of R-value from 0.707 to 0.152) during the CO_2 release demonstrated such a disturbance.

From Fig. 9, we can see that the minimum soil temperature was 9.2 °C for the control site and 9.1 °C for the hotspot site, very similar. However, the maximum temperature was 18.5 °C for the control site and 23.1 °C for the hotspot site, differing by 4.6 °C but for only 10 m spacing. Fig. 6 shows the temperature and soil moisture difference at the hotspot and control sites on a half-hourly basis. We can see that the low temperatures at night are similar for both sites, but there was a large difference in the high temperatures during the day. We speculate that this difference was caused by the difference in evapotranspiration due to difference in stress among the vegetation at the two sites (see Fig. 2). At the hotspot, the vegetation canopy was stressed due to the CO_2 release, evapotranspiration was largely reduced and the soil temperature changed in synchronization with daily solar radiation. While at the control site, vegetation canopy was normal and evapotranspiration was more active. Root zone soil moisture was consumed by evapotranspiration for temperature regulation. This speculation was cross-supported by the evolution of root-zone soil moisture also shown in Fig. 6. At the beginning of CO_2 release, the soil moisture at the control site was even higher than the hotspot, but with time of CO_2 release, the soil moisture at the control site decreased more rapidly and soon became lower than the soil moisture at the hotspot site.

4.3. Relationship between soil O_2 concentration and soil moisture

Soil wetting processing increases microbial activity and reduces soil air-filled porosity and consequently results in a reduction in soil O_2 diffusion coefficient. Water vapor evaporated from the soil liquid water content is one gas component in the soil atmosphere. Although we did not measure directly the water vapor concentration in soil air, we take the soil moisture as a proxy for it since there is more water vapor in soil air when the soil moisture is higher. Strictly, temperature and water vapor (thus soil moisture) should be entangled with each other since evaporation also depends on soil temperature. However, we disentangled the complexity by considering the dependence of soil O_2 on soil temperature and soil moisture separately. The dependence on temperature was discussed in the previous subsection. The relationship between the soil O_2 concentration θ_{O_2} and soil moisture θ_{H_2O} at the control site is shown in Fig. 10. It was found that at the control site, the soil O_2 concentration decreased linearly with increasing soil moisture:

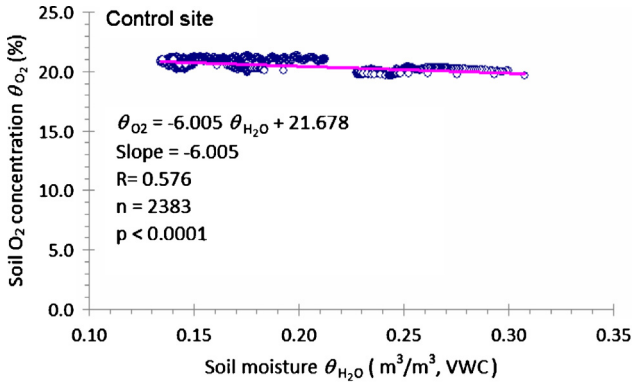

Fig. 10. The soil O_2 concentration versus the soil moisture at the control site for the whole period of observation (7/18–9/15, 2010).

$$\theta_{O_2} = -6.005\theta_{H_2O} + 21.678 \quad (\%) \tag{8}$$

with $R = -0.576$ and p-value <0.0001. θ_{H_2O} is the soil moisture in m^3/m^3. Under normal conditions, higher concentrations of water vapor in soil air resulted in more O_2 being replaced by the water vapor. Thus, soil O_2 concentration is negatively correlated with soil moisture.

The relationship between soil O_2 concentration and soil moisture under normal conditions may be altered by CO_2 leakage. Fig. 11(a) shows the relationship between the soil O_2 concentration θ_{O_2} and soil moisture θ_{H_2O} at the hotspot site during the CO_2 release:

$$\theta_{O_2} = 45.583\theta_{H_2O} + 11.846 \quad (\%) \tag{9}$$

with $R = 0.834$ and p-value <0.0001. The soil O_2 concentration was observed to increase with increasing CO_2 with the slope value being 45.583. This relationship is quite different from that derived from the control site where under normal conditions the gas composition in the soil atmosphere is under stable condition and in equilibrium. CO_2 release resulted in a positive correlation ($R = 0.834$) between the soil O_2 concentration and the soil moisture. This may suggest that the released CO_2 not only depleted soil O_2 but also enhanced evaporation and reduced the soil moisture. Compared with the stable gases such as soil O_2 and N_2 in soil air, water vapor is variable, largely because soil moisture as its source is very variable. The relative humidity in the soil air decreases as CO_2 expands during CO_2 release, pumping more water vapor (enhanced evaporation) from soil moisture and thus reducing soil moisture. Since the soil CO_2 concentration is negatively associated with the soil O_2 concentration during CO_2 release, while CO_2 release also results in reduced soil moisture, thus we expect a positive relation between soil O_2 concentration and soil moisture.

Fig. 11(b) shows the soil O_2 concentration θ_{O_2} versus the soil moisture θ_{H_2O} after the CO_2 release (8/15–9/15, 2010) with $R = 0.622$ and p-value <0.0001:

$$\theta_{O_2} = -6.521\theta_{H_2O} + 20.907 \quad (\%) \tag{10}$$

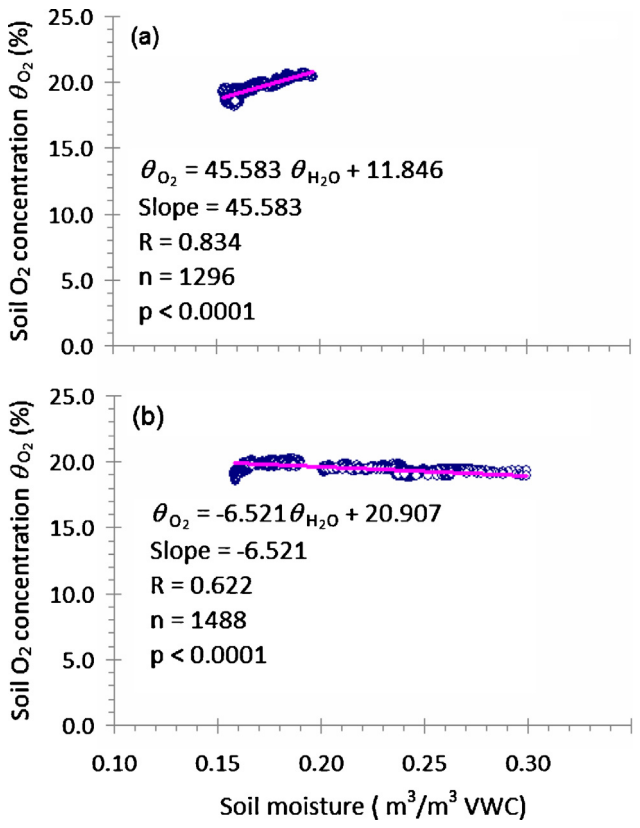

Fig. 11. The soil O_2 concentration versus the soil moisture at the hotspot site for (a) during CO_2 release (7/19–8/15, 2010); and (b) after CO_2 release (8/15–9/15, 2010).

The relationship between the soil O_2 concentration θ_{O_2} and the soil moisture θ_{H_2O} returns to the negative correlation with the slope value being −6.521, much closer to the −6.005 slope value derived from the control site than that (+45.583) derived from the hotspot site for the during-release period of time.

4.4. Relationship of soil O_2 concentration with soil CO_2 concentration, soil temperature, and soil moisture

We assume that a multiple linear model exists linking soil O_2 concentration with soil CO_2 concentration, soil moisture, and soil temperature and is given as follows (Williams, 1992):

$$\theta_{O_2} = b_1\theta_{CO_2} + b_2\theta_{H_2O} + b_3T + a(\pm S) \quad (11)$$

where a, b_1, b_2, and b_3 are model coefficients, S is the standard error in fitting the model to the observation data. The method of obtaining the model coefficients when fitting the model equation to the observed data can be found in Williams (1992). The above equation models the synergetic action among soil CO_2 concentration, soil moisture, and soil temperature in determining the soil O_2 concentration, assuming that each factor contributes to the soil O_2 concentration independently and linearly. Here soil CO_2 concentration, soil moisture and soil temperature are treated as independent variables because their origins are different and unrelated: soil CO_2 concentration is dependent on the CO_2 source, especially in the case of leaking CO_2; soil moisture is mainly controlled by rainfall intensity, frequency, duration, and soil infiltration; and soil temperature is mainly controlled by the atmospheric temperature and solar radiation. The statistical significance of the multivariate analyses is tested with an F test (Pearson and Hartley, 1966).

At the control site, the dependence of the soil O_2 concentration on the soil CO_2 concentration, soil temperature, and soil moisture under normal conditions takes the following form:

$$\theta_{O_2} = -1.084\theta_{CO_2} - 0.501\theta_{H_2O} + 0.116T + 19.605(\pm 0.209) \quad (12)$$

with $R^2 = 0.8605$ or 86.050% of the change in the soil O_2 concentration at the control site can be explained by the change in the soil CO_2 concentration, soil temperature, and soil moisture. Statistical significance holds to $p < 0.0001$ level of confidence. Empirical model Eq. (12) demonstrates the dependence of soil O_2 at the study site under natural conditions.

At the hotspot site, the empirical model equation for during release and post-release periods of time are, respectively

$$\theta_{O_2} = -0.109\theta_{CO_2} + 4.022\theta_{H_2O} + 0.031T + 19.436(\pm 0.213) \quad (13)$$

$$\theta_{O_2} = -0.100\theta_{CO_2} - 9.532\theta_{H_2O} + 0.008T + 21.70(\pm 0.214) \quad (14)$$

Analysis for the pre-release was not performed since there was only one and a half days' data available. For the during-release model, $R^2 = 0.844$, i.e., 84.400% of the change in soil O_2 concentration can be explained by the change due to the 3 independent variables. The statistical significance holds to $p < 0.0001$ level of confidence. The average soil CO_2 concentration, soil moisture, and soil temperature during the release were 12.57%, 0.163 m^3/m^3, and 18.2 °C, respectively. Their average magnitude of the contribution to the variation of soil O_2 concentration is thus 1.370%, 0.660%, and 0.560%, respectively. For the post-release model, $R^2 = 0.636$, i.e., 63.600% of the change in the soil O_2 concentration can be explained by the change in the soil CO_2 concentration, soil moisture, and soil temperature. At the control site, soil O_2 can often be depleted due to respiration by roots and microorganisms and the simultaneous increase of CO_2 concentration.

Table 1 summarizes the ranges of parameter value for the relationships resulted from the analyses discussed above. For instance, Eq. (3) is for the first week of post-release at the hotspot, the ranges for O_2 concentration θ_{O_2} (%) and CO_2 concentration θ_{CO_2} (%) are 18.500–20.300% and 2.50–15.00%, respectively.

Table 1
Ranges of parameter value for Eqs. (2)–(10) and (12)–(14).

Parameter	Hotspot site			Control site
	During release	Post release		Whole observation
		1st week	After 1st week	
θ_{O_2} (%)	18.220 – 20.690	18.500 – 20.300	18.800 – 20.200	19.060 - 21.180
		18.190 – 20.710		
θ_{CO_2} (%)	1.04 – 18.20	2.50 – 15.00	1.30 – 2.70	0.49 – 1.50
		1.04 – 18.20		
θ_{H_2O} (m^3/m^3)	0.153 – 0.197	0.158 – 0.299		0.134 – 0.308
T (°C)	13.2 – 23.1	9.1 – 23.1		9.2 – 18.5
Equations	(2), (9), (13)	(3)	(4)	(5), (6), (8), (12)
		(10), (14)		
	(7)			

5. Conclusions

An artificial release of CO_2 to simulate CO_2 leakage from a geological CO_2 storage site was carried out from 12:35 pm on July 19 to 12:35 pm on August 15, 2010 at the ZERT research facility. Observation of soil CO_2 and O_2 concentrations, soil moisture, and soil temperature was extended from 9:30 am on July 18 to 12:30 pm on September 15, 2010 at a control site and a hotspot site. For development of detection technology of CO_2 leakage, one month of CO_2 release should be enough. However, for environment impact assessment, this may not be long enough for season-sensitive soil processes to be considered.

At the control site, the soil O_2 concentration was found to be negatively correlated with the soil CO_2 concentration and the soil moisture, and positively correlated with the soil temperature, suggests two co-existing processes under normal conditions were involved: (1) production of CO_2 and concurrent consumption of soil O_2 from the normal soil respiration; (2) depletion of soil O_2 by the CO_2 and water vapor in soil air.

At the hotspot site during the whole observation, soil O_2 concentration was found to be negatively associated with soil CO_2 concentration and soil moisture, positively associated with soil temperature. The magnitudes of slope of the linear relationship for both CO_2 concentration and soil temperature were much smaller than that at the control site. The slope of the linear relationship between soil O_2 and soil CO_2 was negative at the control site, but positive at the hotspot site with much larger amplitude. This opposite relationship for the during-release and post-release suggests that the released CO_2 not only depleted soil O_2 but also enhanced evaporation and reduced the soil moisture due to the pumping effect of the released CO_2 gas plume at the interface between the CO_2 plume and the soil liquid water. CO_2 release altered the intrinsic relationship between the soil O_2 concentration and soil moisture under natural conditions.

At the hotspot site during the first week after the termination of the CO_2 release, the soil CO_2 concentration decayed monotonically with time, while the soil O_2 concentration increased, suggesting the recovering process of the soil O_2 to the background level from the re-infusion of the surface air. Increasing soil O_2 concentration was associated with decreasing CO_2 concentration or vice versa, but the decrease of magnitude of slope from 0.124 for during the release to 0.102 for the post-release indicates that the sensitivity of soil O_2 concentration to soil CO_2 was reduced. The following processes may be simultaneously involved: (1) the on-going depletion of soil O_2 by the residual CO_2 from the CO_2 release; (2) replenishment of soil O_2 from the surface air by diffusion that reduced the sensitivity; (3) restoration of microbial and soil respiration activities impacted by the CO_2 release should enhance the sensitivity if we assume the strong relation between the soil O_2 concentration and soil CO_2 concentration at the control site (see Eq. (4)) was primarily due to microbial and soil respiration activities under natural conditions. The overall reduction of the sensitivity indicates that the first two processes dominate over the third one.

For the post-CO_2 release, the soil O_2 concentration is negatively correlated with the soil moisture, similar to the control site. During the post-release phase, disturbance to the gas composition due to the released CO_2 disappeared and slow processes dominated again. Depletion of soil O_2 by water vapor became an important process once again under normal conditions.

In summary, (1) under natural conditions, generation of CO_2 at the ZERT site was primarily due to oxidation of organic matter, the soil O_2 concentration is negatively associated with the soil CO_2 concentration and soil moisture, and positively associated with soil temperature. (2) When there is CO_2 leakage, the soil O_2 concentration is negatively associated with the soil CO_2 concentration, and positively associated with the soil moisture and soil temperature. The observation that the dependence of soil O_2 concentration on soil moisture was reversed from negative to positive when there is CO_2 leakage should be useful for CO_2 leakage verification. Anomalous changes in the soil CO_2 and O_2 gas composition at a CO_2 sequestration site should provide important and direct signature of CO_2 leakage and important information on impacts on the environment, especially O_2 relevant soil respiration processes.

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