COMPARISON OF THE IMPACTS OF ELEVATED CO_2 SOIL GAS CONCENTRATIONS ON SELECTED EUROPEAN TERRESTRIAL ENVIRONMENTS

J. M. West[1], D. G. Jones[1*], A Annunziatellis[2], T. S. Barlow[1], S. E. Beaubien[2], A. Bond[3], N. Breward[1], P. Coombs[1], D. de Angelis[2], A. Gardner[1], V. Gemeni[4], S. Graziani[2], K. A. Green[1], S. Gregory[1], S. Gwosdz[5], S. Hannis[1], K. Kirk[1], N. Koukouzas[4], M. Krüger[5], S. Libertini[2], T.R. Lister[1], S. Lombardi[2], R. Metcalfe[3], J. M. Pearce[1], K. L. Smith[6], M. D. Steven[6], K Thatcher[3] and F. Ziogou[4].

[1]British Geological Survey, Keyworth, Nottingham NG12 5GG, UK.
[2]Universita di Roma "La Sapienza", Rome, Italy.
[3]Quintessa Ltd, Henley-on-Thames, RG9 1AY. UK.
[4]CERTH/Chemical Process and Energy Resources Institute, Thessaloniki 57 001, Greece.
[5]Federal Institute for Geosciences and Natural Resources, 30655 Hannover, Germany.
[6]University of Nottingham, School of Geography, Nottingham, NG7 2RD. UK.

Corresponding author's e-mail address: *dgj@bgs.ac.uk

ABSTRACT

Selected European studies have illustrated the impacts of elevated CO_2 concentrations in shallow soils on pasture. For the first time, general unified conclusions can be made, providing CO_2 thresholds where effects on plants and soil microbiology are observed and making recommendations on how this information can be used when planning projects for CO_2 storage. The sites include those where CO_2 is being naturally released to the atmosphere from deep geological formations; and a non-adapted site, with no previous history of CO_2 seepage, where CO_2 has been injected into the unsaturated soil horizon. Whilst soil gas concentrations will be influenced by flux rates and other factors, the results suggest that a concentration of between 10-15% CO_2 soil gas at 20 cm depth, which is within the root zone, is an important threshold level for observing changes in plant coverage. Site-specific plant 'indicators' are also observed for CO_2 concentrations at ≥35%. Microbiological changes are seen where CO_2 soil gas concentrations are between 15–40%. As part of site characterisation, an evaluation of the risks of leakage and their potential environmental impacts should be undertaken.

Keywords CO_2 storage; leakage; Site monitoring; Leakage detection; Natural systems; Controlled injection; Environmental impacts

1. INTRODUCTION

Carbon dioxide capture and storage is one option for reducing man-made greenhouse gas emissions to the atmosphere. However, the possibility of leakage from the reservoir and any subsequent effects on the environment, need to be considered so that all potential risks can be understood and minimised (Damen et al., 2006; Tian et al., 2013; West et al., 2005). Although studies have been undertaken which examine the impact of increased atmospheric carbon dioxide concentrations on surface ecosystems (e.g. Jossi et al., 2006), such work has limited relevance when considering the possible impacts of increasing CO_2 on ecosystems in the shallow subsurface from upward gas migration. Consequently, the impact of elevated CO_2 soil gas concentrations and fluxes on near-surface ecosystems and soils (to a depth of ~1 m) has been an area of active research, particularly where there are naturally occurring CO_2 releases from volcanic or geothermal areas. These include studies in California, USA (Bergfield et al., 2006; Biondi and Fessenden, 1999; McFarland et al., 2013; Stephens and Hering, 2004); Germany (Frerichs et al., 2013; Krüger et al., 2011, Oppermann et al., 2010); Greece (Ziogou et al., 2013); Italy (Beaubien et al., 2008; Donders et al., 2013;) and Slovenia (e.g. Maček et al., 2005; 2012; Pfanz et al., 2007; Šibanc et al., 2014). Work has also been undertaken at field sites, where CO_2 has been injected into the shallow soil environments, (e.g.; Keith et al., 2009; Male et al., 2010; Moni and Rasse, 2014; Patil et al., 2010; Smith et al., 2013; Spangler et al., 2010; West et al., 2009; Zhou et al., 2013) and at carbon dioxide storage sites (e.g. Jones et al., 2011). Biological monitoring techniques were reviewed by Noble et al. (2012). Other work has examined long-term ecosystem responses to elevated CO_2 concentrations from nearby natural CO_2 seepages from springs and vents in, for example, New Zealand (Kool et al., 2007: Stock et al., 2005), Iceland (Cook et al., 1998) and South Africa (Ross et al., 2000). However, these studies only report time-averaged atmospheric concentrations so it is difficult to determine if the observed effects were directly influenced by elevated CO_2 concentrations in the root zone.

This paper compares and evaluates the results from a number of European studies where we have examined the impacts of elevated CO_2 concentrations in shallow soils on pasture. It evaluates all these results and presents, for the first time, general unified conclusions from these studies, providing CO_2 thresholds where effects on plants and soil microbiology are observed and making recommendations on how this information can be used when planning CO_2 storage projects. The sites include those where CO_2 is being naturally released to the atmosphere from deep geological formations (Florina, Greece (Ziogou et al., 2013); Laacher See, Germany (Krüger et al., 2011); and Latera, Italy; (Beaubien et al., 2008)) and a non-adapted site, with no previous history of CO_2 seepage, where CO_2 has been injected into the unsaturated soil horizon (Artificial Soil Gassing and Response Detection (ASGARD) field site, England) (Smith et al., 2013; West et al., 2009).

2. BACKGROUND ON SITES

A summary of the sites and methodologies used to examine the impacts of elevated CO_2 concentrations on pasture land is given in Table 1. Both Laacher See and Latera contain pasture land located within extinct volcanic calderas. The Latera caldera, located in west-central Italy, is a large elliptical (10 km x 8 km), NNE/SSW trending structure with several eruptive vents located both within and outside of the caldera. A detailed account of the geology and structure of the caldera is given elsewhere, together with a discussion of gas migration along faults in the area (Annunziatellis et al., 2008). Surface lithology throughout the caldera floor is dominated by alluvial sediments, while the overlying soils are highly fertile. The local climate is Mediterranean, with hot (average 22ºC July) dry summers and cool (average 5ºC January) wet winters. Rainfall (652 mm annual average) occurs throughout the year but is highest in winter (84 mm average November) and lowest in summer (24 mm average July; climate information from http://en.climate-data.org/location/117010). The study site is located in the centre of the caldera within a small, flat field used for sheep pasture. The field contains a number of vents, one of which has been extensively characterised in previous studies using geochemical, geophysical and remote sensing tools (e.g. Annunziatellis et al., 2008; Bateson et al, 2008; Pettinelli et al., 2008, 2010). This vent is estimated to have been active for more than 75 years, perhaps much longer (Beaubien et al., 2008) and was selected for further analyses.

The Laacher See volcanic centre is located in the core of the East Eifel volcanic field in Germany, west of the River Rhine in the still uplifting Palaeozoic Rhenish Massif. The Laacher See volcanic centre is morphologically characterised by a basin filled by a lake (Laacher See) with a surface area of 3.3 km^2. CO_2 is produced below the caldera via degassing of the earth's upper mantle and migrates through faults and fractures to the surface. Release is typically from gas vents, characterised by a small core of elevated gas flux (Möller, 2009). One defined gas vent has been studied on the western side of the lake, the age of which is estimated to be less than 150 years (Krüger et al., 2011). The vent is in a large field used for cattle pasture. The local climate is temperate/continental. Average temperature ranges are similar to Latera. Rainfall is spread across the year but most abundant in summer (73 mm average in July at nearby Mendig; http://en.climate-data.org/location/22416).

The Florina basin is a NNW-SSE trending graben in the NW of Greece formed by Neogene coarse clastic sediments. The overlying 800 – 1000 m thick lacustrine deposits consist of conglomerates, marls, sandstone, limestones and clayey caprocks. Natural CO_2 accumulations alternate with lignite seams in these sediments at various depths (Karakatsanis et al., 2007; Ziogou et al., 2013). Carbonate-rich springs and CO_2-rich gas vents occur throughout the Florina basin, resulting from ascent of magmatic-hydrothermal CO_2 along faults and fissures (Ziogou et al., 2013). The studied field is generally flat and is used as pasture for sheep, goats and horses. The field contains a number of gas vents and a grid of soil gas and CO_2 flux measurements was conducted in July 2011 to define leakage distribution and orientation. No information on the age of the vents in the field can be given although interviews with local residents suggested that the vents had been present for over 50 years. The local climate is mountain Mediterranean with long cold, wet winters (average close to 0ºC December/January and average of 106 mm rainfall November) and warm, drier summers (average temperature 21ºC and 37 mm rainfall July). Rainfall occurs through the year and averages 813 mm annually (climate data from http://www.florina.climatemps.com).

Controlled injection of CO_2 has been undertaken at the ASGARD field site in England which is located on the University of Nottingham's Sutton Bonington campus, approximately 18 km south of Nottingham. The site has been previously used for sheep pasture and has remained grassland for over 10 years. The climate is maritime temperate with generally cool summers and mild winters, although extremes in temperature and precipitation are possible. Winter temperatures average between 1 and 7 ºC whilst in summer they are 12-22 ºC (climate data from http://www.metoffice.gov.uk/public/weather/climate/gcrhe9cy8). Total rainfall averages 620 mm annually and occurs throughout the year averaging most in October (61 mm) and least in February (39 mm). Geologically, the site is characterised by up to 1.5 m of head deposits (hillwash and soil creep) overlying mudstones of the Mercia Mudstone Group (Ford, 2006). The head deposit is highly variable but generally comprises a lower clay-dominated facies overlain in the north and east by sandy facies. A thin and highly variable mixed facies up to 60 cm thick (topsoil 'A' horizon and subsoil 'B' horizon) overlies these units across the entire site. This mixed facies is characterised by a gravel-rich base, typically 15 cm thick, in the south and west of the site. Lithological variation also increases with depth. Therefore, to mitigate the effects that this variation may have on gas migration, the depth of gas injection was restricted to 60 cm or less. The ASGARD site consists of a number of plots measuring 2.5 m x 2.5 m with paths (50 cm wide for the original plots and increased to 1 m wide on a new set of plots developed in 2010) between each plot (Figure 1). Some of these plots were kept as pasture whilst the others were planted with agricultural crops and grass/clover mixtures.

3. MATERIALS AND METHODS

3.1. Field campaigns

Two field campaigns were conducted at Latera in September 2005 and June 2006 surveying a 50m long transect across the vent (Figure 1) with measurements including CO_2 soil gas fluxes, soil gas concentrations and composition together with botanical, microbiological, mineralogical and geochemical analyses The vegetation is harvested twice a year for animal feed. Full details of the field campaigns are given in Beaubien et al. (2008).

Surveys near the Laacher See were conducted in September 2007 and July 2008 along a 60 m transect across the vent (Figure 1) which provided a range of different CO_2 soil gas concentrations and fluxes (Krüger et al., 2011). Detailed botanical, microbiological, mineralogical and geochemical analyses were performed at the site in addition to the gas measurements.

At Florina a 25 m transect across a well-defined vent was selected for botanical, microbiological and gas geochemistry studies in September 2011 and July 2012 (Figure 1) (Ziogou et al., 2013).

Intermittent gassing of pasture plot G8 at ASGARD took place between May 2006 and October 2008, with an injection rate of 3 L min^{-1} until September 2006 and 1 L min^{-1} from April 2007 onwards. Continuous gassing of G8 later took place over 24 months between June 2010 and May 2012 at an injection rate of 1 L per minute. Both control pasture plot G7 and G8 were surveyed in spring and autumn between March 2006 and October 2008 and again between May 2010 and October 2012. Detailed botanical, microbiological, soil gas concentration and flux measurements were performed plus limited mineralogical and geochemical analyses. Full details of all the field campaigns are given elsewhere (West et al., 2009; Smith et al., 2013)

3.2. Analyses

Analyses were broadly similar for all the sites and are summarised in Table 2 together with references which provide in-depth descriptions of techniques. Considerable work was undertaken at Latera prior to the environmental impacts studies so the site was well characterised. This was not the case at Florina and Laacher See where rapid and large scale evaluations of CO_2 concentrations in the site were made prior to transect ecological studies. At ASGARD, studies were focused on the plots themselves.

3.3.1. Soil gas measurements

Soil gas and flux measurements were made at all the sites using a variety of field and laboratory methods as detailed in Table 2 and the associated references. Whilst the measurements made at each of the sites differed in detail, a broadly similar approach was adopted at each of the natural CO_2 seepage sites whereby detailed transects were chosen to assess the impacts of the CO_2 based on a more extensive set of measurements that enabled discrete gas vents to be identified.

At Latera, the choice of transect was based on previous regional soil gas and flux studies and detailed work around individual vents. In contrast, at the Laacher See and Florina sites, vents had to first be confirmed by wider areal coverage and more detailed measurements made to define the location of the transects more precisely. At ASGARD detailed soil gas and flux measurements were made over both gassed and ungassed plots during sampling visits. In addition fixed sampling tubes were measured on a weekly basis and long-term continuous measurements were made to assess variability in CO_2 concentrations and fluxes with time and in relation to other parameters, such as temperature, pressure, rainfall, soil moisture and wind speed. These latter factors were recorded either directly on site using a Campbell Scientific automatic weather station or obtained from the University of Nottingham weather station located some 200 m away on the Sutton Bonington campus. Weather observations were also made using the automatic weather station at the Laacher See.

4. RESULTS

4.1. Soil gas and flux

At all the natural CO_2 seepage sites the vents selected for study had well defined centres with CO_2 concentrations reaching 80-100% at depths below about 60-80 cm, whilst atmospheric exchange may reduce these values for the shallower measurements at about 20 and 50 cm depth. The vent cores were typically a few meters to a few tens of meters across with the high CO_2 content of the soil gas being accompanied by higher fluxes of CO_2, with the maximum values ranging normally from a few hundred g m^{-2} d^{-1} to a few tens of kg m^{-2} d^{-1}. The locations of the transects at the three natural CO_2 seepage sites are shown in the context of more extensive gas measurements at each site in Figure 2, Figure 3 and Figure 4.

The O_2 and N_2 levels in the soil gas decrease towards zero as CO_2 approaches 100%, caused by a simple dilution of these gases by the escaping CO_2; this is in contrast to near surface biological processes where respiration consumes O_2 and produces CO_2 in a near 1:1 ratio but with no impact on N_2 concentrations (Romanak et al., 2012; Beaubien et al., 2013). Thus at high CO_2 concentrations there may be an effect caused by anoxia in addition to that due to elevated CO_2. There is also a potential impact at the natural gas seepage sites from other trace gases that may accompany the CO_2. At Latera the CO_2 is associated with up to 1000 ppm of methane, 10 ppm of ethane and more than 200 ppm of H_2S, although these gases are only present in the vent core over the first few metres of the transect. The gas escaping at Florina had up to 3000 ppm of methane and about 1 ppm of ethane and propane, again in the vent centre, but only traces of H_2S (25 ppm maximum recorded at 70 cm depth with the field IR detector). The Laacher See vent traverse had no H_2S that was detectable with the field analyser, or in a small number of samples analysed in the laboratory by gas chromatography (Gal et al., 2011) although this was present in other nearby vents. Methane was not detected in the gas vent but was found in two samples (containing 29 and 150 ppm) 40 m or more from the vent and not on the transect studied (Gal et al., 2011). Trace levels of helium, an inert gas, also occurred as a component of the vent gas at all sites. Food grade CO_2 was injected at the ASGARD site; quality guidelines for this product (ISBT, 2001) specify a purity of at least 99.9% CO_2 with total volatile hydrocarbons and H_2S below 50 ppm and 0.1 ppm respectively.

Repeated measurements at different times of the year, and in different years, show similar patterns of CO_2 concentration and flux at the natural sites (Figures 5, 6, 8 and 15). In general, both concentrations and fluxes are high in CO_2 vents at these sites but they vary in detail and high concentrations can occur for a wide range of flux rates (due to CO_2 storage in the unsaturated zone). Whilst patterns remain similar, the absolute CO_2 concentrations and fluxes fluctuate in response to seasonal and shorter term factors. For example, slightly higher fluxes and concentrations were observed at the Laacher See in September 2007 compared to July 2008 (Figure 5). Differences were also seen at Florina between September 2011 and July 2012 (Figure 6) and soil gas concentrations were in general slightly higher at Latera in September 2005 compared with June 2006 (Figure 15 and Figure 2 of Beaubien et al., 2008). Concentrations at this site were generally higher at all depths in the vent core in 2012 and the gradient of declining CO_2 concentrations away from the vent was much more gradual, compared with the sharply defined edge of the vent in 2011, except at 20 cm depth. It is well known that meteorological and environmental factors affect soil gas concentrations and fluxes in general (e.g. Hinkle 1994; Beaubien et al., 2013) and they clearly influence these parameters in gas vents albeit to a relatively lesser extent. The lower CO_2 levels in September 2011 are consistent with the drier ground conditions during that visit, with freer exchange of atmospheric air into the soil, and lower biological primary production at the end of the growing season.

There are also differences between the natural sites. Whilst CO_2 concentrations, at depths below 70 cm, reach 80-100% in the vent cores at all sites, there are differences in the gas concentrations at shallower depths and in the fluxes. Florina had the highest fluxes with a maximum in September 2011 of 10.6 kg m^{-2} d^{-1} and up to 33.8 kg m^{-2} d^{-1} in July 2012. A maximum of 7 kg m^{-2} d^{-1} was measured at Latera in September 2007 with values between 2 and 3 kg m^{-2} d^{-1} seen on earlier visits. In contrast, the highest flux at Laacher See was only 0.8 kg m^{-2} d^{-1}, and was associated with similarly lower near surface CO_2 concentrations (which only reach 35% at 15 cm). The higher fluxes at Florina gave rise to concentrations at 20 cm depth that were mostly above the Laacher See values in September 2011, and more markedly so in July 2012 when maxima at this depth were above 90%. Similarly high values were also seen at 20 cm on the Latera transect. Therefore, the root zone of most pasture plants is exposed to lower CO_2 exposure levels at Laacher See compared to those at Latera or Florina, but they are generally higher than those observed at ASGARD.

The injection of gas at 1 L min^{-1} in the pasture plots at ASGARD for the RISCS project produced CO_2 concentrations that were generally lower than those at the natural CO_2 sites. The mean/median CO_2 concentrations measured weekly at 30 cm depth, 15 cm from the injection point were 37.6 and 32.3% respectively during gas injection (Figure 7), varying from 7.1% to 86.2% with an interquartile range between 26.3 and 47.8%. Concentrations were appreciably lower 70 cm from the injection point (Figure 7) and much lower and less variable on the ungassed plot. Injection in 2006 at a higher rate of 3 L min^{-1} produced maximum CO_2 concentrations of 70.7 and 85.4% at 20 cm depth on visits when botanical and microbiological investigations were made. Regular measurements for the May-September 2006 injection period gave significantly higher mean values at all locations compared with the later RISCS measurements, for example a mean of 48.0% and median of 52.2% at 30 cm depth 15 cm from the injection point (Figure 7). There was a strong vertical CO_2 gradient from 70 to 50 to 20 cm depth, apparent in more detailed measurements made during all the sampling visits (Figure 8); the maximum values at 20 cm depth for the gassed plot ranged between 7.4 and 35.9%. There was also a marked radial gradient, in both concentrations and fluxes, from the highest values near the centre of the plot to much lower, almost background values at the outer margins (Figure 8). A slight northward offset in the maximum flux and concentration levels suggest some gas escape along the line of the injection pipe. There is some evidence for complex and tortuous movement of CO_2 down and laterally outside the injected plots but the influence of this on the root zone of the control plot studied was not significant.

Temporal variability is very apparent in continuous monitoring data from ASGARD (Figure 9). Fluxes near the injection point averaged 500-800 g m^{-2} d^{-1} between January and July 2011, with most peak values between 1500 and 2000 g m^{-2} d^{-1} but with higher levels between 2800 and 9400 g m^{-2} d^{-1} being observed during 5 short periods during that interval (Figure 9). Post-injection values averaged 22-32 g m^{-2} d^{-1} with a maximum of 200 g m^{-2} d^{-1}. Continuous soil gas concentrations were obtained at 20 cm depth from March to June 2012 (Figure 10). Measurements 0.8 m from the injection point (slightly displaced from the maximum soil gas values) had a mean of 10.0% (median 11.0%) CO_2 but varied between 3.2 and 17.8% (Figure 10). After injection this fell to baseline levels between 0.8 and 2.3%.

It is apparent from the above description that the near surface ecosystem is not exposed to constant fluxes or concentrations of CO_2, either at natural sites or in experiments where the gas is injected at a constant rate. Instead these parameters vary in response to meteorological and soil conditions on diurnal to seasonal and longer timescales.

4.2.Impacts of elevated soil gas CO_2 concentrations on pasture plants

It is clear that at all sites elevated CO_2 soil gas concentrations, and the associated drop in pH, have an impact on vegetation in terms of the plant types present i.e. broad leaf plants (Eudicots or “true dicotyledons” such as clover) and grasses (monocotyledons), and their relative mix and overall coverage.

4.2.1. Impacts at natural CO_2 release sites - Latera, Italy; Laacher See, Germany; Florina, Greece

As described by Beaubien et al. (2008), at Latera (Figure 11– Zone 1) a mix of both dicotyledonous and monocotyledonous plants grow where CO_2 soil gas concentrations are at background concentrations of <2%, although there were differences between the two sampling visits because vegetation was cut for animal feed just prior to the June 2006 visit which prevented the identification of clover. On both sampling occasions there was bare earth with no vegetation in the centre of the vent, where CO_2 concentrations were near 100% and CO_2 flux rates close to 2 kg m^{-2} d^{-1} (Beaubien et al., 2008) (Figure 11 – Zone 3) although fluxes of up to 7 kg m^{-2} d^{-1} have been measured on that vent on other occasions. An acid-tolerant grass (*Agrostis capillaris* L.) started to occur on the edge of the bare-earth core of the vent (i.e. 6–7 m from the start of the profile) where CO_2 soil gas concentrations are ~40% (Figure 11 - Zone 2c). Clover (dicotyledonous plant) appeared at about 13 m from the start of the profile (i.e. about 6 m from the edge of the core) where there was 5% CO_2 at 10 cm depth and 20% CO_2 and 17% O_2 at 20 cm depth (Zone 2b). Finally, although other gases are present in the leaking CO_2 stream, such as <2000 ppm of H_2, CH_4 and H_2S, these reduced and, in the case of H_2S, acidic gases only occur in the bare earth interval (zone 3) and thus they have no impact on the gradational halo which encompasses zones 2c to 2a. (Beaubien et al., 2008). They may however contribute to the impact in the vent core as H_2S toxicity, for example, is well established (e.g. Lamers et al, 2013).

At Laacher See in September 2007, grasses predominated at soil gas CO_2 concentrations below 20%. In contrast, the dicotyledonous plant species *Polygonum arenastrum* Boreau is the main plant present at this site where CO_2 concentrations are between ~10-35% at 15 cm depth and ~35-90% at 60 cm (Figure 12). Overall, however, CO_2 soil gas fluxes are considerably lower at Laacher See (the highest recorded flux being 0.8 kg m^{-2} d^{-1}, Figure 5) than at Latera, or more especially Florina, where the highest CO_2 soil gas flux of all the natural sites was observed (up to 33.82 kg m^{-2} d^{-1} in July 2012 – Figure 6).

At Florina most dicotyledonous plants did not appear to tolerate CO_2 concentrations above 5% or a flux over 0.1 kg m^{-2} d^{-1}. Interestingly, another *Polygonum* species, *P. aviculare* L., is predominant at Florina where CO_2 concentrations are above ~60% at 20 cm depth (Figure 13) and is still observed where concentrations are near 100% (gas flux ~10 kg m^{-2} d^{-1}). Where concentrations are between ~10-50% at 20 cm depth, grasses and *P. aviculare* occur together. A mixture of monocotyledonous and other dicotyledonous plants is then observed where CO_2 concentrations are below 10% at 20 cm depth and where CO_2 flux rates are less than 0.1 kg m^{-2} d^{-1} (Figure 6) This appears to be a higher threshold than that observed at Latera but it should be noted that the depths of analysis were slightly different, with Florina and Latera observations 5 cm deeper than those from Laacher See.

4.2.2. Impacts at controlled CO_2 release site - ASGARD, England

At ASGARD, no specific indicator plants of high CO_2 concentration were observed, probably because soil gas concentrations and fluxes were lower than those observed at the natural sites (Figure 8). Additionally, exposure to elevated concentrations at ASGARD was over shorter time periods (a maximum of 2 years compared to decades of exposure at the natural sites), and thus the plant ecosystem has had less time to adapt to the elevated CO_2 conditions. Nevertheless, when the CO_2 injection rate was higher at ASGARD (3 L min^{-1} at 60 cm depth) there was a rapid response in plant health with change in leaf colour in a variety of plants within 7-10 days (West et al., 2009; Smith et al., 2013). After 2 years of intermittent gassing, with the injection rate dropping from 3 L min^{-1} in 2006 to 1 L min^{-1} in April 2007, resulting in CO_2 soil gas concentrations between 10-30% at 20 cm depth across the transect, monocotyledonous plants (grasses) dominate (Figure 14a). When the injection rate was lower (1 L min^{-1} at 60 cm depth) over a 24 month gassing period, with a resulting overall soil gas concentration below 10%, the domination by monocotyledonous plants across the plot was not observed (Figure 14b and c), even after a period of 24 months of gassing (Figure 14b and c).

It should be noted, however, that these soil gas concentrations indicate impacts at the specific time when the plant coverage was evaluated. Figure 7 shows CO_2 concentrations measured weekly at 30 cm depth, 15 cm from the injection point for the two gas injection rates. For an injection rate of 1 L min^{-1} the mean/median CO_2 concentrations were 37.6% and 32.3% respectively, whereas for injection at 3 L min^{-1} they were 48.0% and 52.2%. Figure 10 shows results from continuous monitoring over a 3 month period in 2012 for G8 at a depth of 20 cm and shows a median CO_2 soil gas concentration of 11% slightly outside the area of maximum concentration. These various results all show the difficulty of assessing impacts based on small numbers of sets of soil gas measurements at a particular site. Continuous measurement over a range of relevant depths at fixed points would be preferable but such intrusive systems will, by their nature, disturb the zone of interest.

4.3. Impacts of elevated soil gas CO_2 concentrations on microbiology

The impacts of elevated CO_2 concentrations on the soil microbiology at all the sites (Figure 15 to Figure 18) are complex but some general trends are clear. At Latera (Figure 15), Beaubien et al. (2008) showed that active biomass, as measured by adenosine triphosphate (ATP) analysis was low within the vent area where CO_2 concentrations were near 100% at 20 cm depth (Zone 3 – Figure 2). This active biomass then rapidly increased over the distance from 8 to 14 m, where CO_2 concentrations decreased from approximately 40% to 15% at 20 cm depth and oxygen and nitrogen concentrations were rapidly rising (Zone 2). Active biomass then decreased to relatively low values in the background area (Zone 1). Such biomass was also low at Florina when CO_2 concentrations were near 100% (Figure 17). However, it should be noted that the apparently anomalous high concentration of ATP at the centre of the vent can be explained by the presence of a dead hedgehog which presumably acted as a major nutrient source for microbial growth. In contrast, the relationship with active biomass (as measured by ATP) was less clear at Laacher See (Figure 16), possibly due to the lower CO_2 soil gas concentrations at this site. Interestingly, at Laacher See, total numbers of organisms determined by direct microscopy (which indicate the size of the microbial community) appeared to increase with increasing CO_2 soil gas concentrations (Figure 16) and soil gas flux (Figure 5) which suggests stimulation of the overall microbial community.

At Latera, numbers of organisms (Figure 15) declined with increasing CO_2 soil gas concentrations, although there was a marked increase in numbers within Zone 2 at 9 m (Figure 11) where CO_2 soil gas concentrations were ~23% in June 2006 (with a flux rate of 195 g m^{-2} d^{-1}) and about 36% in September 2005. This was also reflected in the quantitative polymerase chain reaction (qPCR) results (Figure 15) where Archaea numbers, in contrast to those for Bacteria, remained low at 9 m and were higher only at 50 m. Further work by Oppermann et al. (2010) showed that there were clear changes in the microbial community in the vent zone (Zone 3 – Figure 15) when compared to a reference community (Zone 1 – 15). Microbial carbon fixation changes from heterotrophic (using plant derived material in Zone 1) to autotrophic pathways (with the use of geothermal CO_2 within Zone 3 by methanogenic Archaea and sulphate reducing bacteria). A shift to acidophilic and anaerobic microorganisms within the vent core (i.e. Zone 3) was also seen as a consequence of long-term exposure of the soil environment to elevated CO_2 (plus trace H_2S) concentrations and the associated drop in pH. A similar shift in community composition was also seen within the vent area at Laacher See (Frerichs et al., 2013; Krüger et al., 2011) and Florina (Ziogou et al., 2013). Additionally, at Laacher See, the archaeal community composition changed along the transect, with a predominance of *Crenarchaeota*-and *Thaumarchaeota*- associated genetic sequences in the vent area. Indeed, Frerich et al. (2013) suggested that *Thaumarchaeota* may be considered as ‘indicator species’ for high CO_2 soil gas concentrations.

At ASGARD (Figure 18), West et al. (2009) showed that after 16 weeks of CO_2 injection at 3 L min^{-1} and where soil gas concentrations reached 90%, no active biomass was detected at 70 cm depth. However, after 2 years of CO_2 injection at 1 L min^{-1}, results were not as clear. There was no obvious impact on total numbers or biomass where CO_2 soil gas concentrations were below 10% at 20 cm (Smith et al., 2013). However, where soil gas concentrations vary between 20-40% at 20–50 cm depth, total numbers of organisms appeared to increase when compared to those observed in the ungassed plot. 16S rRNA analyses of Bacteria and Archaea using quantitative real time PCR showed variations in microbial copy numbers over time and depth. However, these variations may not result from CO_2 injection but from changes in weather conditions.

5. DISCUSSION

5.1. Impacts of elevated CO_2 soil gas on terrestrial ecosystems

Each of the sites studied has yielded considerable information on the impacts of elevated CO_2 soil gas concentrations and CO_2 surface flux rates on a range of parameters, including botany and soil microbiology, for pasture in different European climatic conditions. Comparisons of these data broadly show how local conditions can potentially modify the impact of any CO_2 leak.

The impact of CO_2 gas vents on the surface ecosystem at natural terrestrial pasture sites appears to be highly localised and is dependent on the prevailing CO_2 regime. The spatial variations of soil CO_2 concentration and fluxes are generally controlled by a complex interplay of factors such as the migration pathway at depth, the physical and chemical properties of the vadose zone (e.g. permeability, water content, and soil buffering capacity), the features and the hydrogeology of the near surface deposits. Additionally, the depth of measurement with regard to the root zone must also be considered: many dicotyledonous plants have deep tap roots which are not found in monocotyledonous species. Consequently, soil gas analyses, together with continuous monitoring within the soil zone, need to be tailored to the plant species present on a site and the depth to which their roots penetrate the soil. This will be required for baseline characterisation of soil gases and for the design of any near-surface gas geochemistry monitoring program for geological CO_2 storage sites.

In contrast, temporal variations are controlled primarily by the effect precipitation has on water content and effective gas permeability in the vadose zone and by pressure variations like those caused by wind or barometric pumping (e.g. Beaubien et al., 2013; Hinkle, 1994). The issue of how temporal variability of CO_2 concentrations in the root zone may affect plant physiology is complex and has not really been examined thus far but could be looked into using continuous monitoring of the soil gas allied to more frequent assessment of plant health.

Results from botanical research at all the natural sites studied, where pasture plants have been exposed to high CO_2 soil gas concentrations for many years, indicate species-specific responses to high CO_2 concentrations which will be dependent on a number of factors, including temporal and spatial soil CO_2 concentration and flux patterns. Site specific plant 'bioindicators' were observed for concentrations at $\geq$35%, such as *P. arenastrum* Boreau at Laacher See and *P. aviculare* L. at Florina. *Polygonum* spp. can thus be regarded as a bioindicator of elevated CO_2 concentrations at both sites. It is a genus in the Polygonaceae family which, in northern temperate climates, is dominated by species commonly called knotweeds. These are known as weeds of 'waste areas' that thrive in fields and wasteland and in compacted soil. They can survive in drought conditions and are prolific seed producers and consequently have been able to colonise the areas near the vents despite the high CO_2 concentrations and changing flux rates. At Latera, the acid tolerant grass, *A. capillaris* L. can also be regarded as a bioindicator tolerating between 15% and 40% CO_2 concentrations at 10 cm depth (Beaubien et al., 2008). This is a similar tolerance to that observed for grasses at the Stavesinci site in Slovenia where timothy grass (*Phleum pretense* L.) has adapted to the high

CO_2, low pH environment (Maček et al., 2005 Pfanz et al., 2007). At Florina and Latera, monocotyledonous plants (grasses) become increasingly dominant where soil gas CO_2 concentrations at 20 cm depth exceed 10% up until concentrations reach ~30-40%. Interestingly, this was also observed at ASGARD after the pasture plot had been exposed to elevated CO_2 soil gas concentrations between 10% and 30% for 24 months. Similar changes in grass coverage have also been observed at a controlled CO_2 injection site in grassland in Montana, USA (Zhou et al., 2013). The results from all the sites suggest that a concentration of between 10% and 15% of CO_2 in soil gas at 20 cm depth, which is within the root zone, is an important threshold level for observing changes in plant coverage. Flux rates will also be important because these influence soil gas concentrations. However, flux rates are also influenced by other factors, such as soil moisture content, atmospheric pressure and wind speed so determining a threshold will be dependent on site characteristics. Additionally, it must be recognised that plants are not exposed to constant fluxes and/or concentrations of CO_2 so these values can only be regarded as indicative and must be considered in the context of a particular site.

Microbiological analyses at all the natural CO_2 vent sites suggest significant changes in the soil microbial community caused by high CO_2 levels in the soil gas. For example, there is a shift in the microbial community composition in the vent cores towards anaerobic and acid tolerant microorganisms as well as an ecosystem adaption to the CO_2 induced soil biogeochemistry. Such changes have also been observed at mofettes in Slovenia (Šibanc et al., 2014). These differences may be related to long-term adaptation of the microbial ecosystems at the natural sites because they are not observed at ASGARD. Observations at ASGARD are unclear but may suggest that when CO_2 soil gas concentrations are <10%, there is little impact on the microbial ecosystem. Soil gas concentrations between 15 and 40% may enhance biomass and total numbers of organisms (as seen at Latera and Laacher See). Taken together, the results from all the sites suggest that microbiological changes can be observed when CO_2 soil gas concentrations are between 15% and 40%. However, it is not clear how rapidly these changes occur. A relatively short exposure (approximately 24 months) appears to have little immediate impact on the microbial community composition as observed at ASGARD. Such changes are, however, observed at Latera, Laacher See and Florina where exposure to elevated CO_2 concentrations has been taking place over much longer periods. Similar changes were also seen in a simulated CO_2 leaka at the ZERT experimental site in Montana (Morales and Holben, 2013, 2014).

It is also interesting to note that changes in soil geochemistry and mineralogy were observed across the vents at both Latera and Laacher See. Data are not yet available for Florina. At Latera, certain mineral phases (such as K-feldspar, quartz), trace elements (such as As and Cr), and other parameters, such as cation exchange capacity (CEC) and total organic carbon (TOC), all increased towards the vent centre as pH dropped (Beaubien et al., 2008). However, there was no large scale leaching of trace metals from the vent core despite the low pH values, probably because of immobilisation due to increased CEC and total organic matter. At Laacher See, reduced aeration and increased acidification of the soil with depth due to CO_2 concentrations and flux were observed. However, other geochemical changes were less pronounced than those observed at Latera (Frerichs et al., 2012). At ASGARD, the geochemical changes between the control and injected plots were very subtle. After 16 weeks injection of CO_2 at 3 L min^{-1}, pH dropped by 0.5 units at injection depth in the gassed plot. Similar small pH changes were also observed between gassed and control plots in the later experiments with CO_2 injection at 1 L min^{-1}. However, there were no significant changes in soil mineralogical components (West et al., 2009).

Observations at ASGARD between 2010 and 2012 included some extreme weather conditions from very wet to very dry and with wide temperature variations. For example, April-July 2012 were the wettest on record for England and Wales (http://www.metoffice.gov.uk/climate/uk/interesting/april-july2012) and followed an extended dry period when there were concerns about drinking water supplies, with below average rainfall from April 2010 to April 2012. The winter of 2010/11 was severe (http://www.metoffice.gov.uk/climate/uk/summaries/2011/winter) with very low temperatures recorded; grass temperatures at ASGARD dipped below -10 ºC during December 2010 and January 2011. The spring and summer of 2011 were, in contrast, amongst the warmest ever in central England. The effects of these unusual conditions on microbes and plants during the experiments may have been as great as those attributable to the relatively modest soil gas CO_2 concentrations experienced and probably made effects due solely to the CO_2 difficult to decipher.

Other factors might also affect the impact of the CO_2, such as whether manure or other fertilisers have been applied to the pasture. We did not have detailed information on this for the sites studied but it could be examined in future research.

5.2. Implications for CO_2 storage projects

The impacts of potential CO_2 leakage from any terrestrial CCS site will be site-specific – dependent on the geological context, previous history of the site and current land use. Given current regulatory controls, it can be assumed that any leakage from a storage site in any terrestrial environment will have a low probability, provided site selection and operation is carried out correctly with due regard and attention. Nevertheless, although only pasture sites were studied, the work described in this paper shows that increased CO_2 soil gas concentrations do impact on shallow ecosystems, albeit in a very spatially restricted manner. Thus, as part of site characterisation, an evaluation of the risks of leakage and their potential environmental impacts should be undertaken. Such surveys may contribute to the required Environmental Impact Assessments. Results described in this paper suggest that soil gas concentrations and fluxes, plant and soil microbiology surveys should be included in baseline studies in order that the effects of any CO_2 seepage can be separated from those caused by natural site variability caused by, for example, seasonal changes and land use practice.

As is widely recognised, a range of monitoring technologies need to be used to demonstrate site performance over the timescales stipulated by regulatory bodies. Although CO_2 leakage is very unlikely, if it occurs it will most probably be from small point sources, particularly from wells (both known and unknown) (e.g. Damen et al., 2006). This would probably occur early in the lifetime of the project, particularly during and immediately after the injection period (e.g. West et al., 2011). Leakage may also occur through faults (e.g. Damen et al., 2006), as seen at the natural CO_2 sites studied, where the affected zones were again limited in area. Consequently, monitoring techniques have to be selected that are capable of a range of resolutions, from rapid evaluation of a large area (km scale) to assessments capable of determining leakage over the metre scale. They must also be sensitive enough to determine increased values above the spatially and temporally variable background concentrations that should be determined during the site characterisation phase. It would also be preferable for continuous monitoring to involve minimal disruption of the soil, for example by sampling from small diameter tubes at different depths rather than the burial of monitoring probes. Meteorological and other parameters, such as soil moisture, need to also be recorded to both understand changes in the gas concentrations and to assess other factors that may also impact on plant and microbial health. Whichever monitoring technique is selected, the results described in this paper have shown that soil gas concentrations above 10% and surface CO_2 flux rates above ~0.8 kg m^{-2} d^{-1} start to impact on plants and probably on soil microbiology in all the climate areas investigated, and thus might be taken as a trigger level which necessitates additional scrutiny of a site. Plant response to increased CO_2 soil gas concentrations can be very rapid with some species responding within days of exposure. Additionally, certain plant species appear to be potential 'bioindicators' of elevated gas concentrations so could, in themselves, be considered as a possible monitoring tool.

In this regard remote sensing techniques may hold some potential, as air-borne instruments that measure wavelength absorption characteristics of plants (e.g. hyperspectral) can be used as a proxy indicator of plant health/stress. Such work was performed at the Latera site (Bateson et al., 2008); although promising, this research illustrated that plant stress can be caused by factors other than CO_2, and thus ground truthing via direct soil gas measurements is needed to eliminate "false positives". Of the true leakage points defined with the remote sensing approach used by these authors the smallest anomaly had a soil gas concentration at 60 cm of about 10% and a flux of about 60 g m^{-2} d^{-1}, which can be considered as the method sensitivity threshold. The most successful approach achieved a success rate of 47%, with some unknown vents located. However, some known gas vents were not found in this work and there may also be other unknown leakage areas that were not defined. It also identified a number of false positives. This work was extended using geostatistical and probabilistic methods to improve the ability to identify anomalies (Govindan et al., 2011). This unsupervised approach to detecting CO_2 leakages has more recently been applied at the Laacher See (Govindan et al., 2013).

Monitoring of the microbial population and community make-up could also provide early indications of increasing CO_2 on soil ecosystems and could also indicate where there has been long-term undetected exposure. Nevertheless, information from these European studies shows that the spatial scale of these responses is likely to be relatively small although this will be site-specific.

ACKNOWLEDGEMENTS

These studies were undertaken for the project 'Research into Impacts and Safety in CO_2 Storage (RISCS) and for the FP6 European Network of Excellence CO_2GeoNet. RISCS was funded by the EC 7th Framework Programme (Project No. 240837) and by industry partners ENEL, I&I, Statoil, Vattenfall AB, E.ON and RWE. The BGS authors publish with the permission of the Executive Director, BGS (Natural Environment Research Council).

REFERENCES

Annunziatellis, A., Beaubien, S.E., Bigi, S., Ciotoli, G., Coltella, M., Lombardi, S. 2008. Gas migration along fault systems in the Latera natural analogue (central Italy): implications for CO_2 geological storage. International Journal of Greenhouse Gas Control 2, 353-372.

Bateson, L., Vellico, M., Beaubien, S.E., Pearce, J.M., Annunziatellis, G., Ciotoli, F., Coren, S., Lombardi, S., Marsh, S. 2008. The application of remote-sensing techniques to monitor CO_2 storage sites for surface leakage: method development and testing at Latera (Italy) where naturally produced CO_2 is leaking to atmosphere. International Journal of Greenhouse Gas Control 2, 388-400.

Beaubien, S.E. Ciotoli, G., Coombs, P., Dictor, M.C., Krüger, M., Lombardi, S., Pearce, J. M., West, J.M. 2008. The impact of a naturally occurring CO_2 gas vent on the shallow ecosystem and soil chemistry of a Mediterranean pasture (Latera, Italy). International Journal of Greenhouse Gas Control 2, 373-387.

Beaubien, S.E., Jones, D.G., Gal, F., Barkwith, A.K.A.P., Braibant, G., Baubron, J-C., Ciotoli, G., Graziani, S., Lister, T.R., Lombardi, S., Michel, K., Quattrocchi, F., Strutt, M.H. 2013. Monitoring of near-surface gas geochemistry at the Weyburn, Canada, CO_2-EOR site, 2001-2011. International Journal of Greenhouse Gas Control 16, S236-S262.

Bergfield, D., Evans, W.C., Howle, J. F., Farrar, C. D. 2006. Carbon dioxide emissions from vegetation-kill zones around the resurgent dome of Long Valley caldera, eastern California, USA. Journal of Volcanology and Geothermal Research 15, 140-156.

Biondi, F., Fessenden, J.E. 1999. Response of lodgepole pine growth to CO_2 degassing at Mammoth Mountain, California. Ecology 80, 2420-2426.

Cook, A.C., Tissue, D.T., Roberts, S.W., Oechel, W.C. 1998. The detection of concealed faults in the Ofanto Basin using the correlation between soil-gas fracture surveys. Tectonophysics 301, 321-332.

Damen, K., Faaij A.,Turkenburg, W. 2006. Health, safety and environmental risks of underground CO_2 storage–overview of mechanisms and current knowledge. Climatic Change 74, 289-318.

Donders, T.H., Decuyper, M., Beaubien, S.E., van Hoof, T.B., Cherubini, P., Sass-Klaassen, U. 2013. Tree rings as biosensor to detect leakage of subsurface fossil CO_2. International Journal of Greenhouse Gas Control, 19, 387-395.

Ford, J.R. 2006. The geology of the ASGARD site, Sutton Bonington. British Geological Survey Internal Report IR/06/049R.

Frerichs, J., Oppermann, B. I., Gwosdz, S., Möller. I., Herrmann, M., Krüger, M. 2013. Microbial community changes at a terrestrial volcanic CO_2 vent induced by soil acidification and anaerobic microhabitats within the soil column. FEMS Microbiology Ecology 84 (1) 60-74.

Gal, F., Brach, M., Braibant, G., Jouin, F., Michel, K. 2011. CO_2 escapes in the Laacher See region, East Eifel, Germany: Application of natural analogue onshore and offshore geochemical monitoring. International Journal of Greenhouse Gas Control 5, 1099-1118.

Govindan, R., Korre, A., Durucan, S., Imrie, C. E. 2011. A geostatistical and probabilistic spectral image processing methodology for monitoring potential CO_2 leakages on the surface. International Journal of Greenhouse Gas Control 5, 589-597.

Govindan, R., Korre, A., Durucan, S. 2013. Application of an unsupervised methodology for the indirect detection of CO_2 leakages around the Laacher See in Germany using remote sensing data. Energy Procedia 37, 4057-4064

Hinkle, M. 1994. Environmental conditions affecting concentrations of He, CO_2, O_2 and N_2 in soil gases. Applied Geochemistry 9, 53-63.

ISBT Carbon Dioxide Quality Guidelines and Analytical Procedure Bibliography, International Society of Beverage Technologists, USA, March 2001.

Jones, D.G., Lister, T.R., Smith, D.J., West, J.M., Coombs, P., Gadalia, A., Brach, M., Annunziatellis, A., Lombardi, S. 2011. In Salah Gas CO_2 storage JIP: surface gas and biological monitoring. Energy Procedia 4, 3566-3575.

Jossi, M., Fromin, N., Tarnawski, S., Kohler, F., Gillet, F., Aragno, M., Hamelin, J. 2006. How elevated p CO_2 modifies total and metabolically active bacterial communities in the rhizosphere of two perennial grasses grown under field conditions. FEMS Microbiology Ecology 55, 39-350.

Karakatsanis, S., Koukouzas, N., Pagonas, M., Zelididis, A. 2007. Preliminary sedimentological results indicate a new detailed stratigraphy for the Florina sedimentary basin and relate them with CO_2 presence. In: Proceedings of the 11th International Congress, Athens, Bulletin of the Geological Society of Greece, May 2007, 78-84.

Keith, C. J., Repasky, K. S., Lawrence, R. L., Jay, S.C., Carlsten, J.L., 2009. Monitoring effects of a controlled subsurface carbon dioxide increase on vegetation using a hyperspectral imager. International Journal of Greenhouse Gas Control 3, 626-632.

Kool, D.M., Chung, H., Tate, K.R., Ross, D. J., Newton, P.C.D. 2007. Hierarchical saturation of soil carbon pools near a natural CO_2 spring. Global Change Biology 13, 1282-1293.

Krüger, M., Jones, D., Frerichs, J., Oppermann, B.I., West, J., Coombs, P., Green, K., Barlow, T., Lister, R., Shaw, R., Strutt, M., Möller, I. 2011. Effects of elevated CO_2 concentrations on the vegetation and microbial populations at a terrestrial CO_2 vent at Laacher See, Germany. International Journal of Greenhouse Gas Control 5, 1093-1098.

Lamers, L P M, Govers, L L, Janssen, I C J M, Geurts, J J M, Van Der Welle, M E W, Van Katwijk, M M, Van Der Heide, T, Roelofs, J G M and Smolders, A J P. 2013. Sulfide as a soil phytotoxin—a review. Frontiers in Plant Science, 4, 268.

Maček, I., Pfanz, H., Francetič, V., Batič, F., Vodnik, D. 2005. Root respiration response to high CO_2 concentrations in plants from natural CO_2 springs. Environmental and Experimental Botany 54, 90–99.

Maček, I., Kastelec, D., Vodnik, D. 2012. Root colonisation with arbuscular mycorhizal fungi and glomalin-related soil protein (GRSP) concentration in hypoxic soils from natural CO_2 springs. Agricultural Food Science 21, 62-71.

Male, E., Pickles, W., Silver, E., Hoffman, G., Lewicki, J., Apple, M., Repasky, Burton, E. 2010. Using hyperspectral plant signatures for CO_2; leak detection during the 2008 ZERT

CO_2 sequestration field experiment in Bozeman, Montana. Environmental Earth Sciences 60, 251-261.

McFarland, J.W., Waldrop, M.P., Haw, M. 2013. Extreme CO_2 disturbance and the resilience of soil microbial communities. Soil Biology and Biochemistry 65, 274-286.

Möller, I. 2009. Report on joint geoecological research of natural CO_2 sources in the East Eifel, Germany. CO2GeoNet deliverable JRAP-18/4, BGR, Hannover, Library No 0128284.

Moni, C., Rasse, D.P. 2014. Detection of simulated leaks from geologically stored CO_2 with ^{13}C monitoring. International Journal of Greenhouse Gas Control, 26, 61-68.

Morales, S.E. and Holben, W.E. 2013. Functional response of a near-surface soil microbial community to a simulated underground CO_2 storage leak. PLoS ONE, 8, e81742

Morales, S.E. and Holben, W.E.G. 2014. Simulated geologic carbon storage leak reduces bacterial richness and alters bacterial community composition in surface soil. Soil Biology and Biochemistry, 76, 286-296.

Noble, R.R.P., Stalker, L., Wakelin, S.A., Pejcic, B., Leybourne, M., Hortle, A.L., Michael, K. 2012. Biological monitoring for carbon capture and storage – a review and potential future developments. International Journal of Greenhouse Gas Control 10, 520-535.

Oppermann, B.I., Michaelis, W., Blumenberg, M., Frerichs, J., Schulz, H.M., Schippers, A., Beaubien, S..E., Krüger, M. 2010. Soil microbial community changes as a result of long-term exposure to a natural CO_2 vent. Geochimica Cosmochimica Acta 74, 2697–2716.

Patil, R.H., Colls, J.J., Steven, M.D. 2010. Effects of CO_2 gas as leaks from geological storage sites on agro-ecosystems. Energy 35, 4587-4591.

Pettinelli, E., Beaubien, S.E., Lombardi, S., Annan, A.P. 2008. GPR, TDR, and geochemistry measurements above an active gas vent to study near-surface gas-migration pathways. Geophysics 73(1), A11-A15.

Pettinelli, E., Beaubien, S.E., Zaja, A., Menghini, A., Praticelli, N., Mattei, E., Di Matteo, A., Annunziatellis, A., Ciotoli, G., Lombardi, S., 2010. Characterization of a CO_2 gas vent using various geophysical and geochemical methods. Geophysics 75, B137-B146.

Pfanz, H., Vodnik, D., Wittmann, C., Aschan, G., Batič, F., Turk, B., Maček, I. 2007. Photosynthetic performance (CO_2-compensation point, carboxylation efficiency, and net photosynthesis) of timothy grass (*Phleum pratense* L.) is affected by elevated carbon dioxide in post-volcanic mofette areas. Environmental and Experimental Botany 61, 41–48.

Ross, D.J., Tate, K.R., Newton, P.C.D., Wilde, R. H., Clark, H. 2000. Carbon and nitrogen pools and mineralization in a grassland gley soil under elevated carbon dioxide at a natural CO_2 spring. Global Change Biology 6, 779-790.

Romanak, K. D., Bennett, P. C., Yang, C., Hovorka, S. D. 2012. Process-based approach to CO_2 leakage detection by vadose zone gas monitoring at geologic CO_2 storage sites. Geophysical Research Letters, Vol. 39, L15405.

Šibanc, N., Dumbrell, A.J., Mandić-Mulec., Maček, I. 2014. Impacts of naturally elevated soil CO_2 concentrations on communities of soil archaea and bacteria. Soil Biology and Biochemistry 68, 348-356.

Stephens, J.C., Hering, J.G. 2004. Factors affecting the dissolution kinetics of volcanic ash soils: dependencies on pH, CO_2 and oxalate. Applied Geochemistry 19, 1217–1232.

Smith, K., Steven, M.D., Jones, D.G., West, J.M., Coombs, P., Green, K.A., Barlow, T.S., Breward, N., Gwosdz, S., Krüger, M., Beaubien, S.E., Annunziatellis, A., Graziani, S., Lombardi, S. 2013. Environmental impacts of CO_2 leakage: recent results from the ASGARD facility, UK. Energy Procedia 37, 791-799.

Spangler, L.H., Dobeck, L.M., Repasky, K.S., Nehrir, A.R., Humphries, S.D., Barr, Jamie L., Keith, C.J., Shaw, J.A., Rouse, J.H., Cunningham, A.B., Benson, S.M., Oldenburg, C.M., Lewicki, J.L., Wells, A.W., Diehl, J.R., Strazisar. B.R., Fessenden, J.E., Rahn, T.A., Amonette, J.E., Barr, Jon. L., Pickles, W.L., Jacobson, J.D., Silver, E.A., Male, E. J., Rauch, H.W., Gullickson, K.S., Trautz, R., Kharaka, Y., Birkholzer, J., Wielopolski, L. 2010. A shallow subsurface controlled release facility in Bozeman, Montana USA, for testing near surface CO_2 detection techniques and transport models. Environmental Earth Sciences 60, 227-239.

Stock, W.D., Ludwig, F., Morrow, C., Midgley, G.F., Wand, S.J.E, Allsopp, N., Bell, T.L. 2005. Long-term effects of elevated atmospheric CO_2 on species composition and productivity of a southern African C4 dominated grassland in the vicinity of a CO_2 exhalation. Plant Ecology 178, 211-224.

Tian, D., Xin, M., Zha, L-S., Yang, W., Zou, X., Hou, X. 2013. Review of impact of CO_2 leakage from geological storage on near-surface terrestrial ecological system. Journal of Ecology and Rural Environment 29, 137-145. (In Chinese).

West, J.M., Pearce, J.M., Bentham, M., Maul, P. 2005. Environmental issues and the geological storage of CO_2. European Environment 15, 250-259.

West, J. M., Pearce, J.M., Coombs, P., Ford, J.R., Scheib, C., Colls, J.J., Smith, K.L., Steven, M.D. 2009. The impact of controlled injection of CO_2 on soil ecosystems and chemistry of an English lowland pasture. Energy Procedia 1, 1863-1870.

West, J. M., Shaw, R. P., Pearce, J.M. 2011. Environmental issues in the geological disposal of carbon dioxide and radioactive waste. In: Geological Disposal of Carbon Dioxide and Radioactive Waste: A Comparative Assessment Toth, F.L. (Ed.) Advances in Global Change Research, 44, 81-102.

Zhou, X., Apple, M.E., Dobeck, L. M., Cunningham, A.B., Spangler, L.H. 2013. Observed response of soil O_2 concentration to leaked CO_2 from an engineered CO_2 leakage experiment. International Journal of Greenhouse Gas Control 16, 116-128.

Ziogou, F., Gemeni, V., Koukouzas, N., de Angelis, D., Libertini, S., Beaubien, S.E., Lombardi, S., West, J. M., Coombs, P., Barlow, T. S., Gwosdz, S., Krüger, M. 2013.

Potential environmental impacts of CO_2 leakage from the study of natural analogue sites in Europe. Energy Procedia 37, 3521-3528.

Figure 1 Photographs of the study sites: (a) Latera; (b) Laacher See; (c) Florina; (d) ASGARD. Images (a) – (c) show the studied gas vents with bare-earthed vent core and surrounding area with different vegetation. The flagged tape in (a) and (c) show the transects with 0 m in the picture foreground. Image (d) shows the 2.5 m x 2.5 m test plots with plots G8 (injected with CO_2 via the yellow piping) and G7 (no gassing) indicated. The vertical pipes are for gas monitoring.

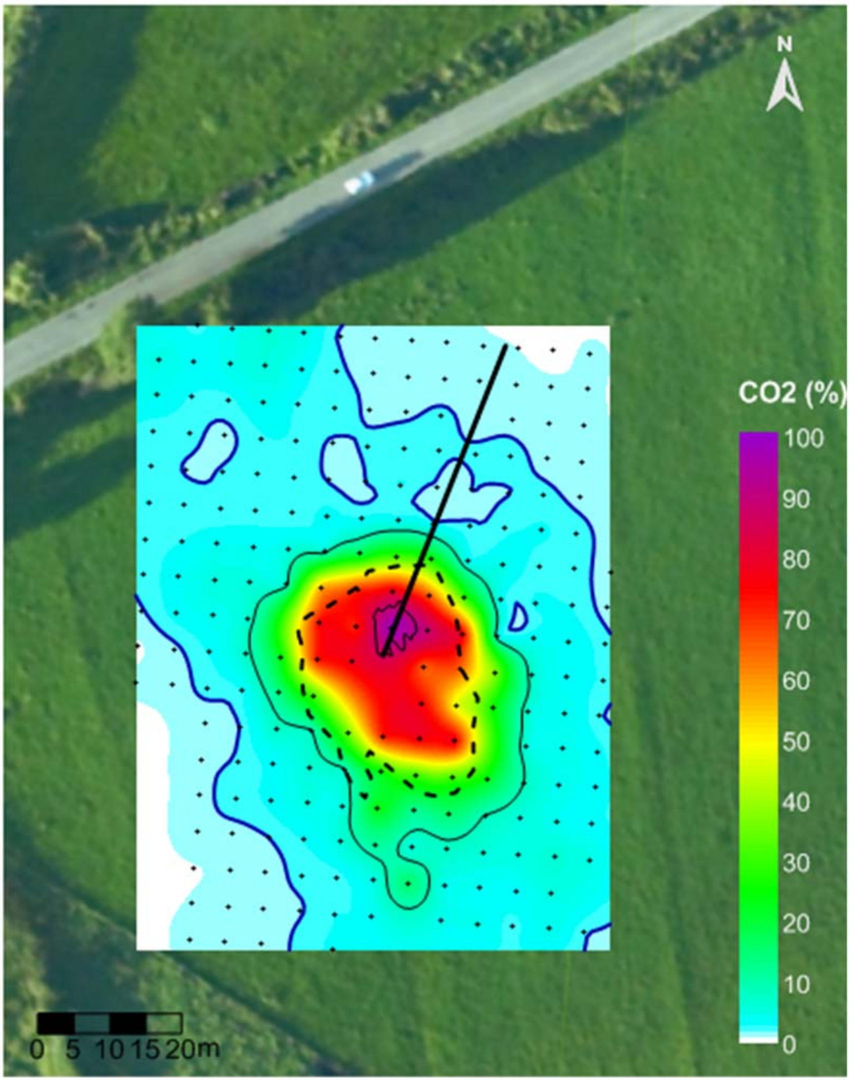


Figure 2 The contoured distribution of CO_2 soil gas concentrations at 90 cm depth at the studied gas vent in the Latera caldera area, with the position of the transect indicated by the black line (data from Pettinelli et al (2010)).

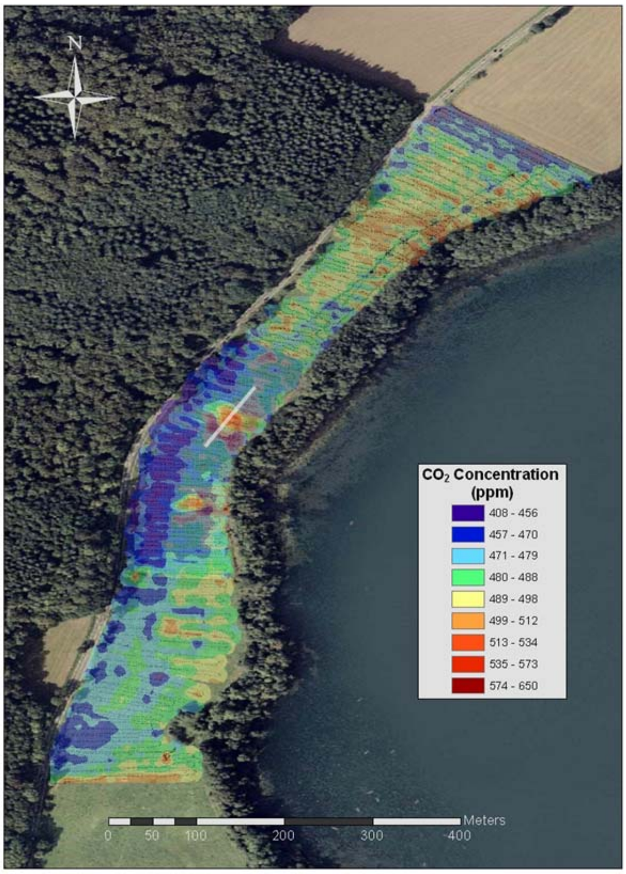


Figure 3 Mobile open path laser measurements of atmospheric CO_2 near the western shore of the Laacher See in September 2007 at a height of about 40 cm above the ground. The vent studied in the centre of the image shows clearly higher CO_2 values. The position of the transect is indicated by the white line in the centre of the image.

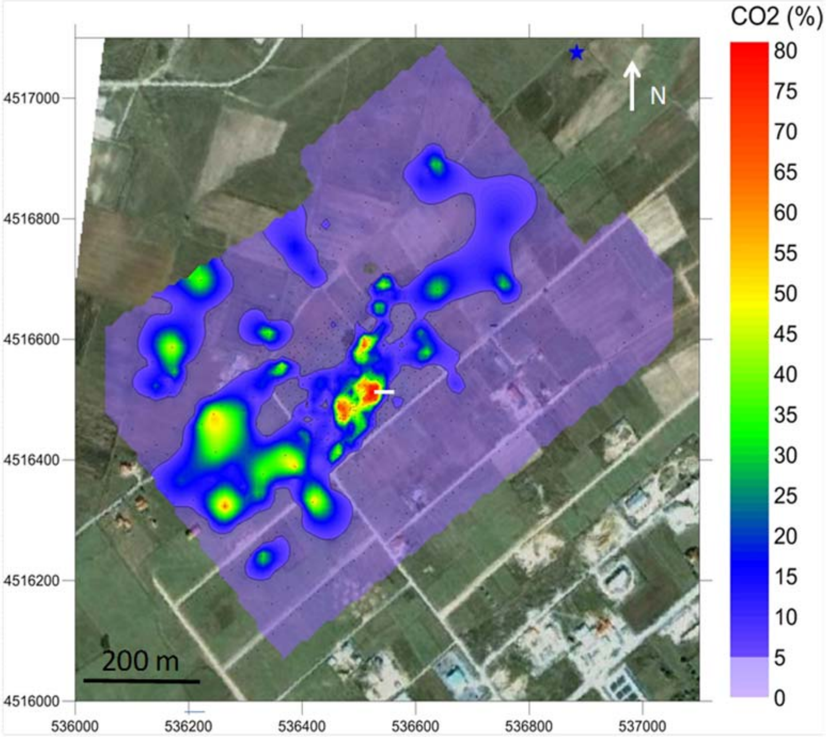


Figure 4 Soil gas CO_2 concentrations at 90 cm depth at the Florina site, July 2011. The transect studied is shown by the white line in the centre of the image

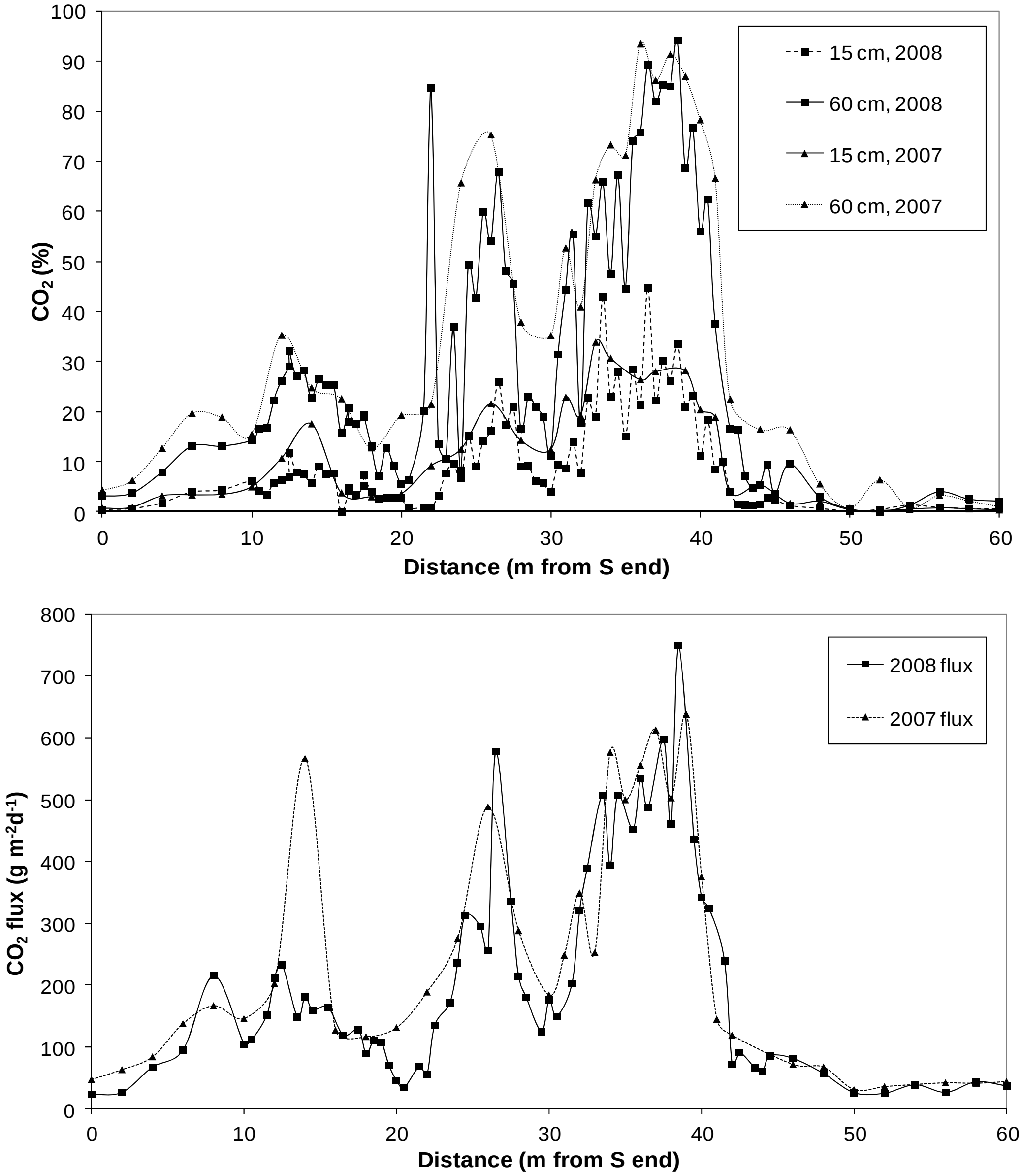


Figure 5 Laacher See data for the transect on the western shore of the lake for September 2007 and July 2008: a) CO_2 concentrations in soil gas at 15 cm and 60cm depth and b) CO_2 flux.

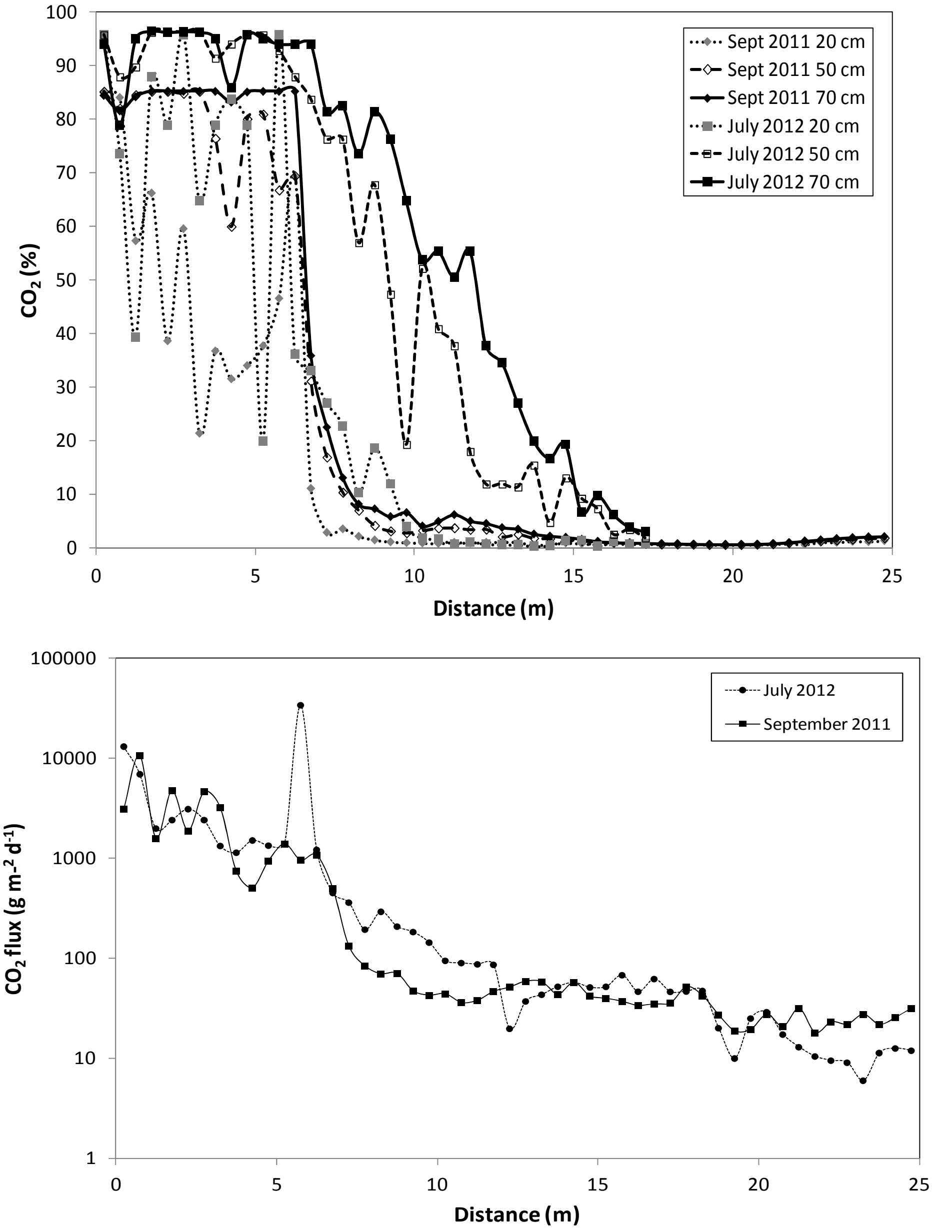


Figure 6 Florina transect data from the September 2011 and July 2012 campaigns: a) CO_2 concentrations in soil gas at 20 cm, 50 cm and 70cm depth and b) CO_2 flux (note log scale)

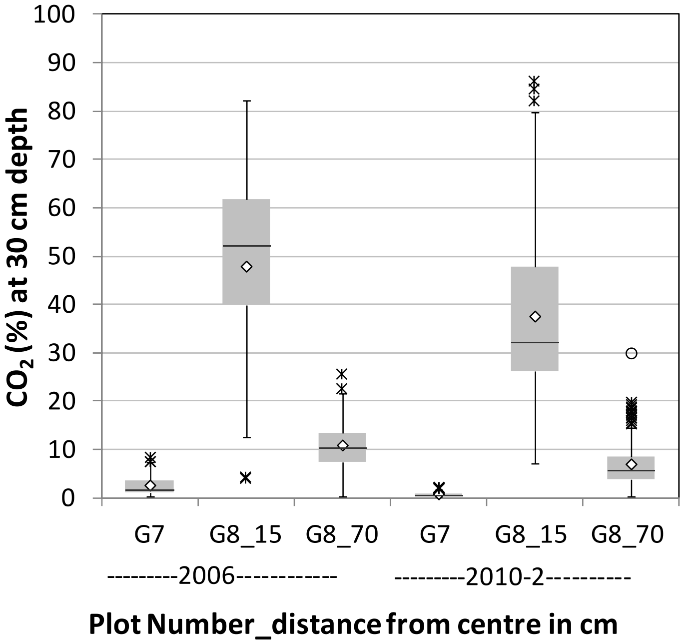


Figure 7 Box and whisker plot of weekly soil gas data for fixed sampling tubes in pasture plots at ASGARD, 2006 (3 L min^{-1}) and 2010-2012 (1L min^{-1}). G7 = ungassed plot; G8 = gassed plot. Means for each location in 2006 and 2010-2 are significantly different (p=0.01).

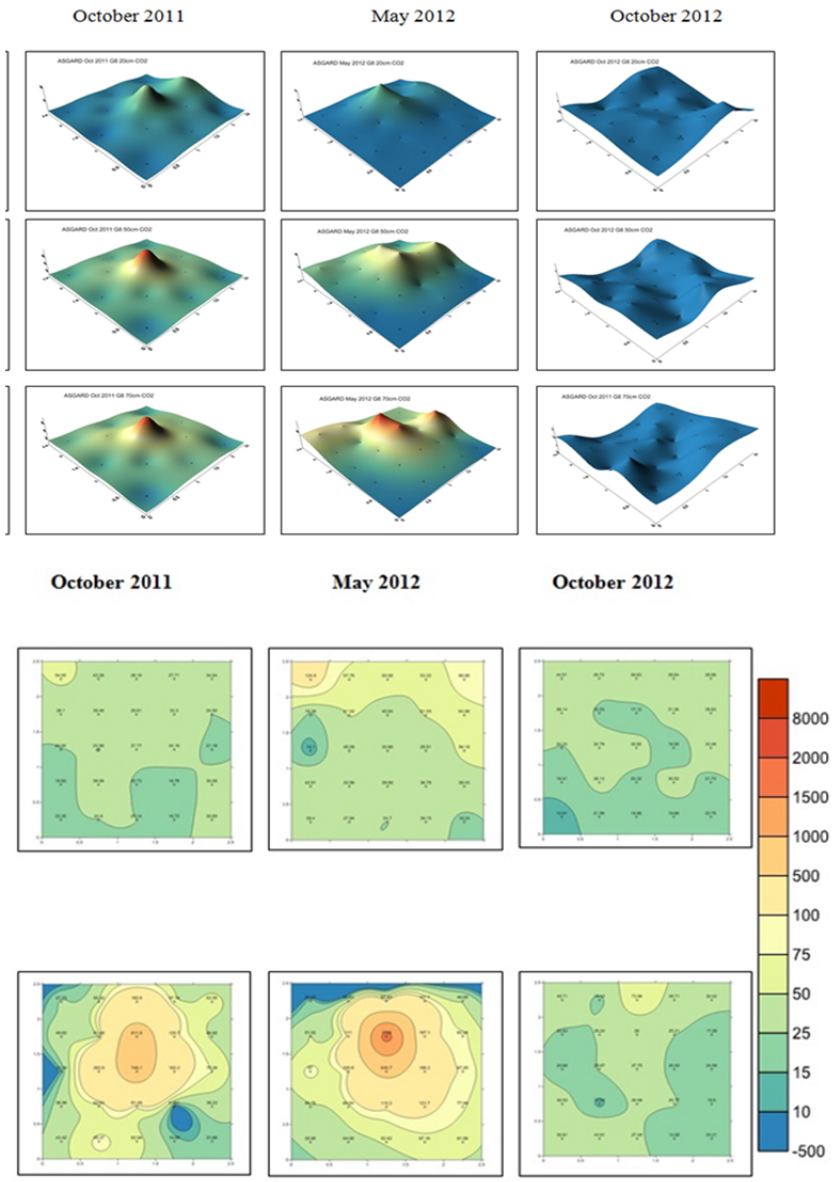


Figure 8 Soil gas CO_2 concentrations (top) in a gassed pasture plot (G8) at ASGARD at depths of 20 cm (top), 50 cm (middle) and 70 cm (bottom) for site visits from October 2011 to October 2012. Vertical scale CO_2 (%) blue <5%, red >70%. Gas injection ceased at the end of May 2012. CO_2 flux (below) for plot G7 (ungassed-top) and G8 (gassed-below) scale in $gm^{-2}d^{-1}$.

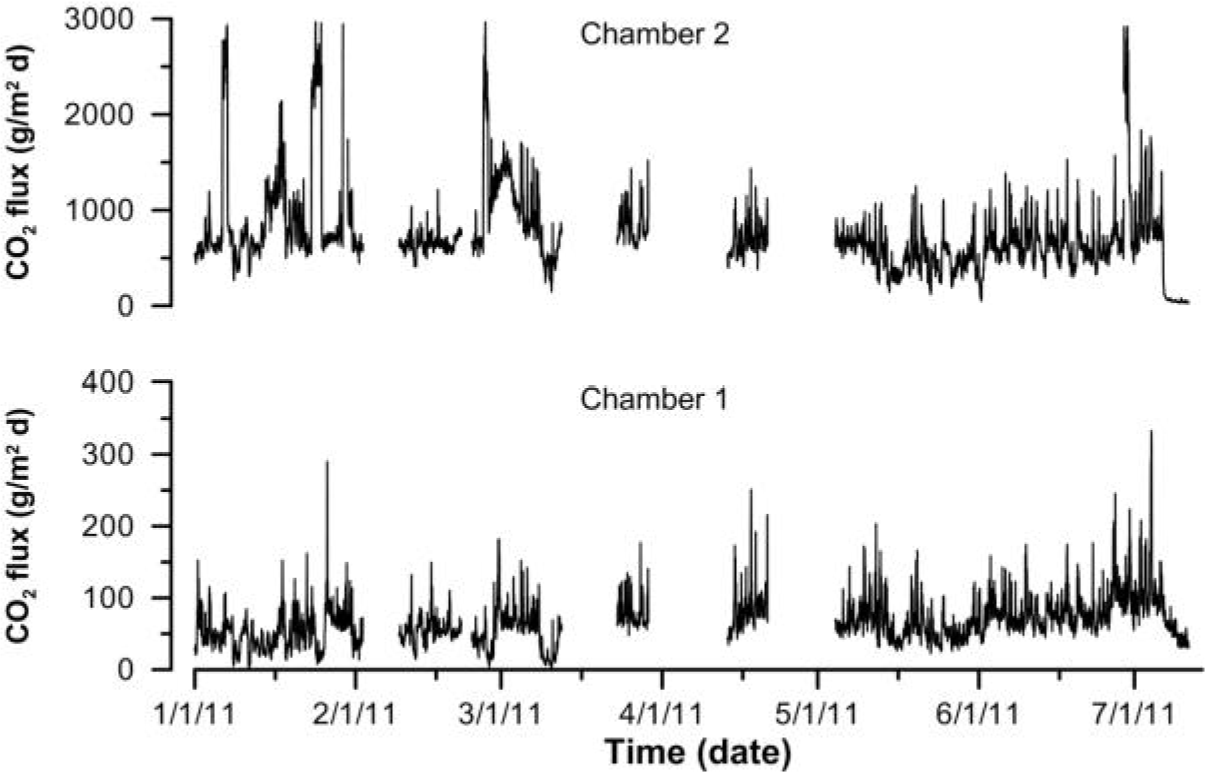


Figure 9 All 2011 data from 2 CO_2 flux monitoring chambers deployed on the gassed pasture plot at ASGARD. Note that data for chamber 2 (10 cm from the injection point) have been clipped at 3000 $g/m^2 d^{-1}$ to better highlight variability at lower flux rates; values exceeded this threshold on 5 occasions up to a maximum of about 8000 g $m-^2 d^{-1}$. Chamber 1 was 90cm from the injection point

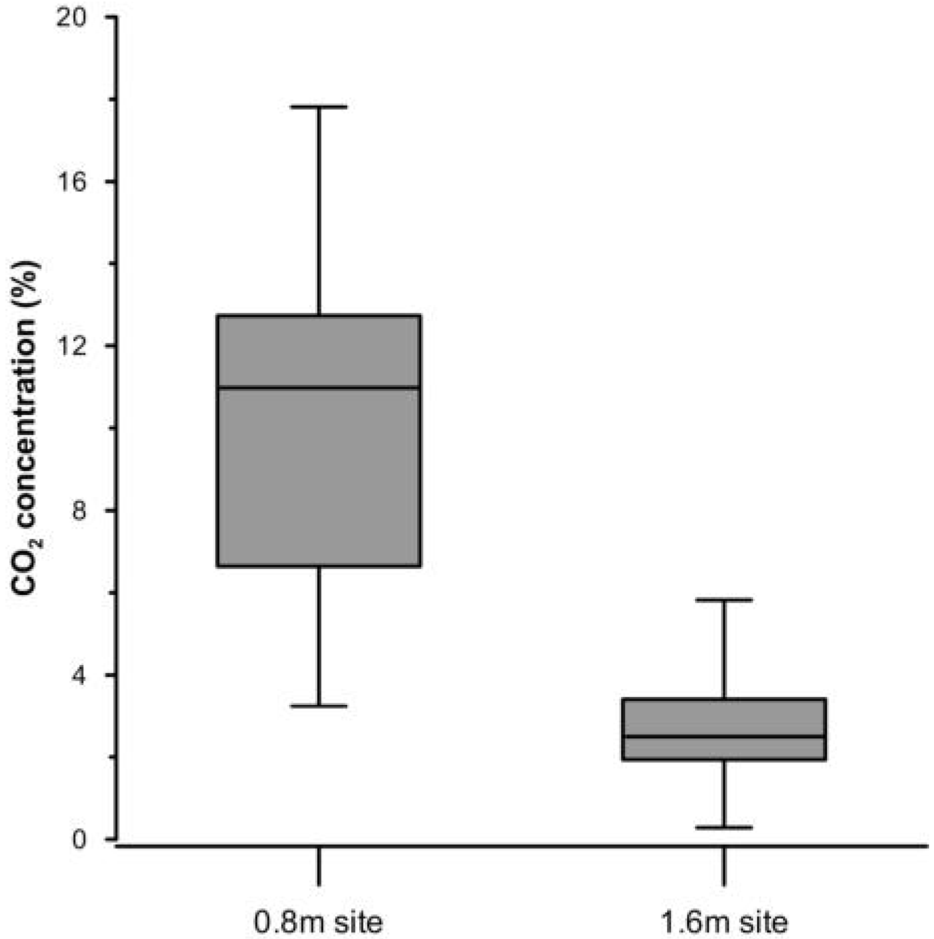


Figure 10 Box and whisker plots of all soil gas CO_2 concentration data measured at ASGARD at a depth of 20 cm by the continuous monitoring probes, over the period from March 3 to June 8, 2012. The 0.8 m site lay just outside the area of maximum concentration and flux whilst the 1.6 m site was near the outer edge of the plot

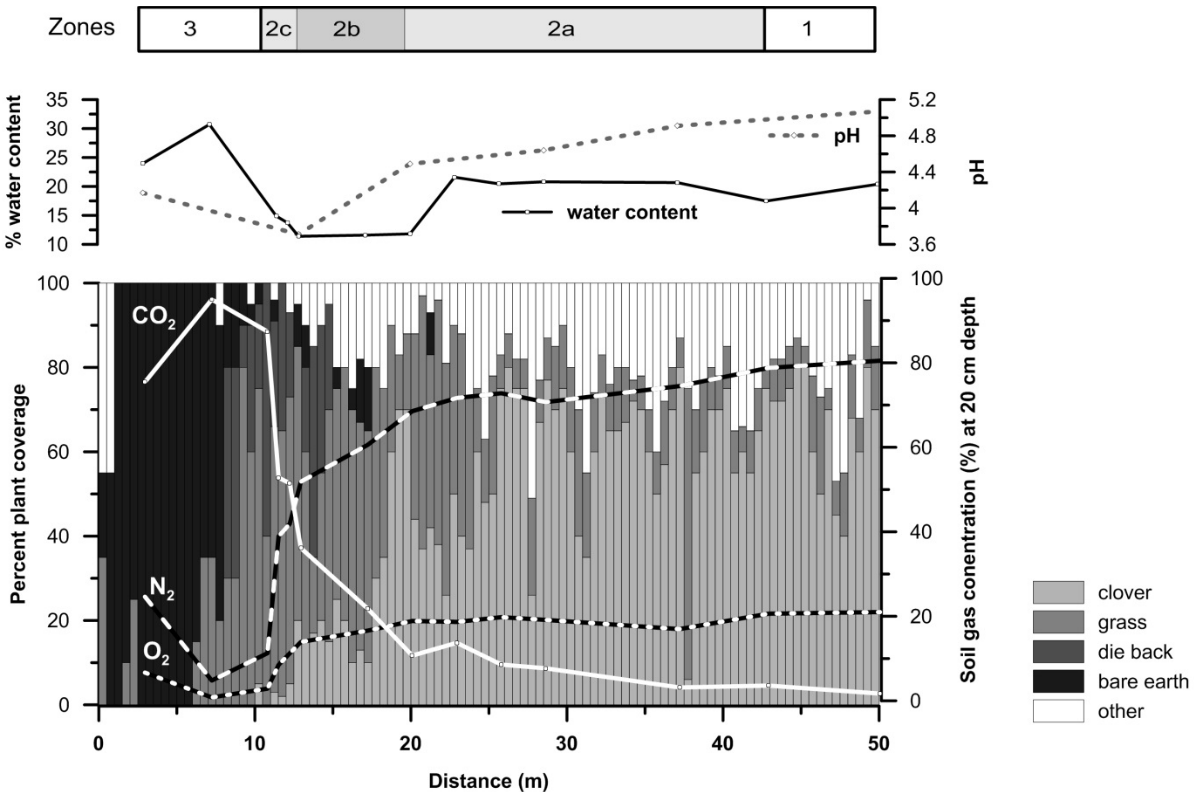


Figure 11 . Latera (adapted from Beaubien et al., 2008 (Figure 6)). Summary of selected parameters from September 2005 dataset. Plots show distribution of various soil gases from 20 cm depth (a) % water content (b)pH and (c) distribution of different botanical groups along the transect along the CO$_2$ vent . Zone 1 Background. Zone 2 Transition. Zone 3 Vent core. Die back is where plants have grown and then died. X axis: location in m from S end.

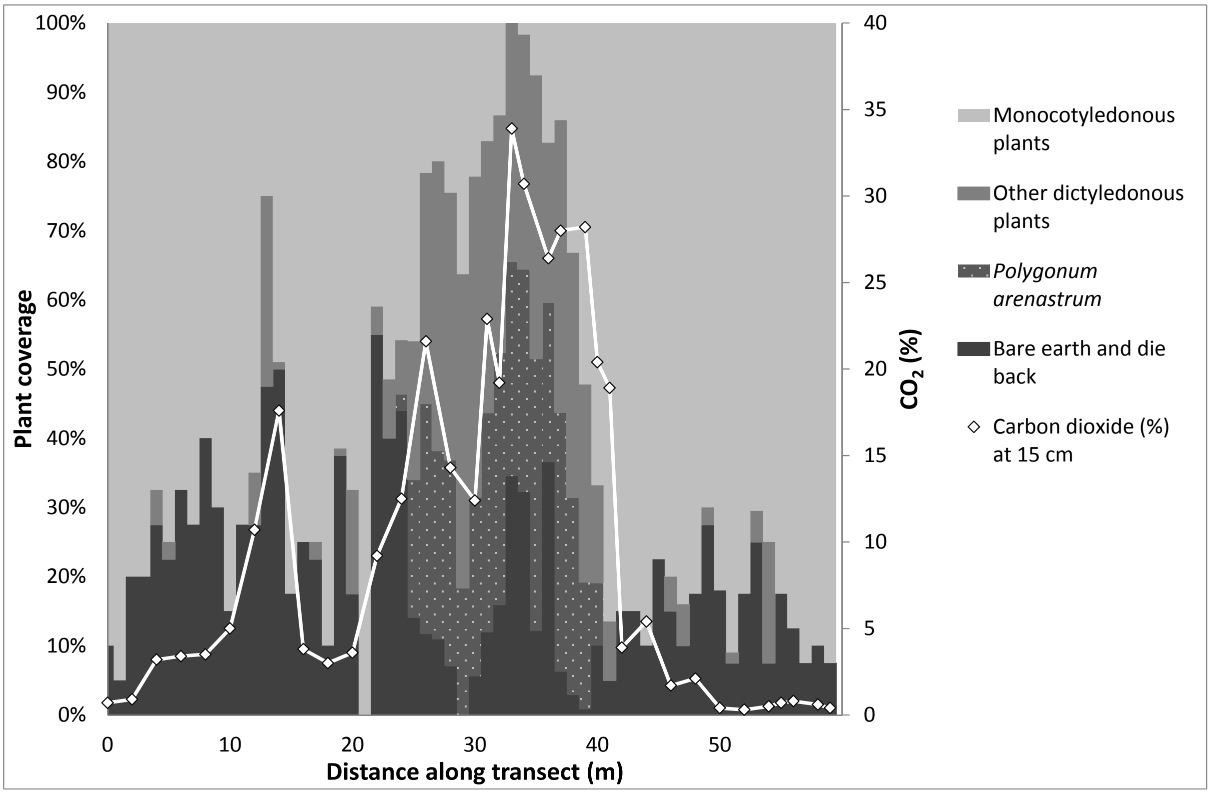


Figure 12 Laacher See (September 2007). Effect of CO_2 emissions on the distribution of different botanical groups/species across the CO_2 vent (centre at approximately 30-35 m). x-axis: location in m from S end, y-axis: coverage

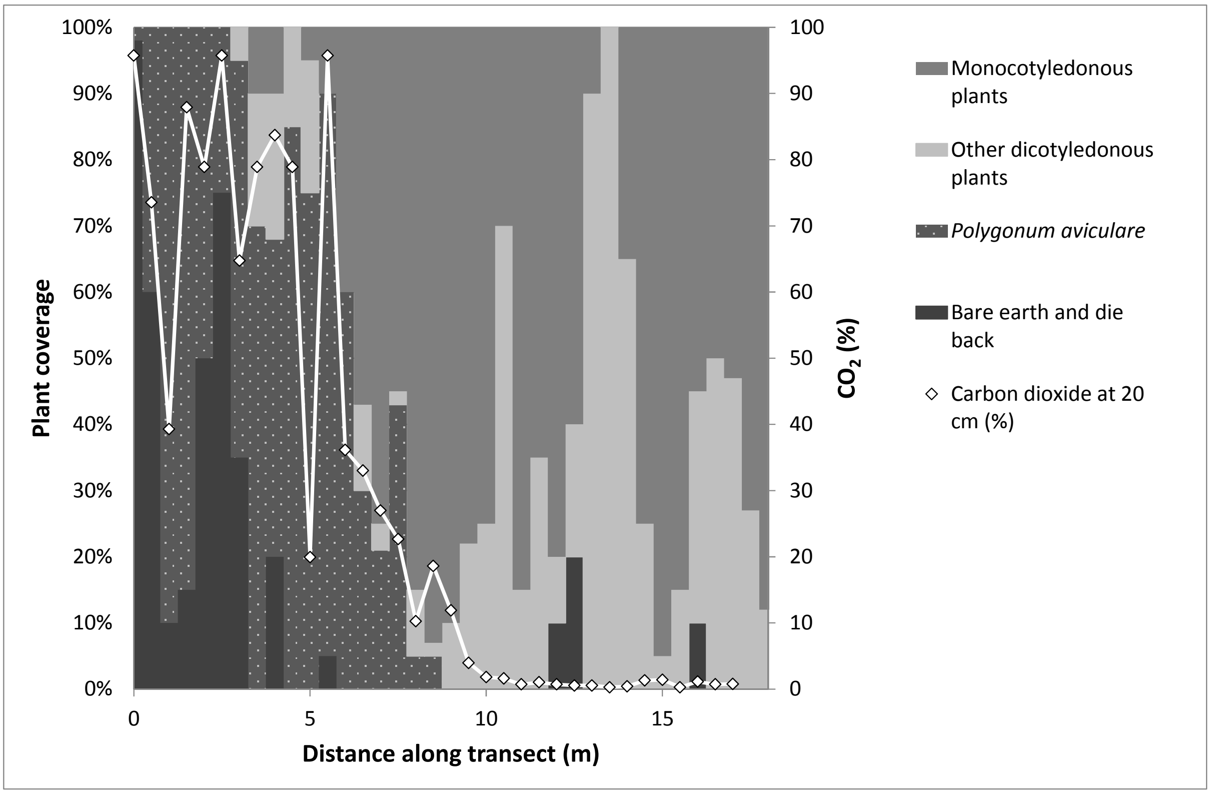


Figure 13 Florina (July 2012). Effect of CO_2 emissions on the distribution of different botanical groups/species along the transect from the CO_2 vent (centre at approximately 1 – 8 m). x-axis: location in m from centre of vent, y-axis: coverage

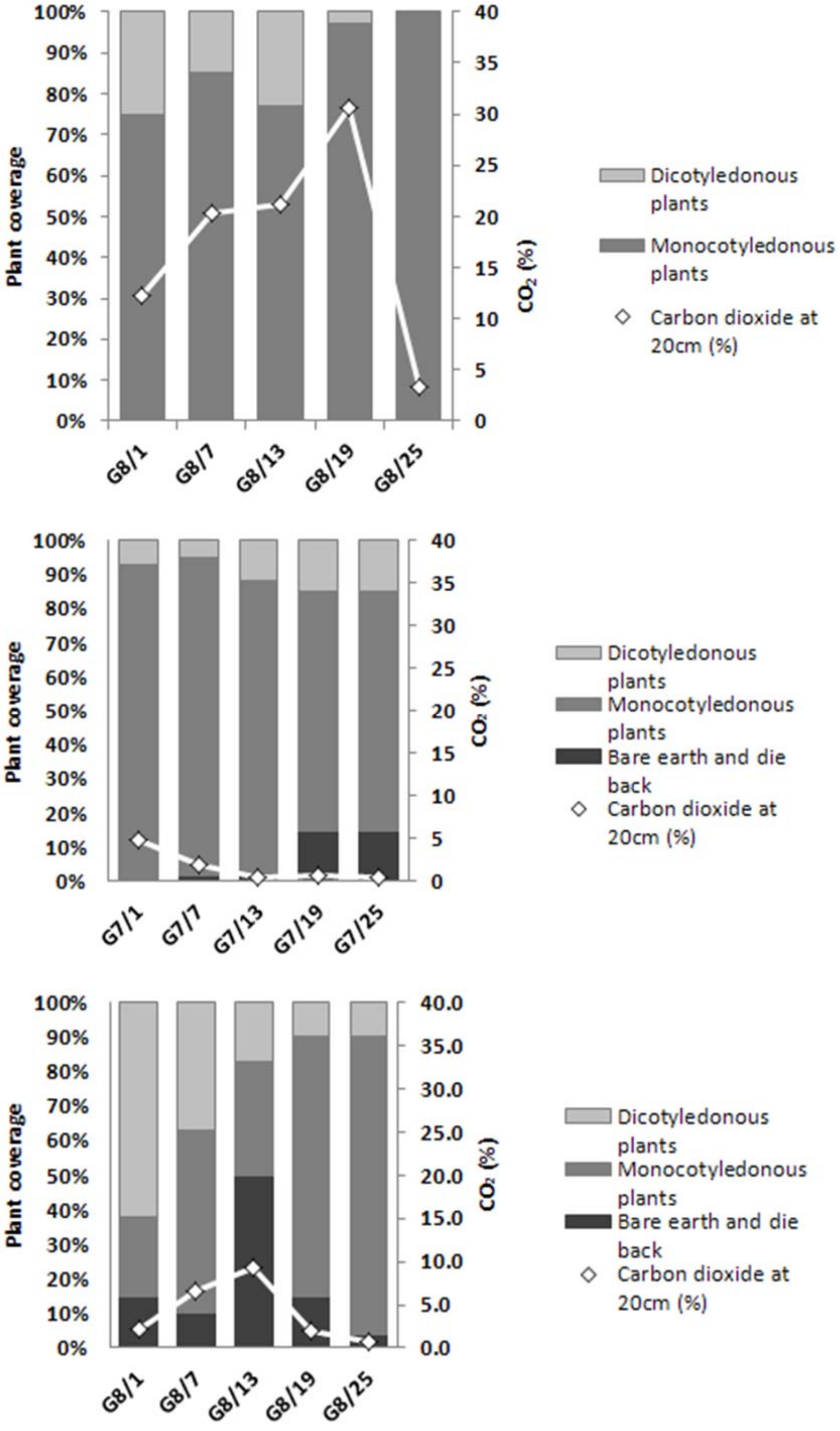


Figure 14 Effect of controlled injection of CO_2 at 60 cm on the distribution of different botanical groups along transects across pasture plots (G7 and G8) at ASGARD. x-axis: position diagonally across the plot, y-axis: coverage
a) September 2008. Transect across pasture plot G8 exposed to intermittent CO_2 gassing from March 2006 to May 2012. Injection rate 3 L min^{-1} at 60 cm depth in 2006 then 1 L min^{-1} from 2007 near position G/13
b) May 2012. Transect across pasture plot G7 which was not exposed to CO_2 gassing at any period from March 2006
c) May 2012. Transect across pasture plot G8 exposed to continuous gassing from June 2010. Injection rate 1 L min^{-1} at 60 cm depth near position G/13

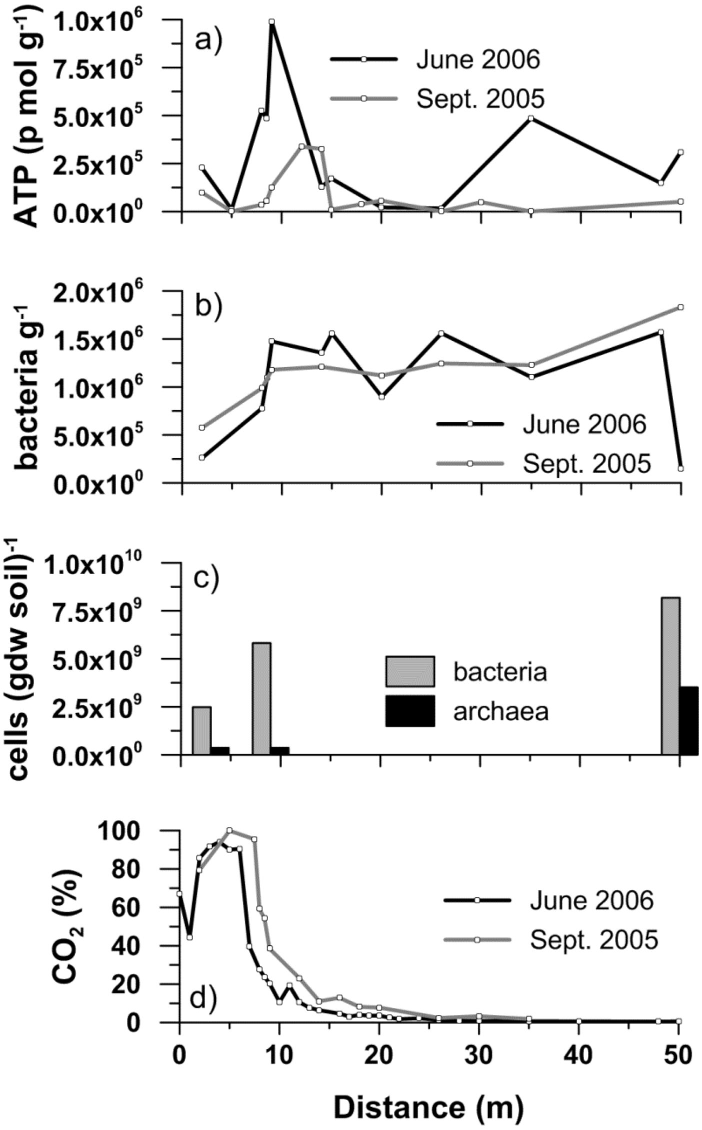


Figure 15 Latera Microbiology (Sept 2005 and June 2006) from Beaubien et al., 2008, Figure 5. Plots showing ATP biomass (a), mean total bacterial counts (b), and qPCR (c) along the profile. Note that the first two plots are for samples collected in the main field campaigns, the qPCR results are from samples collected in July 2005

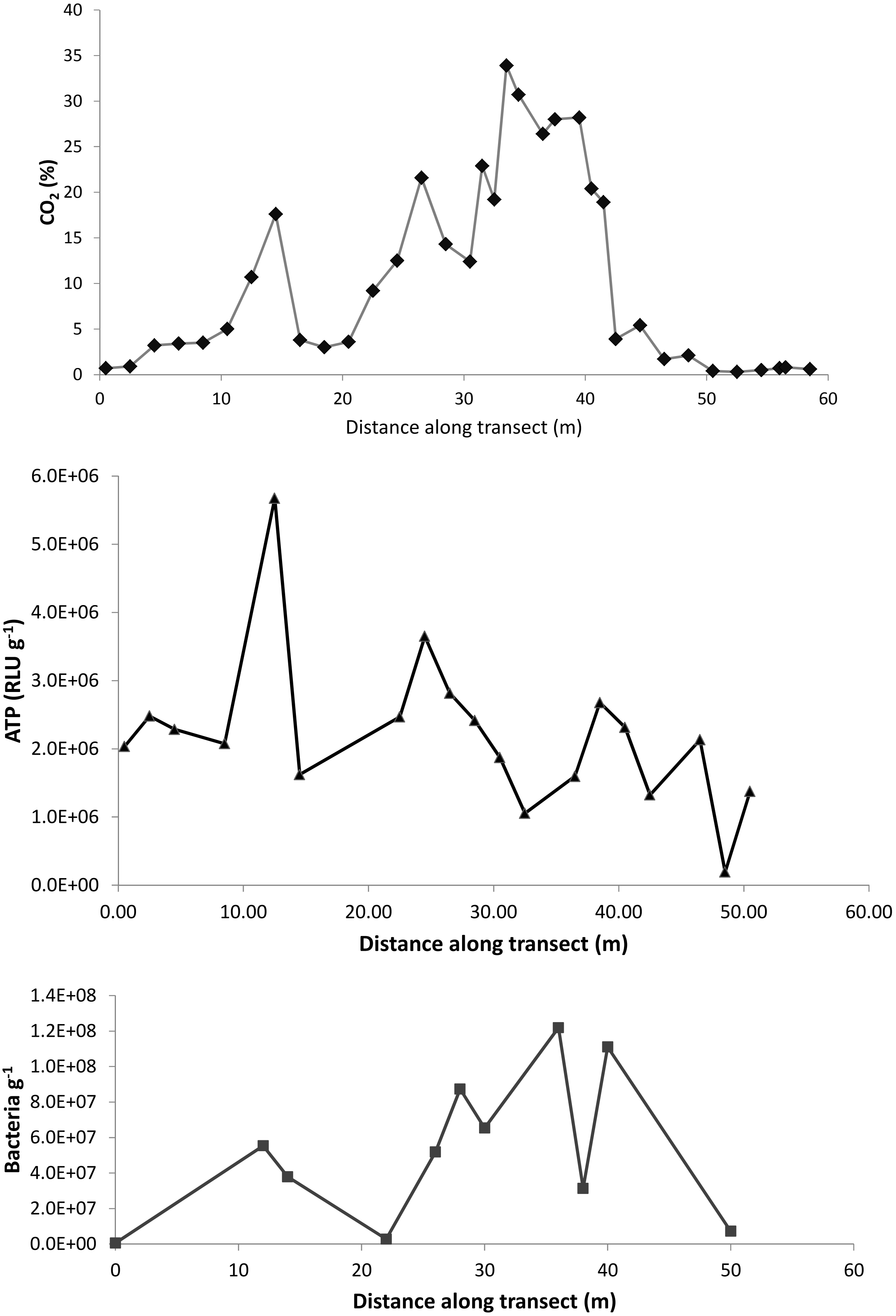
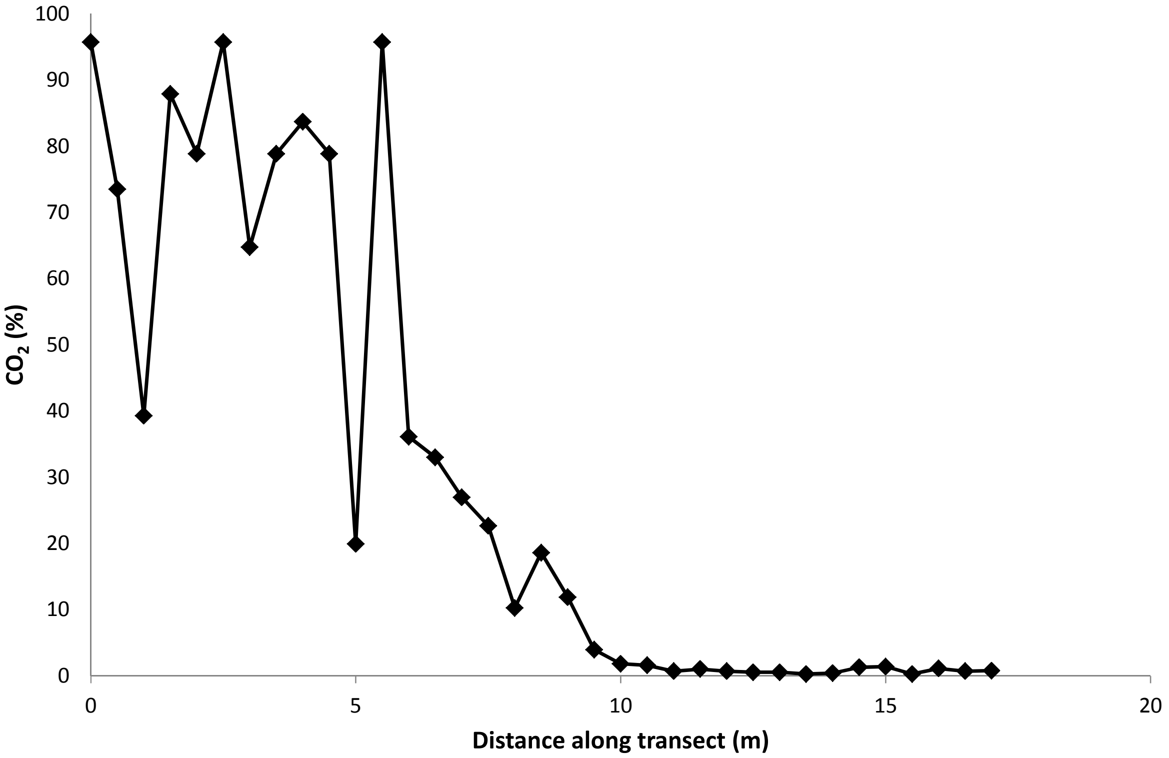


Figure 16 Laacher See (September 2007). Summary of selected parameters. Plots show distribution of CO_2 gas concentration at 15 cm depth (a), ATP biomass (Relative Light Units) (b) mean total bacterial counts (c) across the CO_2 vent (centre at approximately 30-35 m). x-axis: location in m from S end



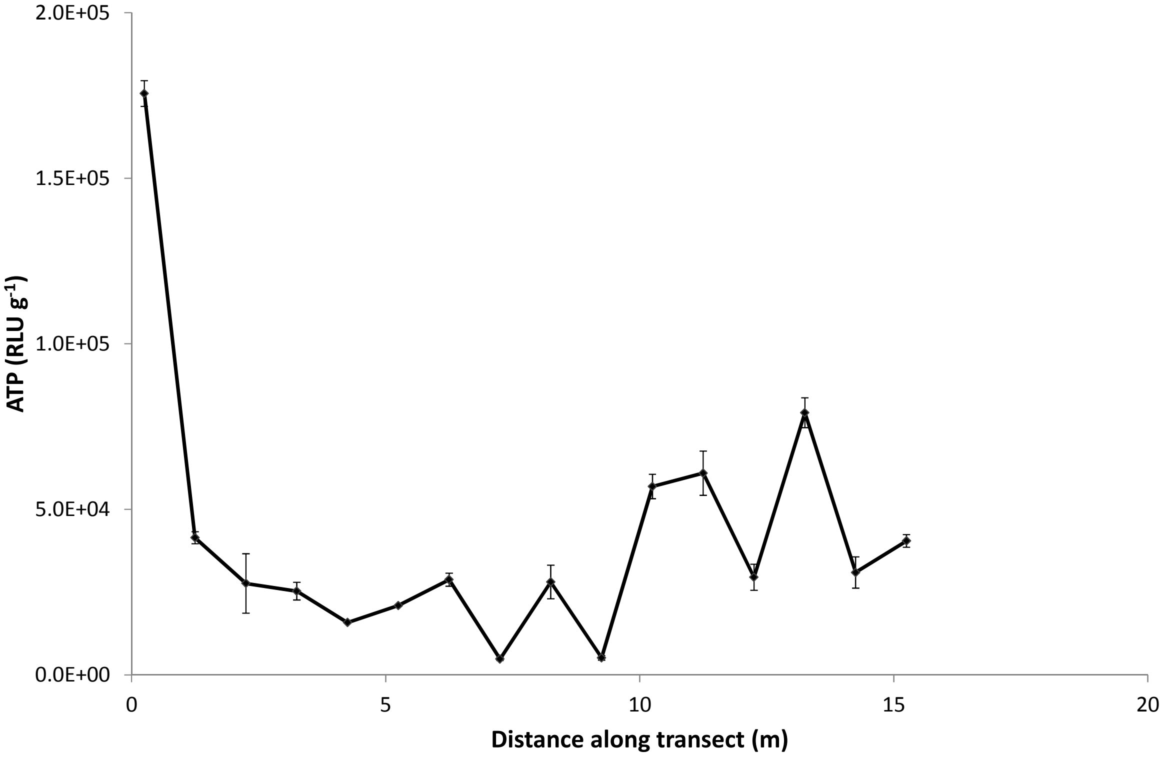
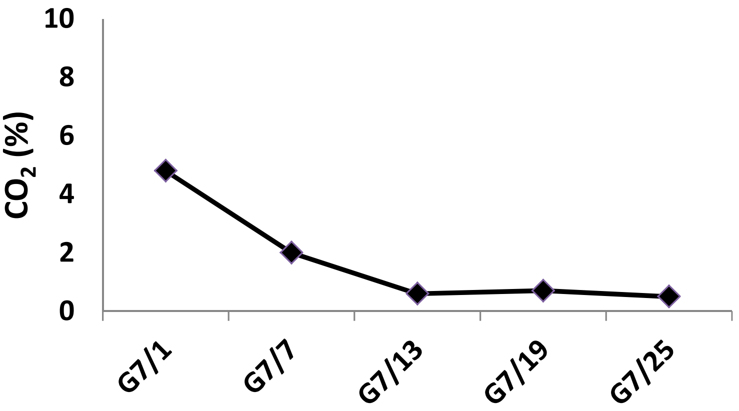
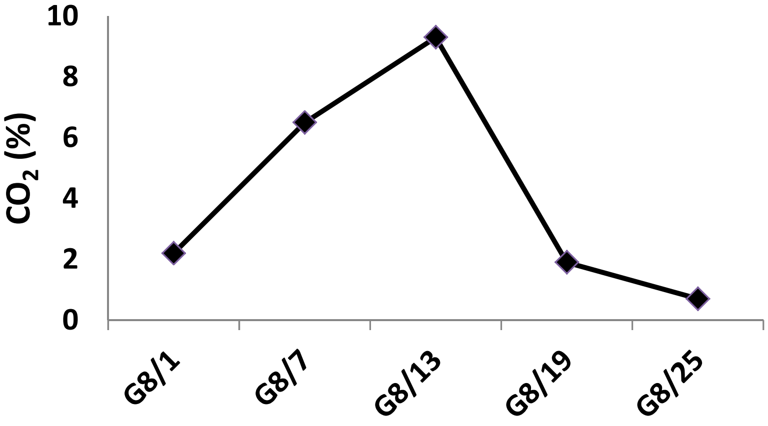
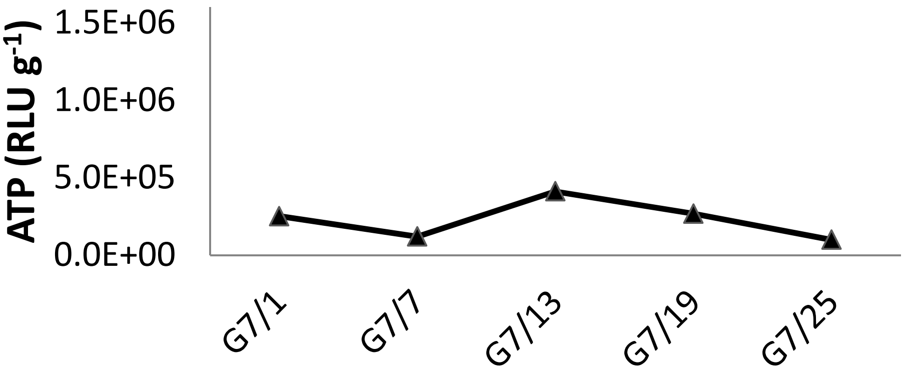
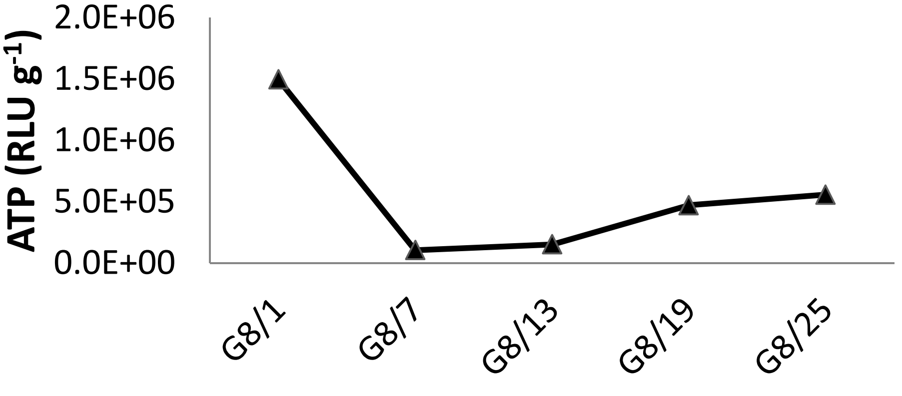


Figure 17 Florina (May 2012) (adapted from Ziogou et al, 2013). Summary of selected parameters. Plots show distribution of CO_2 gas concentration at 20 cm depth (a), ATP biomass (Relative Light Units) (b) mean total bacterial counts along the transect from the CO_2 vent (centre at approximately 18 m). x-axis: location in m from centre of vent


CO$_2$ (%)
10
8
6
4
2
0
G7/1
G7/7
G7/13
G7/19
G7/25


CO$_2$ (%)
10
8
6
4
2
0
G8/1
G8/7
G8/13
G8/19
G8/25


ATP (RLU g^{-1})
1.5E+06
1.0E+06
5.0E+05
0.0E+00
G7/1
G7/7
G7/13
G7/19
G7/25


ATP (RLU g^{-1})
2.0E+06
1.5E+06
1.0E+06
5.0E+05
0.0E+00
G8/1
G8/7
G8/13
G8/19
G8/25

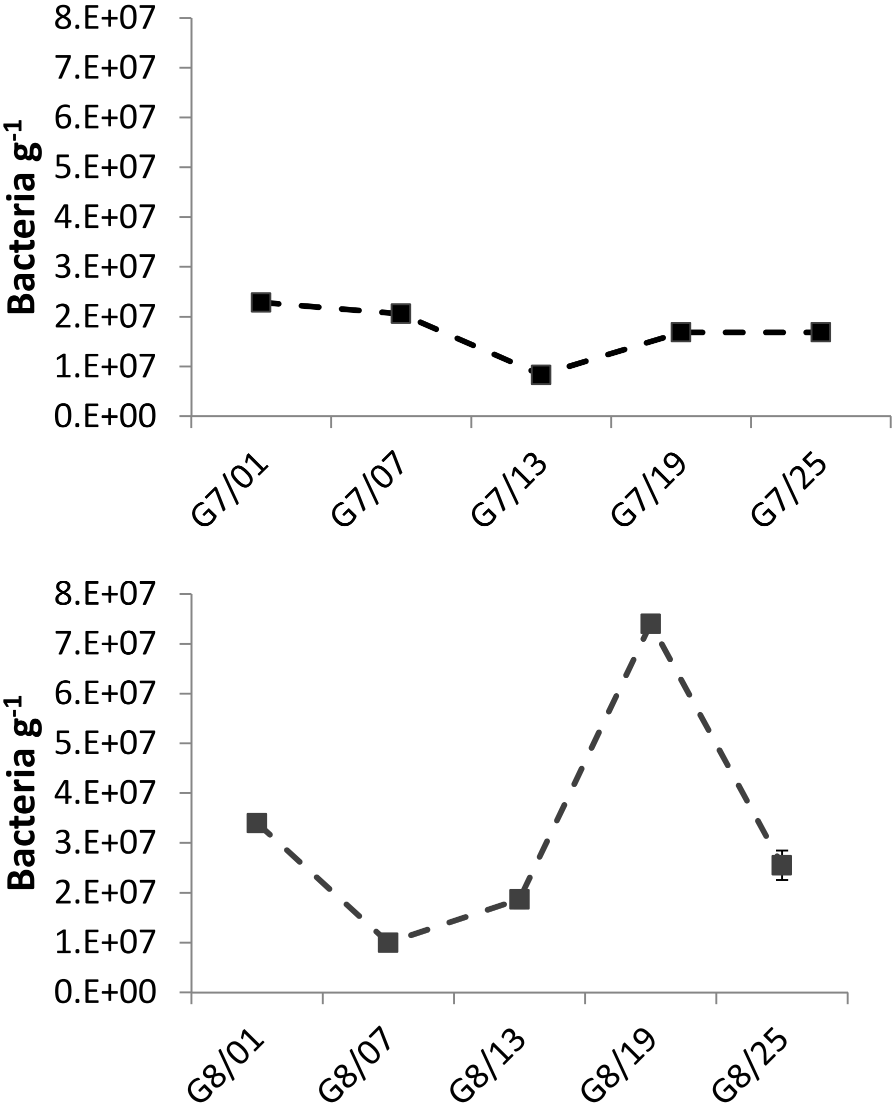


Figure 18 ASGARD (May 2012). Effect of controlled injection of CO2 at 60 cm along transects for selected parameters across pasture plots (G7 and G8) at ASGARD in May 2012. x-axis: transect position across plot. Plot G7 was not exposed to CO2 gassing at any period from March 2006. G8 exposed to continuous gassing from June 2010. Injection rate 1 L min-1 at 60 cm depth near position G/13. x-axis: position diagonally across the plot
a) CO_2 soil gas concentrations at 20 cm for plots G7 and G8
b) ATP biomass (Relative Light Units) for plots G7 and G8 at 15 – 30 cm depth
c) Mean total bacterial counts for plots G7 and G8

Table 1 Summary of European sites used to evaluate impacts of elevated CO_2 concentrations on pasture

Site and sampling dates	Climate	CO_2 source	Methodologies for analysis
Latera, Italy (September 2005 and June 2006)	Mediterranean	Metamorphic alteration of limestones	Transect across surface gas vent Soil gas concentrations and fluxes Geochemical analyses Botanical surveys Microbiological analyses
Laacher See, Germany (September 2007 and July 2008)	Continental	Magmatic	Transect across surface gas vent Soil gas concentrations and fluxes Geochemical analyses Botanical surveys Microbiological analyses
Florina, Greece (September 2011 and July 2012)	Mountain Mediterranean	Magmatic, hydrothermal CO_2 sedimentary basin	Transect across surface gas vent Soil gas concentration and fluxes Geochemical analyses Botanical surveys Microbiological analyses
ASGARD, UK (sampled spring and autumn from 2006 to 2008 and from 2010 to 2012).	Maritime	Controlled injection of CO_2 at 60 cm depth. CO_2 Injection rates: 2006 3 L min^{-1} 2007–2012 1 L min^{-1}	2.5 m x 2.5 m plot evaluations Soil gas concentrations and fluxes Geochemical analyses Botanical surveys Microbiological analyses

Table 2 Summary of analyses used at Latera, Laacher See, Florina and ASGARD

Site	Gas geochemistry	Soil sampling	Mineralogy and other chemical analyses	Botany	Microbiology	Reference
Latera	Soil gas concentrations using field infra-red and electrochemical analysers. (CO_2, O_2, H_2S, H_2). Laboratory analysis by gas chromatography (CO_2, N_2, O_2 + Ar, light hydrocarbons) and mass spectrometry (He) CO_2 flux by accumulation chamber in June 2006 only.	Hand held auger for sample collection.	Whole rock X-ray diffraction (XRD). Clay-XRD. Cation exchange capacity (CEC). Soil pH. Total carbon (and organic and inorganic). Water content and Loss on ignition (LOI). Major and minor oxides using X-ray fluorescence (XRF)	% cover of identified plants at 0.5 m intervals along transect using a 50 x 50 cm quadrat. Field flora books used to identify species.	Total numbers (epifluorescence microscopy) ATP microbial biomass. Eubacteria and Archaea evaluation (Quantitative polymerase chain reaction analyses (qPCR)). Community analysis using Denaturing Gradient Gel Electrophoresis (DGGE). Methane production, methane oxidation and sulphate reduction rates (incubation experiments).	Beaubien et al., 2008. Oppermann et al., 2010.
Laacher See	*Site evaluation:* Atmospheric CO_2 concentrations (mobile open path laser system mounted 40 and 20 cm above ground on a quad bike). *Transect evaluation:* Soil gas concentrations using field infra-red and electrochemical analysers (CO_2, O_2, H_2S) CO_2 flux by accumulation chamber. Limited laboratory	Hand held auger for sample collection.	Total carbon and total nitrogen in soil and plants. Total organic carbon. Total sulphur.	% cover of identified plants at 0.5 m intervals along transect using a 50 x 50 cm quadrat. Field flora books used to identify species.	Total numbers (epifluorescence microscopy) ATP microbial biomass. Eubacteria and Archaea evaluation (Quantitative polymerase chain reaction analyses (qPCR)). Community analysis using Denaturing Gradient Gel	Frerichs et al., 2013. Gal et al, 2011 Kruger et al., 2011.

	determination of CO_2, N_2, O_2 + Ar, light hydrocarbons, by gas chromatography and He and carbon isotope ratios by mass spectrometry.				Electrophoresis (DGGE). Methane production, methane oxidation and sulphate reduction rates (incubation experiments).	
Florina	*Site and transect evaluation:* Soil gas concentrations using field infra-red and electrochemical analysers. (CO_2, O_2, H_2S, H_2). Laboratory analysis by gas chromatography (CO_2, N_2, O_2 + Ar, light hydrocarbons) and mass spectrometry (He) in Sept. 2011. CO_2 flux by accumulation chamber	Hand held auger for sample collection.	Soil water content. Mineralogy by X ray diffraction	% cover of identified plants at 0.5 m intervals along transect using a 50 x 50 cm quadrat. Field flora books used to identify species.	Total numbers (epifluorescence microscopy) ATP microbial biomass. Eubacteria and Archaea evaluation (Quantitative polymerase chain reaction analyses (qPCR)). Community analysis using Denaturing Gradient Gel Electrophoresis (DGGE). Methane production, methane oxidation and sulphate reduction rates (incubation experiments).	Ziogou et al., 2013.
ASGARD	*Site and transect evaluation:* Soil gas concentrations using field infra-red and electrochemical analysers (CO_2, O_2, H_2S) CO_2 flux by accumulation chambers.	Hand held auger for sample collection.		% cover of identified plants at 0.5 m intervals along 2 diagonal transects across plots using a 50 x 50 cm quadrat. Field flora books used to identify species.	Total numbers (epifluorescence microscopy) ATP microbial biomass. Eubacteria and Archaea evaluation (Quantitative polymerase chain reaction analyses (qPCR)). Community analysis	West et al., 2009. Smith et al., 2013.

					using Denaturing Gradient Gel Electrophoresis (DGGE). Methane production, methane oxidation and sulphate reduction rates (incubation experiments).	