

# New and established techniques for surface gas monitoring at onshore CO<sub>2</sub> storage sites

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## Abstract

New methods for the monitoring of CO<sub>2</sub> near the ground surface at geological CO<sub>2</sub> storage sites have been tested over areas of natural CO<sub>2</sub> emission. Mobile open path laser measurements and ground-surface portable infrared measurements show great promise for rapid assessment of large areas. Such techniques would help to focus more detailed investigations needed to verify the extent and source of the gas being emitted. It is envisaged that they would be used in conjunction with established field and laboratory techniques and continuous monitoring methods as part of an overall monitoring strategy for a CO<sub>2</sub> storage site.

*Keywords.* CO<sub>2</sub> storage, surface gas monitoring, CO<sub>2</sub>, rapid methods, open path laser, infrared gas analyzer

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## 1. Introduction

The measurement of gases at or near surface is likely to be a required part of monitoring at geological CO<sub>2</sub> storage sites. It is the ultimate test of leakage to the atmosphere from a site, helps reassure the public and regulators, and may be needed for accounting purposes. Although significant leakage from underground stores of CO<sub>2</sub> is not expected, it is important to study the effects of leaking gases on ecosystems in order to understand their potential impact and to determine appropriate remediation strategies. Gas measurements at natural CO<sub>2</sub> vents have been used to help understand the spatial and temporal distribution of gases and assess their impact on ecosystems.

Commercial storage sites are likely to be of such a scale that the surface monitoring will be over at least tens of square kilometres. Also, by analogy with natural CO<sub>2</sub> vents, the surface footprint of a gas leak may be less than 10 m across. In order to discover such small features in these large areas, rapid monitoring methods will be needed; conventional soil gas techniques that involve single point measurements are likely to be far too time consuming and could miss leaks.

Currently available techniques for the near-surface measurement of gas concentrations include both field and laboratory methods. Field measurements are usually quite rapid (a few minutes per observation) and can provide instant results but tend to be of lower precision. Laboratory techniques, which can be carried out in a field laboratory or mobile facility, or in a fully fledged laboratory, are typically of higher precision but are more laborious and there is some delay in obtaining results. Both approaches usually only provide data for a single point. This means that surveying a larger area is only possible, within a reasonable time frame, using widely spaced sampling intervals.

Studies of sites of natural CO<sub>2</sub> leakage have been undertaken over a number of years [1-6]. They indicate that gas vents can be restricted in size, and may have a surface expression of less than 10 m across. Features of this size would be easily missed by point measurements; unless they were closely spaced. However, very close spacing

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would be impractical for surveying large areas. Areas of more diffuse venting can be 50-100 m across and provide a somewhat larger target, albeit of lower intensity.

In order to cover large areas in a reasonable timeframe rapid methods are required. These ideally need to provide good sensitivity and a dense coverage of closely spaced observations. Several new methods for rapid surveying of surface gas concentrations have been tested in this study; open path laser, ground surface measurement techniques and hyperspectral remote sensing. These have been evaluated alongside existing techniques at two sites of natural CO<sub>2</sub> seepage in Italy and Germany. The airborne hyperspectral work is described by Pearce et al [6] and will not be discussed further here. The work formed part of wider ranging studies for the CO<sub>2</sub>Geonet Network of Excellence [7] and the CO<sub>2</sub>ReMoVe project, both funded through the European Commission

## 2. Methods

Commercial open path laser systems are available for CO<sub>2</sub>, CH<sub>4</sub> and a range of other industrial gases [e.g. 8]. At the start of this study (2006) CH<sub>4</sub> systems were available as tripod-mounted (measuring the gas concentration in air between the instrument and a reflector on another tripod) and airborne or vehicle-mounted options (where the measurement is made over a fixed path length with the laser and reflectors deployed in a probe mounted on the vehicle). The CO<sub>2</sub> system was only available as a tripod mounted configuration. Whilst the mobile CH<sub>4</sub> system had a reported sensitivity of 0.5-1 ppm, the sensitivity for the tripod-mounted CO<sub>2</sub> equipment was quoted at 100 ppm.

A tripod-mounted GasFinder2.0 CO<sub>2</sub> unit (Boreal Laser Inc.) was tested over natural seeps of CO<sub>2</sub> at sites near Latera, Italy. The results of these tests led to the commissioning of a new mobile open path CO<sub>2</sub> laser system based on a shorter wavelength tunable laser diode, with a reported sensitivity of 5-10 ppm and a completely redesigned probe. This equipment was also tested at Latera, and near the Laacher See in Germany in September 2007. Based on early experience of the system, modifications were made before further tests in Germany in July 2008.

Another potential method of rapid surveying was also trialed at Latera. This involved measurements of near-ground gas concentrations at a slow walking pace with a portable pumped infrared analyzer. The results of these trials were tested against more established soil gas methods, including measurements of CO<sub>2</sub> flux and concentrations of a range of soil gases.

Flux of CO<sub>2</sub> was measured by the accumulation chamber technique using a West Systems flux meter with a LICOR LI820 CO<sub>2</sub> analyzer and systems built by SUR, and BGR. Samples of soil gases, for field or laboratory measurement, were obtained using small diameter hollow steel probes or by drilling. Samples were collected at variable depths of up to 1 m, depending on specific requirements and local conditions, such as the depth of the water table. Field analysis of CO<sub>2</sub>, CH<sub>4</sub> and other gases (O<sub>2</sub>, H<sub>2</sub>S, CO) was made using a variety of instruments with IR and electrochemical sensors including, Geotechnical Instruments GA2000, Draeger X-am 7000 and Multiwarn II and ADC LFG20. Radon was measured with a Pylon AB5 or an Algade system, both using ZnS scintillation cells, and He with an Alcatel 100HDS He mass spectrometer. Gas samples were also measured in the laboratory by gas chromatography/mass spectrometry. To assist with the interpretation of data, weather observations were obtained using a Campbell Scientific automatic weather station, providing data on air temperature, barometric pressure, wind speed and direction, solar radiation and soil moisture content. Additional observations in Germany were obtained from local official and private weather stations. A Campbell Scientific eddy covariance system was deployed at the Laacher See in 2007 to measure CO<sub>2</sub> flux near to the gas vents.

## 3. Background on field sites

The Latera caldera is in central Italy, about 110 km NW of Rome. It formed by the collapse of a Quaternary eruptive centre, dating back to about 0.8 Ma [9]. Carbon dioxide and other trace gases, probably produced by thermo-metamorphic reactions in carbonates at depth are being emitted at surface [4, 9]. The gas migration is controlled by faulting and gives rise to gas vents in areas of high flux or zones of more diffuse release to atmosphere

where flow rates are lower [9]. A number of vents occur in the caldera floor, where the gas is passing through tens of metres of alluvium before being finally emitted into the atmosphere.

The Laacher See is a flooded caldera in the East Eifel volcanic region of SW Germany. The lake was created following the only known large explosive eruption in Central Europe during late Quaternary time (at about 12,900 yr BP) [10]. CO<sub>2</sub> degassing from an underlying magma chamber has been known for many years, and helium and carbon isotope data indicate a deep, mantle origin for the gases [11, 12]. Surface gas emissions are known, or suspected, from several locations in and around the lake shore [11, 13]. They occur, at least in part, in areas of the lake that were drained as recently as 1844, following an early reduction in the water level in 1164.

#### 4. Results

Initial tests of the tripod mounted open path laser system took place in summer 2005 over gas vents at Latera. A number of experiments were carried out. One involved measuring different paths across a gas vent. Each path was measured in turn for about 10 minutes and the process was repeated at 2 different heights, 61 cm and 143 cm, to assess vertical mixing and dilution effects. The concentrations measured were all above normal atmospheric levels (> 380 ppm) and showed the effect of the prevailing E to NE wind (Fig. 1). At higher CO<sub>2</sub> levels there was greater variation in the values, reflected by increased standard deviations, caused by wind-induced variable mixing of the escaping CO<sub>2</sub>. Another trial entailed setting the laser on one side of a small creek containing a strong CO<sub>2</sub> vent and the reflector on the other side of the creek at progressively increasing distance from the laser (16-100 m). The anomalous signal related to the vent steadily declined with increasing distance between laser and reflector until at 100 m there was no difference between the observed concentration and that of background measurements well away from any vents. Since the laser measures the average gas content over the whole path length the short distance with elevated CO<sub>2</sub> eventually becomes diluted to such an extent that the value is not distinguishable from background.

These results suggested that the original instrument would only be suitable for monitoring small sites, such as around a well head, and not for surveying large areas rapidly, due to the dilution of even strong CO<sub>2</sub> emissions (up to 2 kg m<sup>-2</sup> d<sup>-1</sup>). This indicated the need for a different approach for large areas using mobile equipment of higher sensitivity.

The first trials of the new mobile open path CO<sub>2</sub> laser system were carried out at Latera and near the Laacher See in September 2007. The equipment in each case was mounted on a quad bike with gas data being recorded every second, in conjunction with positions from a GPS receiver, as traverses were made in areas of known or suspected gas vents. In the first deployment at Latera a survey of a field with known CO<sub>2</sub> vents, including that used for the initial static laser tests, was repeated on two separate days, 5 and 6 September 2007 (Fig. 2). The two surveys showed similar patterns, detecting the two main known vents in the field and suggesting other areas of weaker gas emissions. The results were, however, different in some details. The anomaly related to the main vent was displaced from the vent itself on the repeat survey. Meteorological data, recorded on site, showed that this displacement was consistent with the wind direction at the time; from the SW at up to 4-5 ms<sup>-1</sup> on 6 September compared to up to 5-6 ms<sup>-1</sup> from a northerly direction on the previous day. The gas concentration at a point at any one instant is likely to

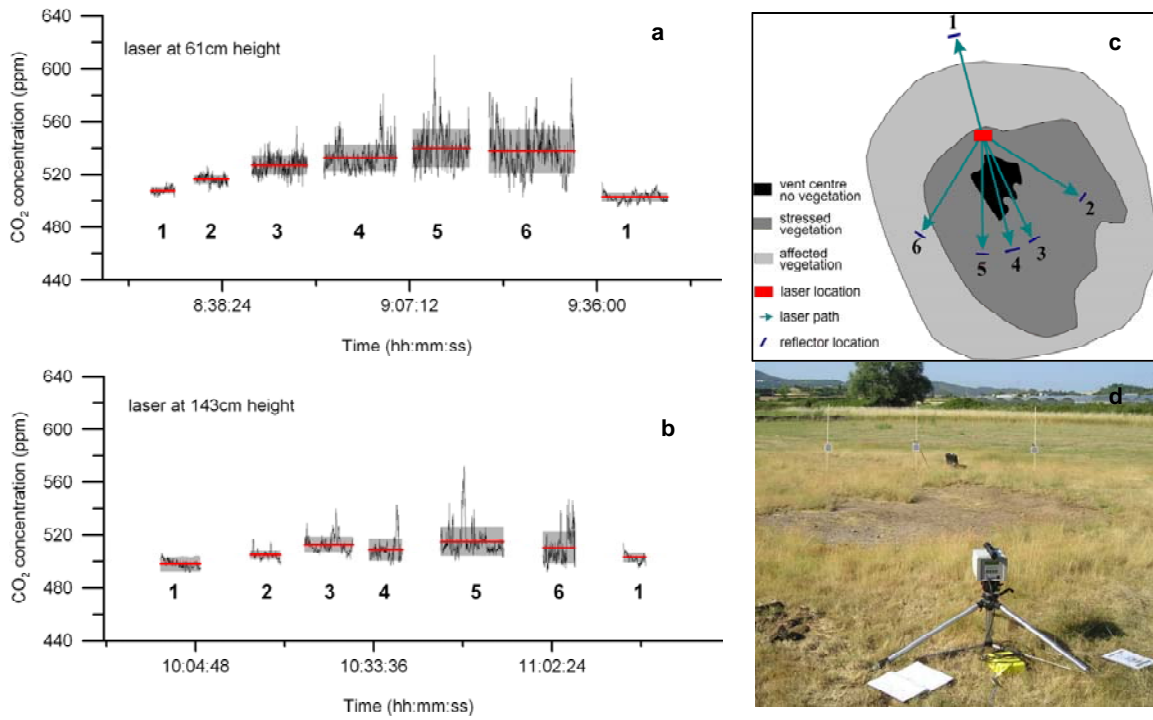


Fig. 1. Results of static laser measurements over a gas vent at Latera at a height of 61 (a) and 143 (b) cm. The numbers indicate the various path directions given in c) the red lines mark the average value while the grey boxes delimit one standard deviation. A photo of the setup d) shows the laser and reflectors 3, 4 and 5 across the bare soil for the gas vent

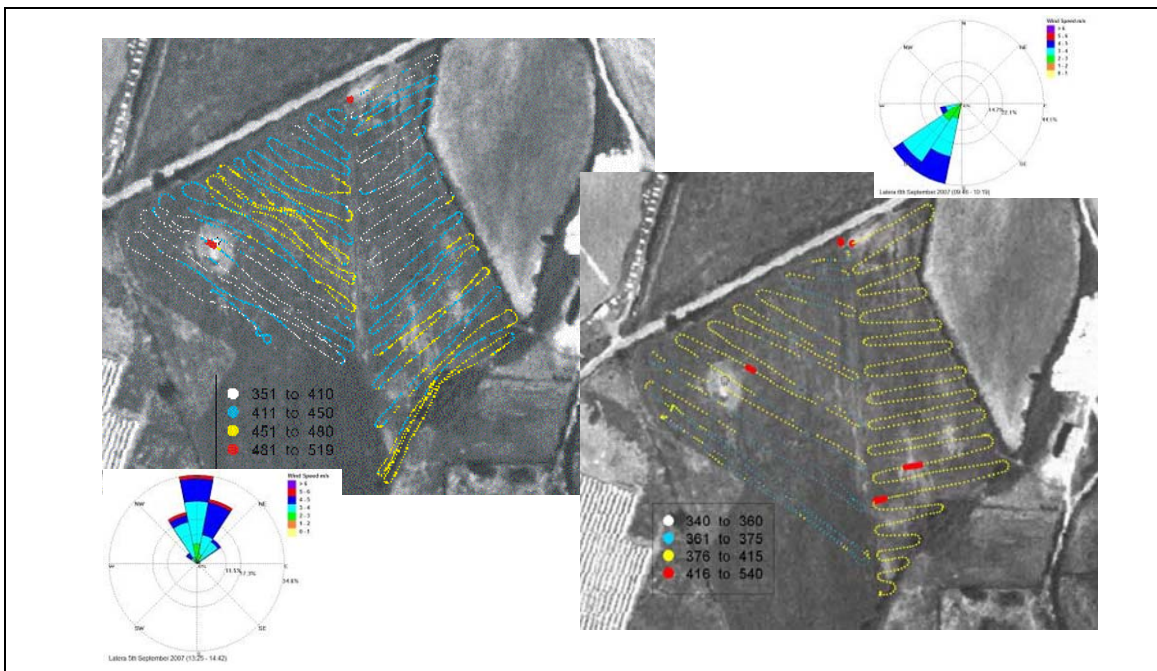


Fig. 2. Results of mobile laser tests at Latera. Separate surveys on consecutive days of a field with 2 major gas vents. CO<sub>2</sub> concentrations (ppm) are overlaid on an air photo showing bare soil/stressed vegetation (pale grey) and wind rose information for each survey

be strongly influenced by the wind. To the north of the vent there is some shelter from tall trees, but the site is more open to the south. There is also a possibility that some of the displacement could be due to positional error, as a simple, low accuracy GPS receiver was used for the trial. The CO<sub>2</sub> levels were also different from one day to the next, but data are too sparse to infer whether this reflects short term variability or longer timescale (diurnal) changes. In addition to the altered wind direction there was a slight increase in soil moisture content (from 19 to 21%) following rain overnight and during the second day. The relative humidity of the air was thus higher on 6 September (32–42% compared with around 30%) although atmospheric pressure and temperature were little different.

Almost 1.5 hours of static observations were made with the mobile system (Fig. 3), within an area of gas escape, but not directly over a vent, during an airborne test of direct detection of CO<sub>2</sub> using hyperspectral remote sensing techniques. These showed marked short term changes in CO<sub>2</sub> concentration similar to those observed on the repeated traverses. The levels were generally well above the average atmospheric CO<sub>2</sub> concentration probably reflecting higher overall values due to the venting of CO<sub>2</sub> in the area. These results suggest, as with the static laser experiments, that the variability of the readings may also be useful as an indicator of gas escape and could be particularly helpful where more diffuse leakage is occurring, and pronounced anomalies might not be observed.

A series of traverses, repeated in different directions, were also completed across the main gas vent (Fig. 4). These showed the influence of short-term changes in the CO<sub>2</sub> concentration at a given height. These can alter the measured contents over short periods (seconds to minutes). Nonetheless, the influence of the vent was seen on each profile, albeit above a variable ‘background’ level.

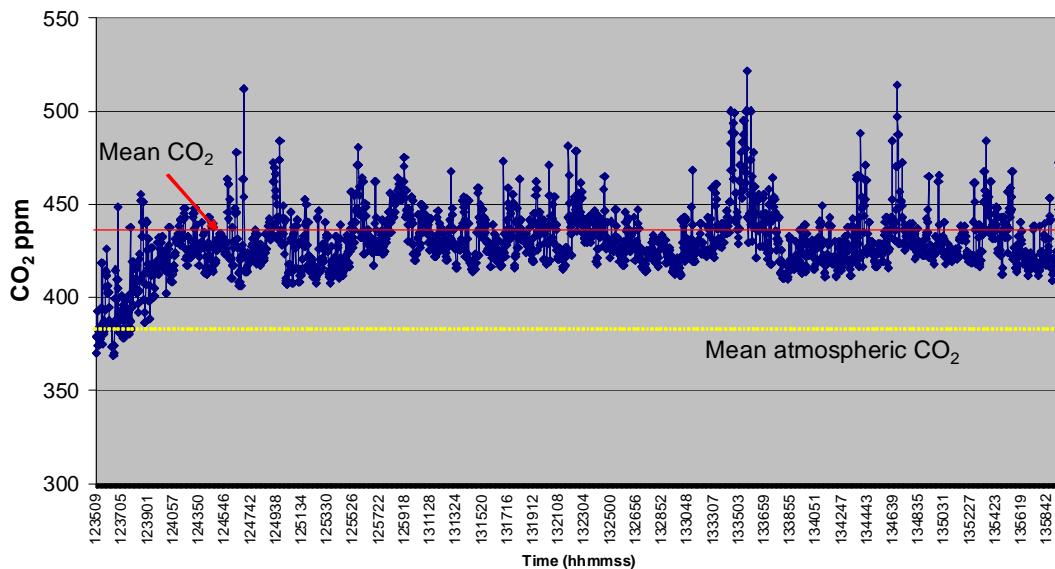


Fig. 3. Gas concentrations in air measured with the mobile laser at one location during a remote sensing overflight at Latera, 5 September 2007

A similar quad bike was used to test the mobile laser equipment around the Laacher See in Germany although, because of slight differences between the bikes, it was possible to mount the laser probe closer to the ground (30 cm) than had been possible in Italy (60 cm). A number of fields on the western shore of the lake were surveyed with the laser system. There was much less known about the gas concentrations and fluxes at this site, but the presence of gas vents was inferred from a small number of earlier measurements and from observed changes in the vegetation.

Five fields along the lake shore (c 100,000 m<sup>2</sup>) were surveyed over the course of 3 days (20–22 September, 2007), with one field, with 2 conspicuous gas vents, repeated on consecutive days to assess the reproducibility of the

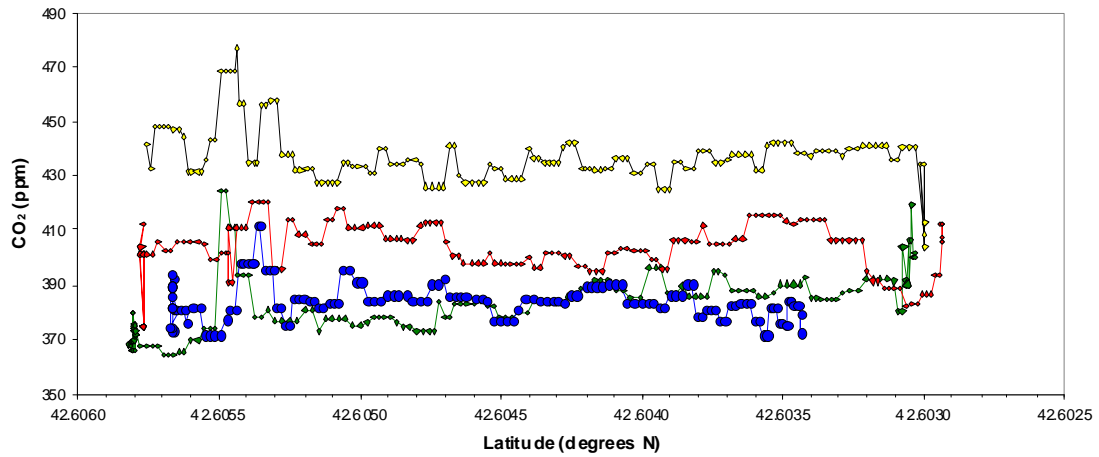


Fig. 4. Repeated N-S traverses with the mobile laser system over the main gas vent (near 42.6055N) at Latera. The figure shows the shift in position of anomalies and overall CO<sub>2</sub> levels over short timescales (minutes)

Fig. 5. (Left) Kriged image of mobile laser data from the western shore of the Laacher See overlaid on an air photo. Data from consecutive days from the central portion are both displayed and show that the 2 main vents were clearly identified on both occasions

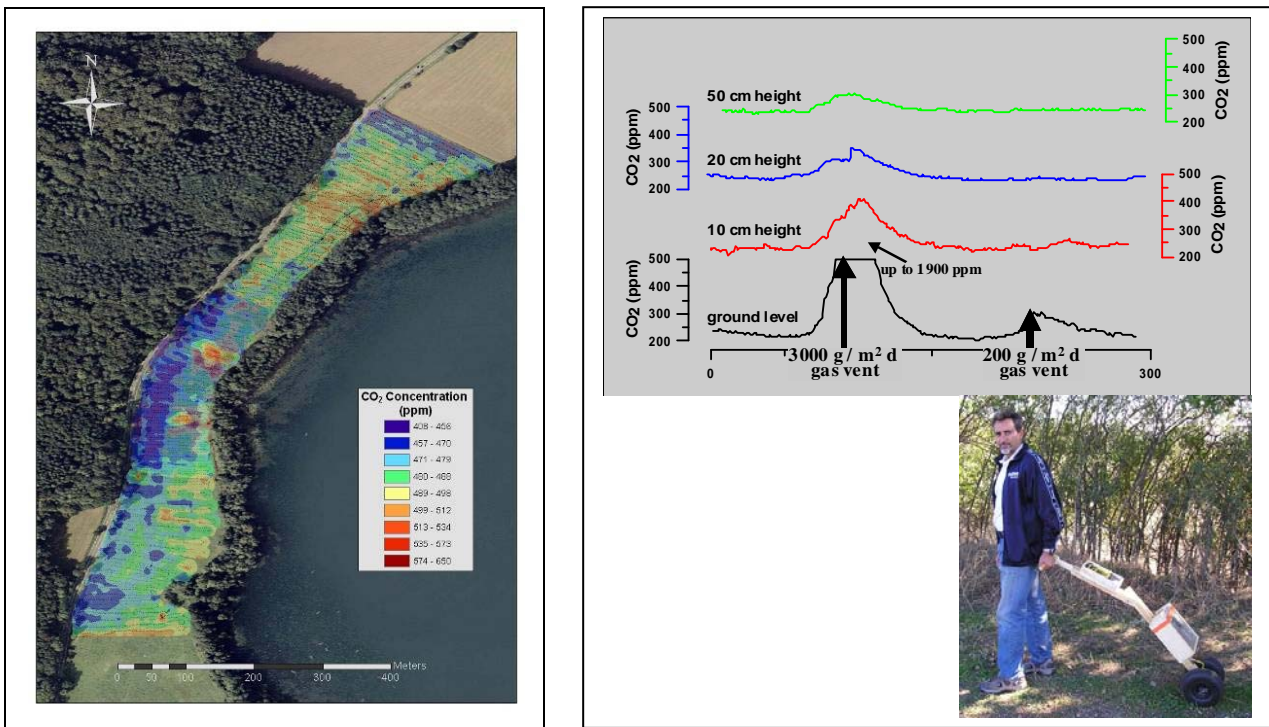


Fig. 6. (Right) Walking traverses over gas vents at Latera with the ground surface measurement system (infrared analyzer) measuring. CO<sub>2</sub> concentrations at different heights show the fall-off in response with increasing height; the weaker vent is not seen at heights greater than 10 cm



method. There was good agreement between the repeat surveys both in terms of the concentrations of CO<sub>2</sub> and the patterns observed. However, the CO<sub>2</sub> levels from the first 2 fields surveyed (the southernmost) were significantly different although there were no appreciable changes in weather or soil conditions over this period.

The 2 principal gas anomalies seen (Fig. 5) were investigated with conventional soil gas concentration and flux measuring techniques. The vent centres were associated with concentrations of CO<sub>2</sub> approaching 100 % at 60-80 cm depth and flux rates ranging from 0.5 to 1.2 kg m<sup>-2</sup> day<sup>-1</sup>. As at Latera these values drop to background within a short distance (usually 10 m or less) from the vent centre. More diffuse anomalies were found to have concentrations and fluxes that were lower but clearly above background, although this could not be established in all cases. This may suggest false positives or the difficulty in relocating the positions accurately with a handheld GPS.

The same fields were re-surveyed in July 2008 and the survey area was extended to include an area south of the lake. Preliminary data suggest very similar patterns to those obtained in 2007, with atmospheric gas anomalies over the 2 known vents and further weaker features in the northernmost field closest to the lake. The latter were not associated with bare soil or obvious vegetation changes and were harder to directly link to higher soil gas concentrations and fluxes. However, fluxes ranged from 23-54 g m<sup>2</sup> day<sup>-1</sup> and concentrations up to 9.1 % CO<sub>2</sub>. By comparison with values for sites with similar vegetation, but no CO<sub>2</sub> escape (typically < 30 g m<sup>2</sup> d<sup>-1</sup> and < 4 %), the results are suggestive of diffuse gas escape.

Initial testing of the ground-surface measurement system involved an assessment of the effect of sampling height on sensitivity. To this end, a series of traverses were conducted across two gas vents at the Latera test site at 0, 10, 20, and 50 cm above ground surface (Fig. 6); the surveys were performed at a slow walking pace, resulting in a sample spacing of about 75 cm. There was no indication of the weaker gas vent at heights greater than 10 cm, and the response to the stronger vent declined markedly with height, so subsequent tests were all done at ground level. It was found that the stability of the infrared detector was critical to differentiating areas with weak CO<sub>2</sub> leakage from background. The time for the detector to return to background values and dilution were found to be significant, and thus new sensor types and general system design are being examined to try to minimize these effects. Finally, to evaluate the potential of the method for rapid reconnaissance mapping, a series of parallel lines 10m apart (with 50 cm sample spacing) were measured over an area of about 80,000 m<sup>2</sup>; this mapping exercise took about 5 hours. Results highlighted all known vents and located 2 vents that were previously unknown. Work is ongoing to improve survey speed, test the instrument under different meteorological and plant growth conditions, and to better understand the detection limit of the method.

## 5. Conclusions

Mobile open path laser techniques have been tested in areas of known CO<sub>2</sub> release. They successfully identified zones of significant gas venting and located areas of weaker gas flux at lower concentrations. Early results suggest that, in addition to obvious anomalous values, a statistical analysis of datasets could also be important. There appears to be a greater degree of variability in near surface atmospheric CO<sub>2</sub> concentrations in areas of gas venting. This is reflected in a higher standard deviation for these datasets compared with those from background areas. More comparative data are needed from true background sites where no gas escape is occurring. Limited data from sites in the UK show much reduced ranges of CO<sub>2</sub> values compared with the volcanic terrains described here. It would be important to define the baseline gas concentrations at a storage site, prior to any CO<sub>2</sub> injection, and to assess their variability i.e. in different seasons and weather conditions.

Simple, inexpensive surveying of near-ground atmospheric gas concentrations, with portable infrared analyzers, has also been tested successfully and improvements to the design of the equipment are underway. Dispersion and dilution of CO<sub>2</sub> emissions with height above the ground means that measurements should be made close to the ground surface. The variability of concentrations with time suggests that rapid survey methods are perhaps best suited to location of features requiring follow-up investigation with other techniques.

A high level of positional accuracy is desirable when mapping gas concentrations as this makes verification of apparent anomalies much easier. It is evident from natural CO<sub>2</sub> vents that the target can be very small, perhaps only a few meters across. The inherent accuracy of handheld GPS receivers is such that matching point observations to the rapid survey results can be difficult; sub-meter positional accuracy is desirable and was used for our latest work

Such rapid methods have great promise for monitoring for CO<sub>2</sub> leakage at sites of geological CO<sub>2</sub> storage. It is not envisaged that these techniques would remove the need for more conventional point measurements and sampling for laboratory analysis as any anomalies identified with these methods would have to be verified and the source of the anomaly defined. It is also possible that leakage may not be continuous, but vary over time due to subsurface and near surface conditions (e.g. pressure variations). Discontinuous pulses of gas escape could be missed by rapid large area methods that provide only a snapshot series of observations. Thus there is likely to a need for continuous monitoring at a number of locations, using methods such as eddy covariance or soil gas monitoring stations. These locations would be chosen on the basis of the results from wide area surveys and using site-specific knowledge of potential pathways for gas migration from depth, such as indications of faults or fractures or well sites.

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