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Continuous monitoring of natural CO₂ emissions near Rome – lessons for low-level CO₂ leakage detection

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Abstract

Continuous monitoring has been carried out at a fluvial flood-plain site near Rome for over a year. There is a mix of biogenic CO₂ and deep geogenic CO₂ at the site at relatively low concentrations and fluxes compared with other natural CO₂ seepage sites studied previously. Factors such as temperature and soil moisture clearly affect the CO₂ concentration and flux and seasonal and diurnal influences are apparent. Statistical approaches are being used to try to define these relationships and separate out the two gas components, which would be necessary in any quantification of leakage from CO₂ storage.

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1. Introduction

Regulations for geological storage of CO₂ (such as the EU Directive on Geological Storage of CO₂ and that covering the Emissions Trading Scheme) require monitoring for leakage detection and quantification of any emissions to the atmosphere or marine water column [1, 2]. Whilst early indications of migration within the storage reservoir and storage complex, and leakage from the storage complex, may be provided by deep-focussed monitoring, the ultimate detection of surface emissions and their quantification will need to be made by near-surface measurements.

There have been no significant leaks from CO₂ storage sites operated to date at pilot, demonstration or larger scales that range up to more than 1 Mt of CO₂ injected per year and totals stored in excess of 20 Mt. In the absence of such leaks, assessment of leakage detection technologies has been undertaken at controlled injection and release sites, such as the ZERT site in Montana, USA [e.g. 3], Ginninderra in Australia [e.g. 4] or the CO₂ Field Lab in Norway [5, 6], or at sites of natural CO₂ emission [e.g. 7, 8]. At many such sites the gas emissions occur at clear seepage points, restricted in areal extent (a few metres to tens of metres across) and with CO₂ concentrations in the soil, fluxes across the soil-to-atmosphere interface and concentrations in the near surface atmospheric boundary layer that are readily distinguishable from background values [e.g. 9]. However, there is also some evidence for more subtle emissions, from isotopic data or gas ratios, that can fall within normal baseline ranges and are therefore more difficult to detect [6]. If such low-level emissions occurred over large areas they could represent a significant loss of stored CO₂.

Previous studies of natural CO₂ seepage, including our own, have focussed on strong seepage points and spatial variability. Instead, for the current study we wanted to find a site where more subtle features could be examined and where we could use continuous monitoring techniques to concentrate on the temporal variability of seepage. By investigating weaker seepage features we hope to better define detection limits for the discovery and quantification of seepage.

1.1. Background

In 2013 a geotechnical borehole was drilled through a clay layer at about 40 m depth near the town of Fiumicino, west of Rome, Italy. This resulted in the leakage of CO₂ trapped below the clay at a rate sufficient to create a small crater at the surface. Although the borehole was soon plugged, concern over this event, and other similar gas releases in recent years, led to the commissioning of a soil gas and flux survey of the area to better determine the spatial extent of the problem for risk assessment purposes [10].

The survey found CO₂ anomalies in the soil gas with concentrations of up to 86%. Stable carbon isotope analyses indicated a deep geological origin for the gas. The soil gas anomalies were aligned along normal faults that could be seen on a seismic reflection line along the Tiber River, which defined the migration pathways of the gas from depth.

The search for a suitable study site for the present research not only had to meet scientific criteria related to gas seepage features, but also had to satisfy logistical requirements for long-term access to a secure site, ideally with mains power available. Having identified a site that met these criteria, just south of the main Rome airport, it was then necessary to characterize the site by more detailed soil gas and flux measurements in order to choose locations for continuous monitoring equipment.

1.2. Methods

Initial soil gas measurements used a probe consisting of an 8 mm diameter (4 mm ID) stainless-steel tube onto which two solid steel cylinders were welded to act as pounding surfaces when installing and removing the probe with a co-axial hammer. Prior to insertion, a sacrificial tip was fitted to the bottom of the probe to prevent blockage.

The probes were inserted to a depth of 50-90 cm depending on local soil conditions. In situ soil gas measurements of CO₂, H₂S, CH₄, and O₂ concentrations were made using Draeger X-am 7000 or Geotechnical Instruments GA2000 portable gas analysers. Samples of soil gas were also collected for laboratory analysis. A plastic syringe was used to transfer approximately 50 ml of soil gas from the probe into pre-evacuated, 25 ml volume, stainless-steel sample canisters. Samples were analysed for hydrocarbon species (C1-C3 alkanes and C₂H₄) and permanent gases (N₂, O₂ + Ar, and CO₂) using two Fisons 8000 gas chromatographs (GC). Note that O₂ and Ar are not chromatographically separated on the packed GC column used for these analyses. The detection limit of the GCs for hydrocarbon gases is about 0.05 ppm with an accuracy of ±3% at the 2 ppm level, while the resolution for the permanent gases is about 100 ppm with an accuracy of ±2% at atmospheric concentrations.

Samples were also collected in the same way for stable carbon isotope analysis. Aliquots of sample gas were extracted from each sample canister by syringe via the septum. These aliquots were then injected into a glass vacuum line where CO₂ was extracted from the gas by trapping in liquid nitrogen, with any permanent gases being pumped away. The CO₂ was subsequently dried by passage through a dry ice/methanol trap. Samples were stored in a glass tube vessel with high-vacuum stopcocks. The C isotopes composition of the CO₂ was determined by analysis using a VG Optima mass spectrometer.

CO₂ flux measurements were taken using a West Systems portable flux metre with a LICOR LI-820 IR detector connected to a palm-top computer (PDA) with built-in GPS. Measurements took 1–3 min depending on the soil flux rate. Flux was also measured using an in-house unit equipped with an Edinburgh Instruments GasCard II detector. Flux was normally measured before soil gas adjacent to the soil gas points.

For continuous soil gas monitoring a GasPro soil gas monitoring station was deployed with four CO₂ / T probes buried horizontally at a depth of about 40 cm. The depth was dictated by a clay layer discovered when installing the station. By sitting the probes on top of this layer a closer link to the surface flux measurements was expected. A continuous flux monitoring station was also installed, consisting of a Licor Li-8100 system with a Li-8150 multiplexer and four accumulation chambers controlled by the Licor automated operating and data-logging system. The chambers were mounted on the surface next to the buried GasPro probes. Soil moisture and temperature probes were placed at 5 cm depth, close to each chamber and linked into the data logging for the system.

Atmospheric CO₂ flux was determined using the eddy covariance (EC) method. A Campbell Scientific EC system mounted on a tripod at a height of 2 m measured wind vectors, using a three-axis sonic anemometer, CO₂ concentration, using a Li-7500 infrared gas analyser, air temperature, pressure and relative humidity all at 10 Hz. The EC was sited at the north-western edge of the property where prevailing winds from the west would be least disturbed by buildings and mature trees. The data were post-processed using the software tool EdiRe [11] which produces a range of corrected means, deviations and fluxes after a number of de-spiking, filtering and correction processes. Data were, in general, computed for 30-min intervals.

Rainfall data from the Isola Sacra meteorological station, located about 2.5 km to the SW of the study site, was provided by the Ufficio Idrografico e Mareografico of the Regione Lazio.

1.3. Results

1.3.1 Background measurements

A reconnaissance survey of the site in December 2013, immediately prior to deployment of the continuous monitoring equipment, defined a range of CO₂ soil gas concentration values from 0.3 to over 30% CO₂ and of CO₂ flux values from 20 to more than 120 g m⁻² d⁻¹. The higher values were seen along a profile measured in an unused field adjoining the main property (Figure 1). On the basis of these results, three points were selected for continuous monitoring in the unused field (numbers 2 to 4 in Figure 1) and one point was chosen in the area adjoining the

buildings, covering the range of soil gas and flux values. The EC tower was deployed at about 70 m to the NW in a more open area.

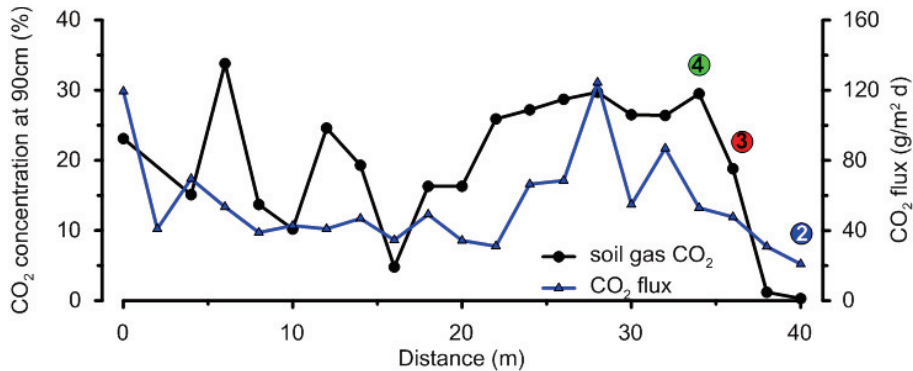


Figure 1 Soil gas and flux data collected along a profile in an unused field at the site. The numbers show values at three of the monitored sites; site 1, located just beyond the end of this traverse had values intermediate between those for sites 2 and 3.

Soil gas ratios [12, 13] from all four profiles are indicative of both in-situ biogenic (respiration) CO₂ and the leakage of geogenic CO₂ from depth, and mixtures of both sources of gas (Figure 2a). This mix of biogenic and geogenic gas is also consistent with stable carbon isotope data, which suggests that shallow samples, above the clay layer, consist of 0–25% deep gas, whilst deeper samples, below the clay layer may have up to 90% deep gas (Figure 2b). The geogenic end-member is particularly well defined in the results from an added point collected 20 m away from point 4, where CO₂ concentration was about 70% and $\delta^{13}\text{C-CO}_2$ was about -1.2‰.

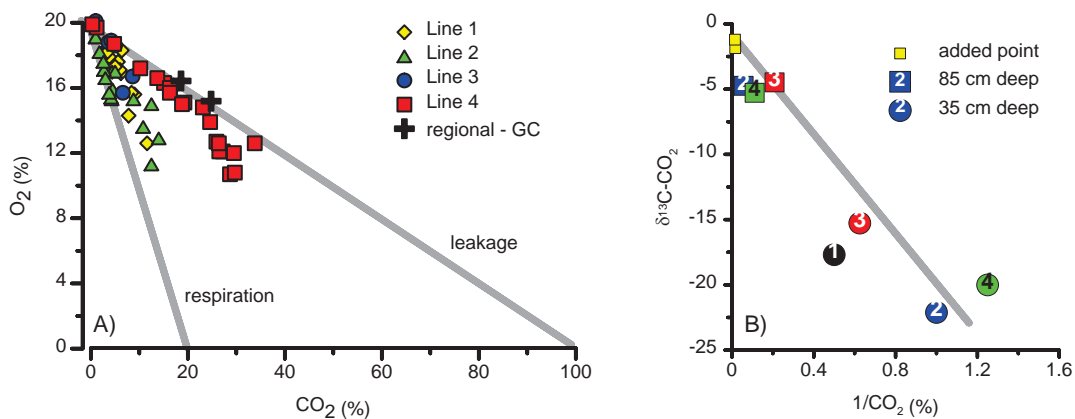


Figure 2 A) CO₂ versus O₂ plot for soil gas from the site showing the variable mix of geogenic (leakage) gas from depth and near surface biogenic gas (respiration) at the site. B) Keeling plot showing a simple mixing of 2 end members having a $\delta^{13}\text{C}$ of -2‰ (geogenic CO₂) and -22‰ (biogenic CO₂). Square symbols represent samples from 85 cm depth below the clay layer while the circles represent samples from 35 cm depth above the clay.

1.3.2 Continuous measurements

Continuous monitoring covered the period December 2013 to January 2015. There were some gaps because of power failures at the site. The multichamber flux system developed a serious fault and did not operate beyond August 2014. There were also problems with one of the GasPro probes so data from that instrument were also more

limited. Overall the data show clear seasonal trends with higher CO₂ concentrations (Figure 3) and flux in the summer when diurnal variability is also greatest.

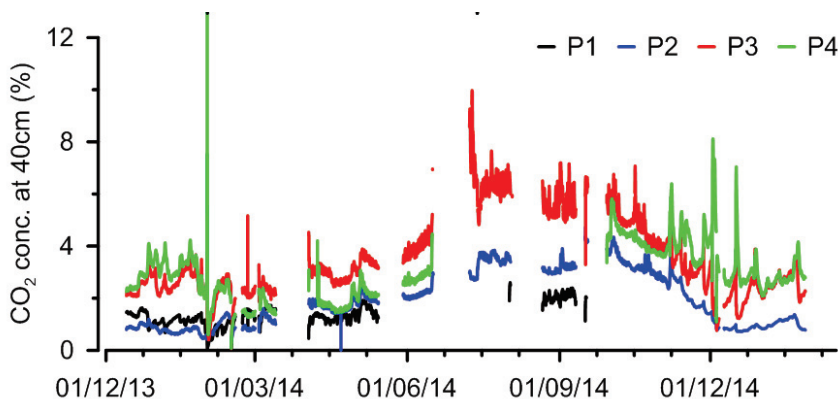


Figure 3 Full soil gas CO₂ dataset for the monitored period showing seasonal and diurnal variations with superimposed events

Superimposed on those trends are marked short-term increases, which can be tied to particular events. For example, in December 2013 a weather system passed through the area, with lower atmospheric pressure, increased wind speeds and significant rainfall. This produced a short-term rise in flux at one chamber, followed by a decline at all chambers as soil moisture increased. This generally caused an increase in soil CO₂ concentration, which gradually declined over the next few days. Diurnal variations are still apparent with daily CO₂ peaks lagging a short time behind atmospheric and shallow soil temperature highs.

Not all rainfall events had a consistent effect on near surface gas values. For example, rainfall on 19-20 January 2014 (approximately 12 mm in total on the 19th and several lighter showers on the 20th) caused a marked reduction in flux (from highest values of about 15 g m⁻² d⁻¹ to 5 g m⁻² d⁻¹ or less) but had a more limited effect on soil gas concentrations, which rose slightly at 2 sites (maximum change from around 3.5% to 4%) whilst at the other sites the concentrations stayed more or less constant at about 1%.

On the other hand intense rainfall at the end of January 2014 (up to 25 mm an hour over several hours) had a pulse-like effect. At one monitoring location (point 4), the onset of precipitation resulted in an immediate drop in flux and a very large increase in CO₂ concentration at 40 cm depth (from 2 to 14%), which was then followed by a peak in flux while soil gas concentrations were decreasing to values lower than those prior to the storm (Figure 4). The concentration peak may have been due to a combination of the advancing wetting front compressing soil gas in the permeable upper sand as well as creating an impermeable cap that allowed accumulation of leaking geogenic CO₂, whereas the flux peak may be a pulse release of some of this accumulated gas. Interestingly, only P4 showed this behaviour. At P3 a similar concentration peak was observed but without a corresponding flux peak, whereas P1 and P2 actually showed decreased concentrations at the onset of the rainfall event. These results highlight the dynamic three-dimensional behaviour of gas movement in the vadose zone.

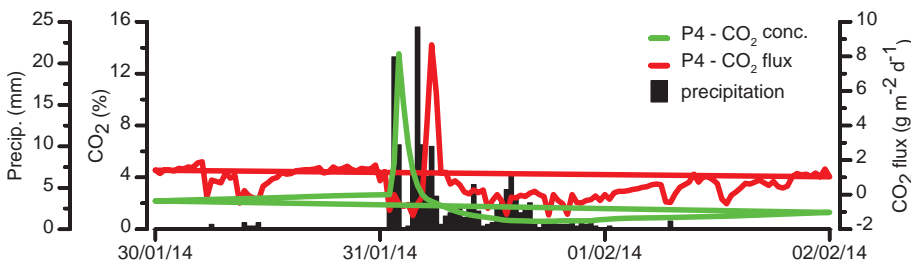


Figure 4 CO₂ soil gas concentration and CO₂ flux response during a very heavy rainfall event.

Temperature appears to be the main control on diurnal variations in CO₂ concentration and flux. The daily peaks in CO₂ flux coincide quite closely, in general, with peaks in air temperature and near surface (5 cm depth) soil temperature. The peaks in CO₂ concentration tend to fall between those of near-surface temperature and the soil temperature at the depth of observation (40 cm). However, this relationship does not always hold true. In August 2014 peaks in CO₂ concentration corresponded with peaks in soil temperature and an increase in wind speed from 1 to 5 m s⁻¹. At the same time diurnal trends were present in data from the EC and one flux chamber, matching temperature changes, whilst 2 other chambers showed no diurnal variation.

The relationship between soil gas concentration and flux and other environmental factors such as air and soil temperature and soil moisture, is being investigated in more detail through the use of cross correlation function (CCF) to identify time lags between parameters. Preliminary results indicate that soil temperature shows a positive correlation with CO₂ concentration, with the CO₂ often anticipating temperature peaks by about 3-4 hours. This relationship becomes stronger and more cyclic towards the stable weather conditions in summer. All 4 soil gas probes show a similar relationship regardless of location. In contrast there is a strong synchronous negative correlation between CO₂ flux and soil moisture for all four flux chambers.

Data for different periods were also standardized ((value-mean)/standard deviation) to investigate couplings to environmental factors. In this way the regular daily cycling, which follows temperature trends, can be separated from other events, where increases in soil gas concentration or flux might be a response to other environmental factors, such as rainfall, or the addition of CO₂ from depth to background biogenic gas. An example from October 2014 (Figure 5) shows an increase in CO₂ concentration that is not part of the daily temperature cycle but appears to precede the main rainfall event. This could be the result of the rainfall data being from a site 2.5 km away from the monitored area, such that rain could have fallen earlier at the monitored site, or it may be that the increase is due to geogenic gas and the near synchronicity with rainfall is coincidental.

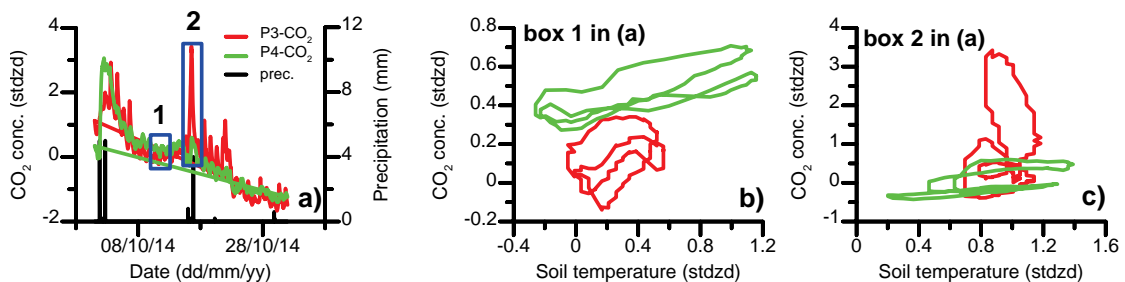


Figure 5 Data for 2 soil gas probes from October 2014 (a), with standardized concentration and soil temperatures compared for the two periods (b, c) that are outlined in blue boxes in (a). The earlier interval (b) shows daily CO₂ cycling in relation to temperature whilst the later example (c) shows a decoupling from temperature trends for P3

1.4. Discussion and conclusions

Ratios of CO₂ and stable carbon isotope data both show a clear mix of biogenic and geogenic CO₂ at the site. However, at low CO₂ concentrations the distinction becomes more difficult to establish unequivocally. At certain CO₂ storage sites, such as Weyburn, stable carbon isotopes have not been found to be useful for source attribution because the injected CO₂ signature is within the modern biogenic range [12].

Continuous monitoring data show clear seasonal and diurnal effects. The biogenic component is strongest in summer and shows the most regular diurnal change at that time of year. It is weaker in winter giving a greater chance of separating out a geogenic component, or leakage from a storage site. Klusman [14] has argued strongly for winter monitoring because of this, although there may be problems at some sites because of frozen ground [12].

The influence of air and soil temperature, rainfall and soil moisture and atmospheric pressure and wind speed on CO₂ concentration and flux are all apparent in the datasets. These influences, noted by previous workers [e.g. 15], are being explored more rigorously using statistical methods such as standardization and cross correlation. There is a direct inverse correlation between flux and soil moisture, as the filling of the soil pore space by water will impede the flow of gas. Conversely, the lowering of flux can lead to a build-up in soil gas concentrations.

If leakage from CO₂ storage is to be detected only from monitoring CO₂ concentrations then the background biological variations, and those caused by meteorological effects and other changes to environmental parameters, need to be filtered out. Further statistical evaluation is being undertaken to see if this can be achieved for the Fiumicino datasets.

If fluxes of CO₂ leakage are to be quantified accurately then the baseline signal needs to be removed and temporal variability accounted for by a period of continuous measurement. This would be in addition to defining the spatial variability.

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