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Innovative tools for rapidly mapping / quantifying CO_2 leakage and determining its origin

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Abstract

Although deployment of onshore CO_2 storage will be crucial to reach the EU's ambitious goal of an 80% reduction in greenhouse gas emissions by 2050, some stakeholders are concerned about potential risks if CCS is situated on land near populated areas. The EU-funded, Horizon 2020 project ENOS (ENabling Onshore CO_2 Storage in Europe) is addressing many of these concerns about onshore storage by demonstrating best practices through pilot-scale projects and field laboratories, integrating CO_2 storage in local economic activities, and creating a favorable environment through public engagement, knowledge sharing and capacity building/training. As part of this work, ENOS is using sites where natural, geologically produced CO_2 is leaking to the surface, to test innovative monitoring tools and to better understand gas migration pathways and early warning signs that could be detected in the unlikely event of CO_2 leakage. At least four natural leakage sites are being used in central Italy, including the well-known Latera caldera as well as San Vittorino valley, Ailano, and Fiumicino. All sites exhibit the leakage of almost pure CO_2 along bedrock faults and through overlying sediments prior to release to the atmosphere, but each has unique characteristics related to the origin of the leaking gas, the composition of the local bedrock, depth to water table, soil properties, and ground surface conditions. Results from recent ENOS field campaigns at these sites are presented, focusing on data and interpretation related to i) large area, rapid leakage mapping and quantification tools; ii) innovative methods to determine the source of a CO_2 anomaly; iii) CO_2 leakage style as a function of near-surface conditions.

Keywords: CCS; near-surface monitoring; leakage mapping and quantification, CO_2 source identification.

1. Introduction

Estimates made based on geological capacity as well as financial feasibility have shown that if Carbon Capture and Storage (CCS) is to make a meaningful contribution to the reduction of anthropogenic greenhouse gas emissions, both offshore and onshore sites must play an important role. However, onshore sites have, in the past,

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faced resistance from some stakeholders due to concerns related to the safety of such installations near populated areas. The EU-funded, Horizon 2020 project ENOS (ENabling Onshore CO_2 Storage in Europe) is addressing many of these concerns.

Figure 1. Study site locations in central Italy.

Within a wide research portfolio that encompasses most issues related to onshore storage, ENOS is also working to understand potential leakage processes and develop monitoring tools to minimize risk. The present paper details some of this research, conducted at four sites in central Italy (Figure 1) where natural, geologically produced CO_2 is leaking to the surface, including: the well-known Latera caldera (volcanics), San Vittorino valley (carbonate bedrock, sinkholes), Ailano (carbonate bedrock, very large leakage volumes, co-migration of CH_4), and Fiumicino (Tiber river fluvial deposits). All sites exhibit the leakage of almost pure CO_2 along bedrock faults and through cover sediments prior to release to the atmosphere. The advantages of such sites include a wide range of leakage rates, different geological and surface settings (lithology, structure, topography, leakage style, vegetation, etc.), large-scale processes, and almost constant accessibility.

The present research takes advantage of these constant leaks of deep-origin CO_2 to test rapid mapping techniques and quantification tools, to examine innovative methods that help distinguish the origin of a CO_2 anomaly, and to better understand gas migration processes and patterns as a function of near-surface conditions.

2. Leakage mapping and quantification tools

Although soil gas and flux measurements are the most accurate way to determine surface leakage, the fact that they require individual point measurements means that mapping resolution is limited by the number of samples that can be taken in a given time for a given budget [e.g., 1]. Other methods have been developed to overcome these limitations, such as eddy covariance or remote sensing [2,3], however they too can be limited by, for example, insufficient sensitivity, potential for false positives, high data processing requirements, and high costs.

To address this we have looked for a compromise between speed, resolution, sensitivity, and cost by developing mobile tools that measure CO_2 or CH_4 concentrations at or near the ground surface, extending previous research conducted by the present authors [4,5] and others [6,7]. In addition, work has also been conducted to look into the potential for using these rapid mapping techniques as a proxy for leakage quantification. Field testing of this mobile platform was conducted by personnel from BGS and Sapienza University at the Latera and Ailano sites (Figure 1). Three different fields were studied at Latera, each having natural CO_2 leakage areas of different sizes and strengths (i.e., flux rates) as well as different ground conditions. At Ailano work was conducted in a single small field in which two CO_2 leakage areas were found, one of which also had measureable CH_4 leakage.

Figure 2. a) Cart with instruments mounted for spatial mapping. b) close-up of cart showing the Mapper system, with the pump, CO_2 sensor, batteries and electronics highlighted in the yellow circle and the sampling tube that is dragged below the cart shown by a dashed yellow line.

2.1. Methods

Ground to air flux measurements were made for CH_4 and CO_2 (WestSystem) and CO_2-only (in-house Sapienza unit) every 2 to 10 m along individual transects or irregularly spaced orthogonal grids to define "true" leakage size and intensity (based on that spatial resolution) to help interpret the results from the mobile platform instruments. The mobile system (Figure 2) consists of a hand cart on which are mounted two open path lasers (Boreal Laser Inc.) that measure CO_2 and CH_4 at a height of about 20 cm above the ground, a low-cost GasPro Mapper unit (in-house Sapienza unit) that measures CO_2 at the soil-atmosphere boundary layer, and a sonic anemometer (R.M. Young 81000 ultrasonic anemometer) that measures 3D wind properties. The mobile platform was hand pushed along the profiles and grids that were previously mapped by the flux measurements, with the mounted instruments providing data more rapidly and at a much higher horizontal resolution (about one measurement per 2 meters). In addition, "static" measurements were also made; these involved leaving the mobile system at fixed locations for 5-10 minutes to determine the temporal variability of the measured parameters at both leaking and non-leaking sites.

Each laser system consists of a 1.5m long "probe" that encompasses the gas volume being monitored (black tubes with yellow boxes mounted at each end of the cart, Figure 2a), batteries and the laser source. Data was directly logged to a laptop computer together with integrated GPS coordinates. Note that the laser systems gave data for CO_2 at Latera and CH_4 at Ailano, as the Latera CH_4 flux rates were too low to give measureable values while the CO_2 laser system had technical problems during the Ailano campaign. The GasPro Mapper system was mounted in the center of the cart (Figure 2b). It consists of two small electrical boxes housing the batteries, sensor, pump, and electronics (green circle) connected to an 80 cm long piece of 6 mm diameter polypropylene tubing that was dragged below the cart (dashed yellow line) to sample the gas in the surface boundary layer. The Mapper was operated via software installed on the portable computer, with data transfer via a radio antenna. The sonic anemometer was mounted at the front of the cart (Figure 2a) to minimize operator interference and with a known orientation so that the horizontal wind components could be corrected and to take into account cart motion.

2.2. Results and Discussion

As stated, a number of "static" measurements were made with the mobile system at various leakage and background points. In a non-leaking, background location where concentrations are expected to be relatively constant, this test gives an estimate of the stability of the measurement system, which in turn can be used to estimate its sensitivity. At a leaking location, where variable wind conditions can change the degree of mixing between leaking and atmospheric air, this measurement indicates the range of values that might be expected above a given leakage point as a function of time and wind strength.

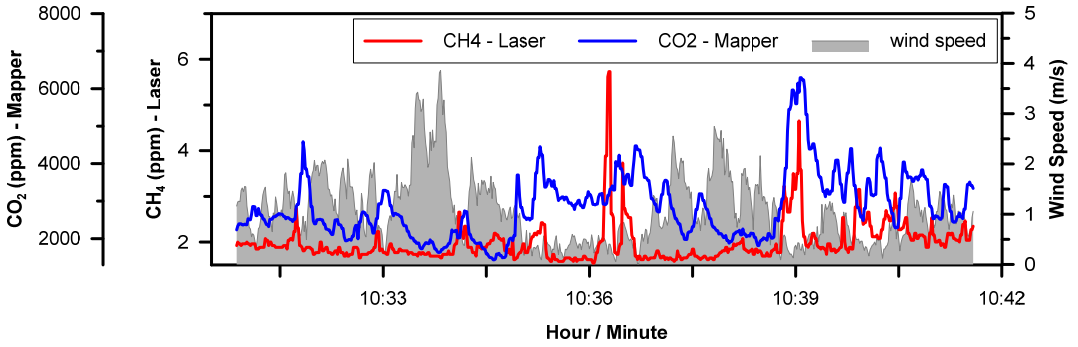

Figure 3. Results from the fixed deployment of the mobile platform at the non-vegetated center of the main gas leakage point studied at Ailano. Measurements were made at ground surface (Mapper), 20 cm height (laser) and c. 1.5 m height (anemometer).

An example of a static measurement is shown in Figure 3 using data from the center of the main gas leakage point studied at Ailano. This point had an extremely high CO_2 flux rate of about 8000 g m^{-2} d^{-1} and a much lower CH_4 flux rate of about 5 g m^{-2} d^{-1}. These results clearly show an inverse relationship between wind speed and gas concentrations, with peaks of both Mapper-measured CO_2 and laser-measured CH_4 in correspondence with moments of low wind conditions. On average the CO_2 baseline values are around 2000 ppm (which is much higher than background atmospheric values of about 400 ppm) while peak values range up to 7000 ppm. Many of these peaks are sustained in time, in part due to the fact that the sampling interval is closer to the ground (thus more potential for accumulation) and in part due to the slower response time of this pumped, laminar-flow system. The CH_4 baseline tends to be relatively close to concentrations in air (about 2 ppm); the CH_4 peaks are narrower due to the rapid response time of the open path system and tend to be more restricted to periods with the lowest wind speeds (typically <0.3 m/s) due to the higher deployment height. In addition there is a very good correlation between the occurrence of anomalies for both gases. These results highlight how a mobile survey over a leakage point may measure different gas concentrations as a function of wind variability, although it should be pointed out that this monitoring point had no vegetation and thus there was no barrier to wind mixing.

A number of profiles crossing gas leakage points of different strengths were measured repeatedly at a slow walking speed of about 0.6 m/s to compare the response of the two instruments and to determine the reproducibility of the mobile platform approach. It should be noted that because of the slower response of the Mapper version used for this study, a 10 second shift in the data was required to correct the spatial distribution of the data; instead, the more rapid response of the laser meant that no such correction was necessary for this instrument.

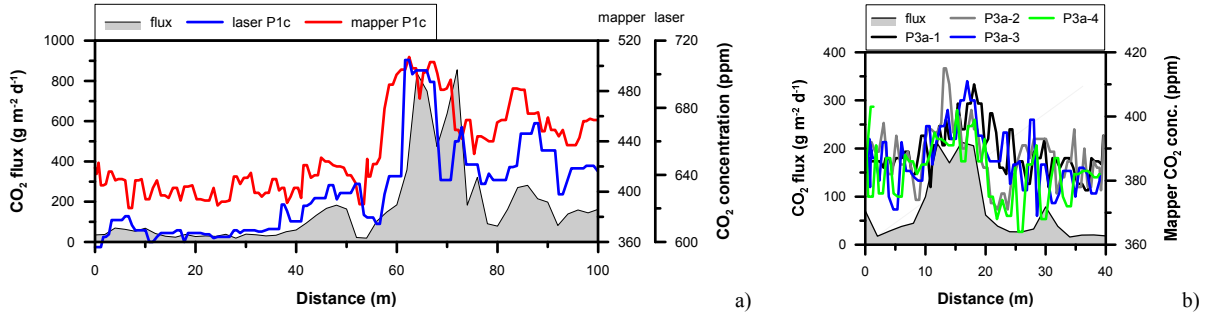

Figure 4. Results from Profile 1 (a) and Profile 3 (b) at the Latera test site. In addition to point CO_2 flux measurements, the Profile 1 plot also reports Mapper and laser CO_2 data while the Profile 3 plot gives Mapper CO_2 results only for 4 repeat surveys.

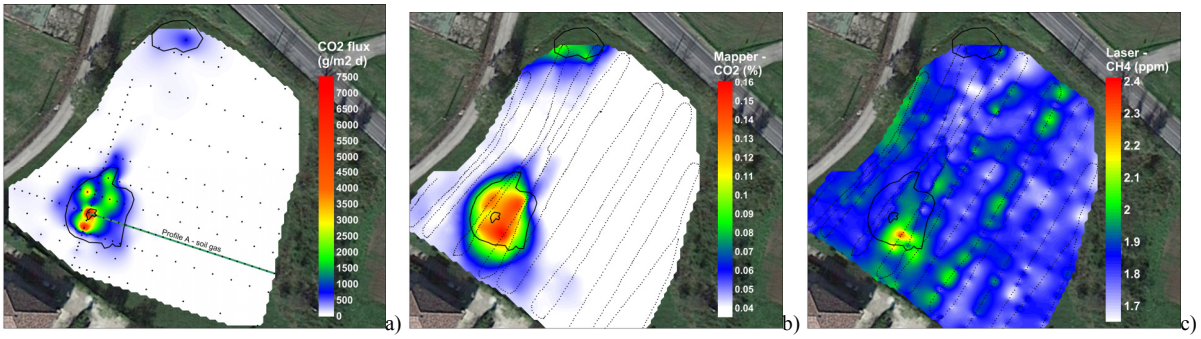

Figure 5. Contoured data from the study field near Ailano showing point CO_2 flux measurements and location of the soil gas profile (a), as well as mobile platform data for CO_2 from the Mapper (b) and the CH_4 laser (c). Note that the black outlined polygons reported in all three maps are at the boundaries of vegetation changes linked to the gas leakage and are given only as a spatial reference.

Profile 1 from Latera was approximately 100 m long in total, with flux measurements every 2 m identifying three main leakage areas (Figure 4a) having peak values of 180, 800, and 280 g m^{-2} d^{-1}. Data from one survey across the profile (P1c) shows an excellent correlation between the flux values and the CO_2 results from both the Mapper and the laser (Figure 4a). Both instruments show a similar interval from background to maximum peak values (about 100 ppm), which is surprising considering that the Mapper samples much closer to the ground and that static measurements at the maximum anomaly point (at 65 m) showed much higher Mapper values. The lower than expected Mapper peak values are likely due to the slower response of the system which does not allow equilibration with the surrounding concentrations while moving. Work is ongoing to increase the response time in the next Mapper version. Three repeat measurements of Profile 1 yielded more reproducible results for the Mapper compared to the laser, due to the influence of the different sampling heights on the two instruments. An example of this reproducibility is shown for Mapper results from Profile 3 (Figure 4b), which crosses weaker leakage points of about 100 – 200 g m^{-2} d^{-1}. While the response from the larger leak is clearly seen in all 4 surveys, any response from the smaller leak is lost in the noise of the system (note that a value of 3σ = 22 ppm was calculated using background measurements).

In addition to profiles, entire fields were surveyed to determine the capability of the mobile platform to rapidly find and delineate a gas leakage area. One such field in Ailano was first surveyed by conducting a total of 190 CO_2 point flux measurements (Figure 5a) on an irregular orthogonal grid to define, at least at that sample spacing, the spatial distribution and strength of leakage. The field was then surveyed twice with the mobile platform, once moving along a NE-SW direction and the other along a NW-SE direction. Results from the first grid direction show an excellent correlation between CO_2 flux and the 10 second shifted Mapper CO_2 results (Figure 5b), although memory effects (i.e., slow washout time of the sensor volume) caused smearing of the anomalies. The laser CH_4 results also show a clear spot anomaly in the location of the main gas vent (Figure 5c), which is a promising result considering that CH_4 flux anomalies (not shown) are much weaker and only occur in a very small area in the high CO_2 flux core of the leakage area (small inner black polygon in Figure 5a).

Finally it is important to note that each of the two mobile platform grids took about 20-25 minutes to measure, which is significantly less than the estimated 9.5 hours needed to perform all 190 point flux measurements used to characterize leakage throughout the entire field (i.e., 190 points x 3 minutes per flux measurement = 570 minutes / 60 minutes/hour = 9.5 hours).

3. CO_2 anomaly source determination

Anomalous CO_2 concentration or flux values in the near surface environment can potentially be caused by biological or chemical processes in the soil itself, via leakage of natural, deep-origin geogenic CO_2, or the leakage of anthropogenic CO_2 stored deep in the subsurface. Clearly it is critical that the true origin of an anomaly is defined, both for safety and carbon credit auditing purposes.

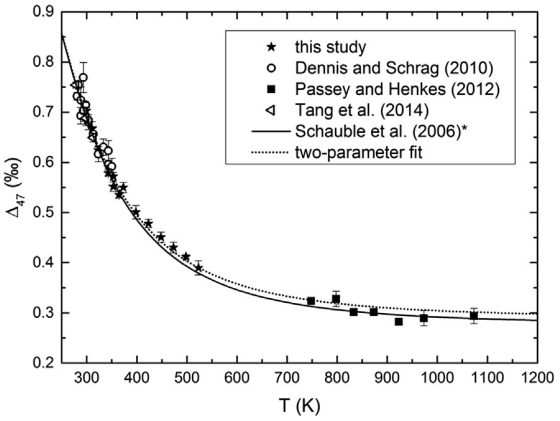

Figure 6. Relationship between Δ47 and temperature from isotopologue studies [9 and references therein].

In this regard CO_2 isotopologue analyses were conducted on leaking gas samples from Latera, San Vittorino and Ailano (Figure 1) to see if this innovative method can be used to determine the depth of origin (i.e., source) of the gas. This is because the formation temperature of CO_2 determines the abundance of rare CO_2 isotopologues (abundance of ^{13}C and ^{18}O bonds in CO_2), with temperature being controlled by the local geothermal gradient.

The identification of the CO_2 source with the stable carbon isotope method strongly depends on the $\delta^{13}C$ value of the injected/leaking CO_2. Thus, the source of CO_2 may be easily identified at one locality but can be more problematic at other sites; for example, the isotopic signature of injected CO_2 from a coal-fired power plant will likely have a $\delta^{13}C$ value that is in the same range as that of biogenic CO_2 produced in the soil horizon. This study was aimed at testing whether CO_2 isotopologues, also referred to as 'clumped' isotopes, may be more indicative of the CO_2 source. The 'clumped' isotope geochemistry relies on multiply-substituted isotopologues of naturally occurring molecules that are primarily analyzed on mass 47 [8]. At low temperatures the heavy ^{13}C and ^{18}O isotopes tend to clump together, resulting in a heavy CO_2 isotopologue. The abundance of ^{13}C and ^{18}O bonds in CO_2 is compared to its stochastic distribution at high temperatures (>1000°C) and the difference is expressed as Δ47 [9].

The Δ47 value is inversely proportional to temperature, with greatest sensitivity in the lower temperature range from ambient to about 400°C (Figure 6). To date, the majority of research on CO_2 clumped isotopes has focused on carbonate minerals to determine the carbonate crystallization temperature [10,11,12]. If isotopologues can be used to determine the temperature of CO_2 gas formation and its origin, they could discriminate whether the CO_2 is leaking from deep reservoirs and thus from stored CO_2 or if it is being produced in soil or groundwater in the shallow environment. The main difficulty with determining the leaking CO_2 gas with the isotopologue method is that the oxygen of CO_2 can equilibrate with the oxygen of H_2O from the aquifer and surface waters [13]. This would result in a Δ47 depicting a temperature at or close to that of the groundwater.

3.1. Methods

The sampling campaign was carried out by TNO and Sapienza University at the Latera, San Vittorino and Ailano sites (Figure 1), where natural CO_2 leakage was identified. To minimize possible sample alteration in the unsaturated zone or contamination with atmospheric air, all sample points consisted of leaking gas bubbling in surface water (creeks or ponds). The gas was pumped slowly from a funnel placed over the gas leakage point, through a drying agent filled with $Mg(ClO_4)_2$, and into the sample vessel (Figure 7). The vessel was flushed with 3 volumes of gas, determined based on filling of the downstream sample bag, and then sealed. In addition, five water samples were taken from gas leakage points occurring in ponds or creeks: Latera 2, Latera 3, Ailano 2, San Vittorino 6B and San Vittorino 18.

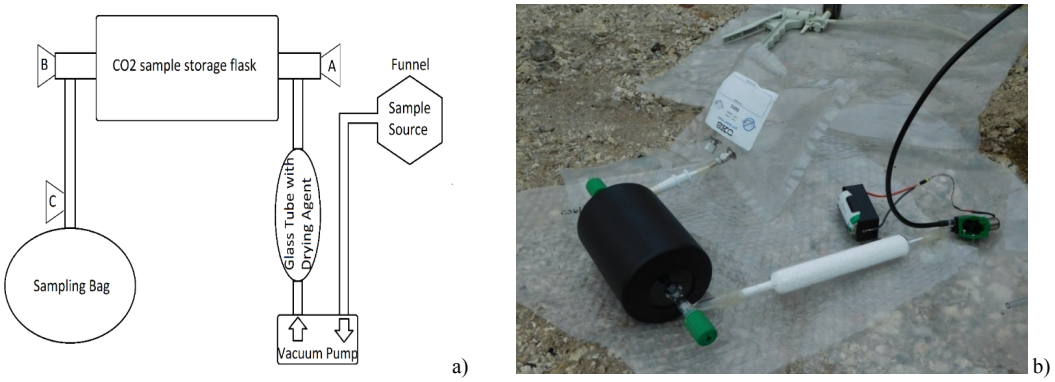

Figure 7. (a) Schematic of sampling set-up & workflow; A, B and C are valves. (b) Photograph of the setup

For the isotopologue measurements the samples were diluted with N_2 and purified in a cryogenic and chromatographic line connected to a mass spectrometer. The isotope measurements were performed on a Thermo-Finnigan mat 253 dual inlet isotope ratio mass spectrometer (IRMS), adapted with a 5th faraday cup to simultaneously collect mass 47.

3.2. Results and Discussion

Although several measurement attempts were made the purification line was not stable, leading to loss of CO_2 or an unacceptable standard deviation. Only four samples were measured successfully. Due to fractionation in the purification line a number of corrections had to be made, which resulted in large error margins.

The four samples measured for Δ47 do not show the expected deep reservoir signals (Figure 8a). Three samples fall within the range of average groundwater temperatures (13 to 15°C) while one value shows somewhat higher temperature of ~38°C. The data indicates that the leaking CO_2 does not reflect the isotopologue composition of the original CO_2 formed at depth. Although some of the CO_2 at the San Vittorino site may have derived from methane oxidation at the surface, the majority of the CO_2 at all sites has leaked from a deep, considerably hot (>150°C) reservoir [14,15].

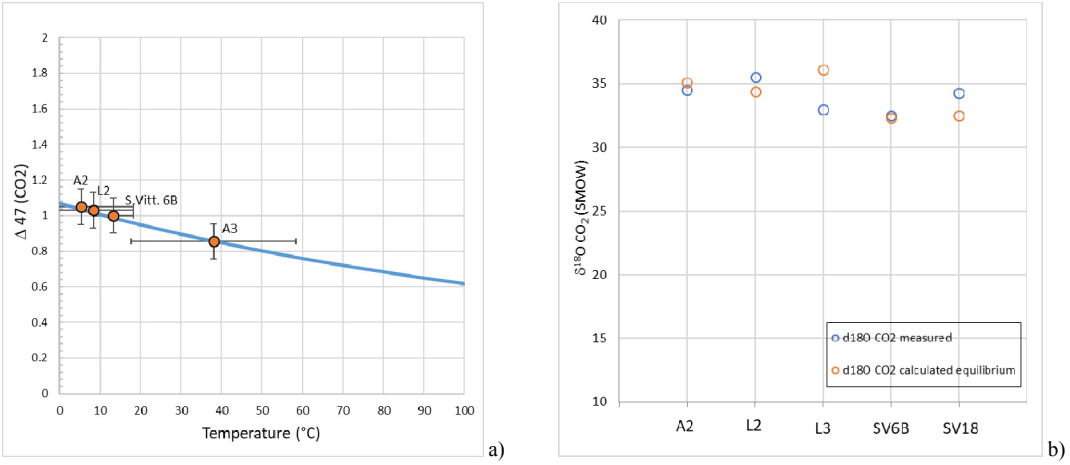

Figure 8. (a) Δ47 values of the four measured sample plotted on the temperature calibration line (in blue); (b) Measured and calculated $\delta^{18}O$ values of CO_2. L2 and L3 were samples at Latera, A2 at Ailano and SV6B and SV18 at San Vittorino.

The main reason for the resetting of the Δ47 signal is thus the re-equilibration of CO_2 with groundwater along its flow path. Although only the oxygen isotope composition of CO_2 is affected by the exchange between CO_2 and H_2O, the Δ47 will still shift towards higher values and the original signal will be lost. This can be exemplified by comparing $\delta^{18}O$ of the groundwater H_2O and venting CO_2. Groundwater $\delta^{18}O$ was used to calculate the equilibrium reaction with CO_2. The measured and the expected values are very close together (Figure 8b), indicating that a re-equilibration took place in all samples. At Latera 3 re-equilibration may have not been complete but had nevertheless a large effect on the oxygen composition. Groundwater could not be sampled at Ailano 3, which prevents us from studying the effect of the re-equilibration at this site.

4. Leakage style on the ground surface

The style of leakage on the ground surface will have a great influence on both the potential for impact and risk, as well as the size and strength of a leakage target to be searched for with a given monitoring technology. This is because if leakage is more diffuse the target will be larger but the anomalous values (and impact) will be smaller, whereas the contrary would be true for more discrete spot leakage of the same total amount of gas. This issue is of particular importance where shallow sediments overlie deeper bedrock leaks through faults or boreholes, as the typical sub-horizontal layering of units of alternating permeability (e.g., sands and clays) can result in complex lateral movement in both the saturated and unsaturated zones. Interpretation is further complicated by the fact that any leaking CO_2 will mix with near-surface, biogenic CO_2, thereby diluting the signal. To address these issues, work within ENOS at Latera and Ailano, performed by Sapienza University and BGS, included detailed soil gas and soil sampling, isotopic analyses, and shallow geophysics to infer processes controlling movement in the soil that controls the eventual footprint of leakage on the surface.

4.1. Methods

Transects were established across known leakage areas at Latera and Ailano (Figure 1). Samples were collected at irregular distances (from 2 to 20 m, depending on site conditions) along each profile. Flux measurements were performed for CO_2 using a closed-loop system developed in-house by the Sapienza research group, or for CH_4 and CO_2 using a West System portable flux analyser. Soil gas samples were collected at the same points by pounding a 8 mm tube to the depth of interest (between 10 to 90 cm, depending on the scope of the study and ground conditions) and drawing gas to surface for field analysis of CO_2, O_2, and CH_4 using a X7000 sensor (Drager) or for transfer into pre-evacuated stainless steel containers for laboratory analyses. Laboratory analyses of light hydrocarbons, CO_2, O_2, N_2 were performed by Sapienza University using a Carlo Erba 8000 series gas chromatograph, while $\delta^{13}C$-CO_2 isotope analyses were performed at the University of Waterloo (Canada). Ground penetrating radar (GPR) measurements were performed using a PulsEkko system (Sensors and Software Ltd.) with 250 MHz antennas and a trace spacing of 5-10 cm; this gave information on the shallow stratigraphy which could control lateral gas migration.

4.2. Results and Discussion

One of the main goals of this part of the research is to use stable carbon isotopes in CO_2 to better understand migration of leaking CO_2 in the unsaturated zone and its mixing with biogenic CO_2, and to use this information to determine leakage styles in different geological, structural, topographic, etc. settings. Although this work is at a preliminary stage, initial results from two sites (Figure 9) show clear differences resulting from near-surface conditions.

In the Latera Caldera a 250 m long profile was conducted across a gas leakage area located near the boundary between a forested area upslope and a cultivated field downslope. The profile starts upslope of the gas vent in the wooded area and then continues down a gentle slope across the field. Soil gas samples for concentration and isotope analyses were collected at 60 cm depth. CO_2 flux, concentration and isotope results show a highly asymmetrical distribution (Figure 9a), with a very rapid change in values over the first 20 m approaching the vent from the upslope forested site (left side in plot), followed by a much more gentle decrease over the next 150 m.

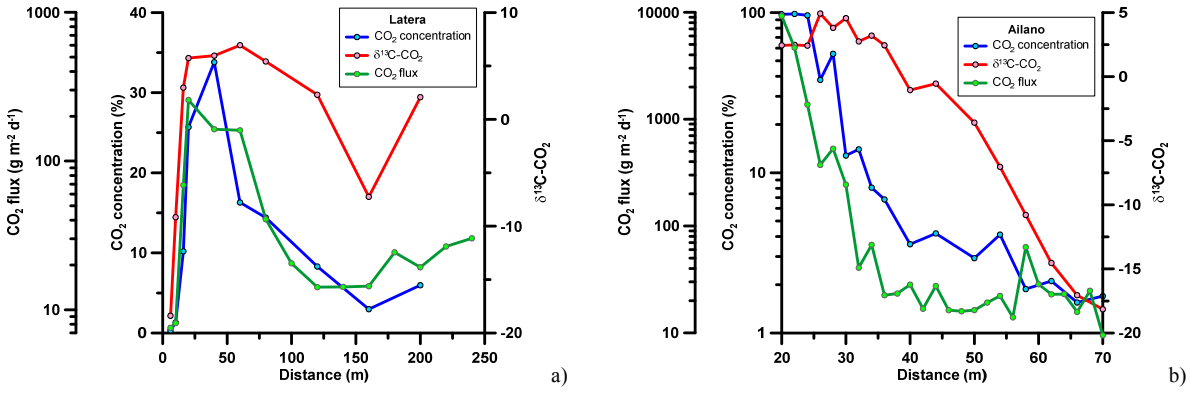

Figure 9. Profile data from gas leakage areas in Latera (a) and Ailano (b) showing soil gas CO_2 concentration and $\delta^{13}C$-CO_2 values as well as CO_2 flux on surface. Note that flux values for both sites are plotted on a log scale as is the CO_2 concentration results at Ailano. Note also the much longer horizontal scale at the Latera site and the much higher CO_2 concentration and flux values at the Ailano site.

Towards the end of the profile values start to rise again, indicating that a second vent leakage point has been encountered before background levels were reached. Despite the very large size of this anomaly the maximum measured values are not particularly high, with CO_2 concentrations up to 35% and CO_2 flux up to 300 g m^{-2} d^{-1}. The stable carbon isotopes start the profile with low values (c. -18 ‰) that likely represent biogenic production, rise sharply up to 6.9 ‰ in correspondence with the core of the vent, and then start to trend towards more negative values (indicating mixing between the two biogenic – geogenic end-members). These results highlight the importance of topography in controlling the size and location of the leakage footprint, as gas leaking at the forest-field boundary can migrate downslope within the unsaturated zone due to density effects but cannot move upslope. The effect of infiltrating meteoric water and/or unconfined groundwater migrating downslope, dissolving CO_2 in the vent area and then degassing it down gradient, may also contribute to this distribution, however it is not possible to assess this mechanism with the present data.

A much shorter, 50 m long profile was performed across an isolated gas vent within a flat field at the Ailano study site (see Figure 5a for location). Based on a grid of flux measurements (Figure 5a) this vent is sub-circular and relatively symmetrical. The profile starts within the center of the gas vent core and moves in an ESE direction. Samples were collected every 2 or 4 m, with soil gas being collected from a depth of about 70 cm. There are a number of clear differences between the Ailano profile (Figure 9b) and the Latera profile described above (Figure 9a). To begin with, this feature is symmetrical, likely due to its occurrence in a flat field. Next, measured values in the vent core are much higher, with CO_2 flux over 9000 g m^{-2} d^{-1} and CO_2 concentration near 100%. Despite this greater flow, this gas vent is much smaller than that measured at Latera; again this may be linked to the topographic differences between the two sites, although depth to water table and/or sediment permeability properties may also have an impact. Finally, because this feature is smaller and more isolated from other leakage points, it is easier to examine the relationship between the three parameters. Despite being measured at the same depth, CO_2 concentration decreases much more rapidly (note log scale) than the isotope values. That said, these two parameters essentially return to near-background values at the same distance (c. 70 m along profile), thus defining a similar leakage footprint. In contrast, the CO_2 flux data (also plotted with a log scale) appear to show a much smaller footprint, with values stabilizing beyond about 35 m at what appear to be background levels near 20 g m^{-2} d^{-1}. This implies that beyond a certain distance the geogenic contribution to surface CO_2 flux becomes very minor despite its presence deeper in the soil column.

5. Conclusions

Research conducted at a number of sites in central Italy where naturally produced CO_2 (± CH_4) is leaking at the ground surface has provided large scale, real-world laboratories in which to conduct experiments. Three principle questions were addressed during field campaigns conducted by ENOS consortium partners in 2017, including how can a leak be located quickly and accurately, what innovative tools can be used to distinguish a leak from natural background noise, and how will gas migration processes in the surface sediments affect the size and strength of a leakage anomaly?

Rapid mapping was addressed by testing a multi-sensor mobile platform that measures CO_2 and CH_4 just above the ground surface (open path IR laser) or at the ground surface (in-house developed GasPro Mapper system using a Non-Dispersive InfraRed sensor). Both methods were capable of locating leaks in a fraction of the time needed with point flux measurements, while their combined application (together with wind strength monitoring) yielded highly complementary data. The laser system has a very rapid response time, little memory effect, and a stable background that makes it highly sensitive, however it was more strongly influenced by wind conditions and the system, in its present form, is relatively expensive and bulky. The Mapper is much less costly and the measurement of gas directly within the boundary layer between the ground and atmosphere (which is less influenced by wind) means that measured anomalies are higher, however the NDIR sensors are less stable and the slower response times of the sample delivery system caused smearing in the spatial data and decreased maximum response. Both systems are presently undergoing continued development to address these shortcomings.

Distinguishing leakage versus background anomalies was addressed through an innovative application of CO_2 isotopologues at the natural leaking sites to determine if this method could be used to estimate formation temperature and thus, by inference, CO_2 origin. Unfortunately, the clumped $\Delta 47$ isotopic signature measured at these sites indicates that this method is unlikely to be a relevant application for depicting the source of leaking CO_2 because the reaction rates of CO_2 equilibration with groundwater along the leakage pathway are too fast, which results in a distortion of the true $\Delta 47$ signature.

Finally, migration processes in the near-surface environment was addressed by detailed studies of horizontal profiles crossing leakage points and the associated analysis of soil gas concentrations, isotopes, and surface flux rates. Results highlight the complexity of CO_2 isotopes in the soil due to the combined effects of leakage, CO_2 production in the root zone, and diffusive fractionation. Whereas migration in the bedrock fault is primarily vertical along the structural discontinuity, the local topography, hydrogeology, and shallow stratigraphy of the sediments that bury a fault can potentially cause lateral movement away from the main leakage pathway and influence the size and strength of the leakage anomaly. This is important both in terms of the size of an eventual monitoring target as well as estimating leakage rates for quantification purposes. Results presented here for two different gas leaks highlight, in particular, the potential effect of topography on the size of a leakage area.

Acknowledgements

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