NEAR-SURFACE GAS GEOCHEMISTRY TECHNIQUES TO ASSESS AND MONITOR CO_2 GEOLOGICAL SEQUESTRATION SITES

The use of natural analogue sites in Italy as field laboratories

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Abstract: As is well known the long-term effects and stability of a man-made CO_2 geological storage facility is very difficult to predict with laboratory or modeling experiments due to the size and long time scales involved. Instead attractive additional sources of information are natural sites where CO_2 produced at great depths is either trapped in porous reservoirs or leaks to the surface. These sites can be considered as "natural analogues" of what may occur over geological time spans within an engineered CO_2 geological storage site. The study of these sites can be subdivided into three broad fields: i) understanding why some reservoirs leak while others don't; ii) understanding the possible effects of CO_2 should it leak into the near-surface environment; and iii) using the leaking sites to develop, test and optimise various monitoring technologies. The present article summaries many of the near-surface gas geochemistry results obtained in central Italy during the EC-funded NASCENT project (Natural Analogues for the Storage of CO_2 in the Geological Environment). These include a comparison of leaking (Latera) and a non-leaking (Sesta) CO_2 reservoirs, detailed soil gas surveys to outline migration pathways, the development of a geochemical continuous-monitoring station to study temporal changes in CO_2 concentrations, and field experiments involving the injection of a gas mixture in the shallow subsurface to outline migration pathways and to understand the behaviour of various gas species based on their different chemical-physical-biological characteristics. Put together this data provides useful information for site selection, risk assessment and monitoring techniques, which is needed if CO_2 geological storage is to become an accepted and widely-applied technology.

Key words: soil gas surveys, geochemical monitoring stations, injection tests, leaking – non-leaking natural CO_2 reservoirs

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1. INTRODUCTION

The geological storage of anthropogenic CO_2 has long been considered one of the safest and most technologically feasible methods for the short-term reduction of atmospheric loading of this greenhouse gas. In fact, geological sequestration has the potential to provide mankind with a finite period of time in which to change its energy strategy (through improved efficiency of energy production, transfer and use, energy conservation measures and the eventual move from fossil fuels to renewable sources of energy) while at the same time attaining immediate CO_2 reductions

However in order to convince legislators, environmental groups, industry and the public at large that this is the proper path to follow, the method must be shown to be safe and effective over geologically significant periods of time. Traditionally laboratory and modeling experiments have been performed to try and predict the possible fate of various engineered systems, however both approaches suffer from limitations related to scaling up their results to large natural systems over thousands to millions of years. Another approach which can address these difficulties are natural analogues, in other words natural sites where the studied phenomenon has already been occurring over extremely long periods of time. In the case of CO_2 geological storage sites there are numerous locations world-wide where CO_2 is (or has been) produced at depth, with the resulting gas either being trapped in deep reservoirs (analogous to hydrocarbon reservoirs) or is leaking to surface along preferential migration pathways like faults or fractures.

Work performed during the EC-funded NASCENT project (Natural Analogues for the Storage of CO_2 in the Geological Environment) addressed this issue through the study of a number of natural CO_2 sites in Europe (Pearce, 2004). These sites were used as natural laboratories, with the analysis of water, rock and gas samples with various geochemical, geophysical and modeling approaches. The resulting database and associated studies are a unique tool for the better understanding of the various physical and chemical processes involved, as well as for the development of new tools for site assessment and monitoring of any eventual CO_2 geological storage site.

The present article summarises some of results obtained during NASCENT on three natural analogue sites in central Italy, focusing on near-surface gas geochemistry as a tool to understand the micro and macro scale migration of gas, the possible effects of CO_2 leakage on the shallow environment, and the development of tools and instruments for site selection and/or subsequent monitoring. The three site include Sesta, a non-leaking site, and Latera and San Vittorino, two leaking sites. Work involved soil gas and gas flux surveys, as well as an injection test and the development of a geochemical continuous-monitoring station.

2. METHODS

2.1 Soil gas

The probe used to collect soil gas samples consists of a modified ¼ inch, thick-walled, stainless-steel tube. The bottom end of the tube is closed with a sharp drive point, while small lateral holes are drilled along the first 5cm of this end to act as sampling ports. The other end is left open so that a septum can be attached, while two steel cylinders are welded on the outside wall to act as pounding surfaces when installing and removing the probe with a co-axial hammer. The probes were generally placed at a depth of 50 to 90 cm in order to avoid any atmospheric input. Once the probe was in place a septum holder was attached to the open end of the tube, and a needle and 60ml plastic syringe were used to draw off gas. The first two 60ml volumes were discarded to clean the system, and then a 60ml sample was drawn for field analysis of radon while a second was placed in a previously evacuated, 25ml volume, stainless-steel canister for subsequent laboratory analyses.

All soil gas samples were analysed in the field for Rn^{222} using a Scintrex EDA200 alpha scintillometer. All soil gas samples were also analysed for hydrocarbon species (C1-C4), sulphur species (COS and SO_2) and permanent gases (N_2, O_2 and CO_2) using two Fissons 8000-series bench gas chromatographs. All samples were also analysed for helium using a Varian Portatest leak detector (model 938-41); helium concentrations are expressed as ΔHe (i.e. $\Delta He = He_{sample} - He_{atmosphere}$).

2.2 Gas Flux

Gas flux measurements were conducted using the chamber technique, whereby the open end of a container was placed on the soil surface and measurements of CO_2 concentrations were made every second via a connected infra-red analyser. The non-destructive analyser was connected to the chamber via an inlet and an outlet tube such that air was recycled through the chamber via a pump in the instrument, thereby guaranteeing a constant internal pressure during the measurement. In the present study a 13 x 13 x 9 cm Plexiglas chamber was used along with a Draeger Multiwarn infrared analyser equipped with CO_2 (0-25%), H_2 (0-1000ppm) and H_2S (0-

100ppm) sensors. Measurements were conducted for no more than 75 seconds in order to ensure that the natural flux rate from the soil was not affected. Data was then transferred to a PC and the flux rate was calculated using the following formula from Hutchinson and Livingston (1993)

$$f = (C_{final} - C_{initial})\, V / \Delta t\, A$$

Where f is the flux in $m^3\ m^{-2}\ s^{-1}$, V is the volume of the chamber (m^3), A is the surface area measured (m^2) and Δt is the time difference (sec) between the first and last measurements of the CO_2 concentrations (ml/ml). Values were then converted into kg $m^{-2}\ d^{-1}$.

3. LEAKING VS NON-LEAKING CO_2 RESERVOIRS

Due to the fact that the Italian peninsula is still tectonically and volcanically active there are numerous sites where CO_2 produced naturally at depth either becomes trapped in permeable but isolated strata or migrates to surface via faults and is released to the atmosphere. Recent work on leaking (Latera) and sealed (Sesta) sites in central Italy with near-surface geochemical techniques have attempted to explain such different behaviours, despite the fact that both occur in faulted, geothermal areas. Clearly understanding these two types of systems will be highly useful for predicting the safety and long-term isolation of man-made CO_2 geological sequestration sites.

3.1 Latera

The Latera geothermal field is located in the west-central part of the Italian peninsula within the Latera caldera. Although studied since the early 1970s for geothermal energy, the area was well known long before that for carbonate rich springs and CO_2-rich gas vents which inferred the occurrence of CO_2 production / reservoirs at depth. The great age of these gas reservoirs (more than 0.1 Ma old) and the fact that local inhabitants have lived for thousands of years above these reservoirs and associated gas vents means that the Latera site is an excellent natural analogue of what might happen at surface in the unlikely event of leakage from an engineered geological storage site for anthropogenic CO_2.

Locally the geology consists of a metamorphic basement, “Tuscan” limestones, “Ligurian” flysch, volcanic units and post-orogenic sediments. Formation of the local geothermal reservoir was likely due to the combination of compressional tectonics during the Eocene to Miocene (which formed the subsurface structural high within the host Tuscan limestones - Bertrami et al., 1984; Barberi et al., 1984) and subsequent volcanic activity and tensional tectonics (which supplied the necessary fluids and high heat flow for the thermo-metamorphic formation of CO_2 - Duchi et al., 1992). Finally the collapse structures associated with the various stages of local volcanism have either remained open for fluid flow (resulting in springs or gas vents on surface) or have become sealed by fault gouge or secondary mineral precipitation (thereby isolating entire blocks and creating heat/water convection cells).

Extensive work has been performed on the Latera test site by the authors during the NASCENT project, including regional, detailed and highly detailed soil gas surveys, detailed gas flux measurements, electrical tomography surveys, gas vent characterization and aqueous geochemistry. This research has been conducted to outline major gas migration pathways and to quantify the amount of gas reaching the atmosphere. Only some of the gas geochemistry data will be discussed here; the interested reader is referred to the final reports of the project itself (Pearce, 2004) for a more extensive treatment of the data.

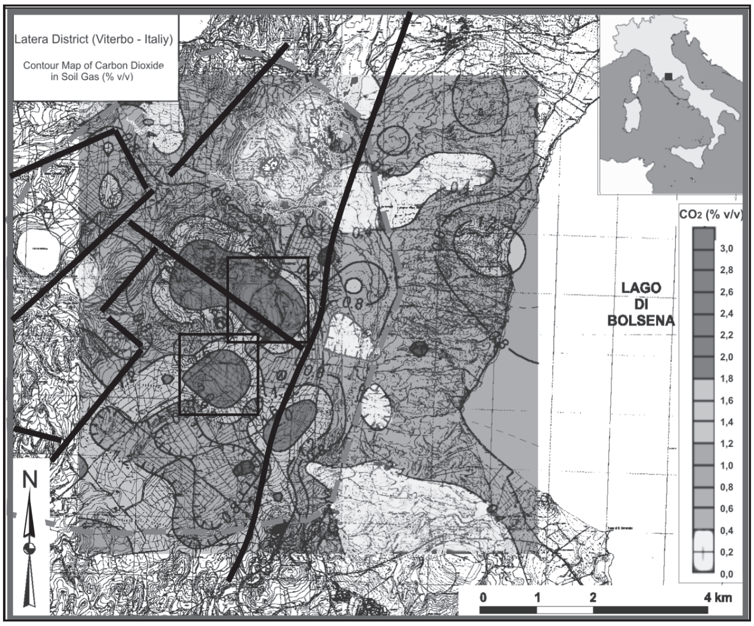

Figure 1. Soil gas CO_2 concentration distribution obtained during a regional geochemical survey in the Latera area. The two small squares in the central portion of the map indicate the location of the two detailed soil gas surveys.

A preliminary, regional soil-gas survey was conducted in the western sector of the Latera caldera with the goal of locating the fault systems which dissect the collapsed area and form the main route of gas migration towards the surface. Sampling was performed in an area of about 65 km^2 using a uniform distribution of about 2 samples/km^2 for a total of 110 samples. The CO_2 contour map shows the spatial distribution of this gas species (Fig. 1). The major anomalies occur in the central and south-western parts of the Latera caldera, in good correspondence with mapped structural elements shown in the figure. Previous geophysical investigations in these areas highlighted a series of NW-SE and NE-SW oriented discontinuities which offset the carbonate substratum and formed the structural high hosting the geothermal reservoir. Elevated values are likely due to gas migration along these geochemically active faults, which result in the clearly anisotropic CO_2 anomalies. This migration of deep (magmatic) gases is also indicated by the presence of He and Rn anomalies in the same area (not shown).

Two subsequent detailed surveys (locations shown in Figure 1) were conducted in areas which exhibited elevated soil gas CO_2 concentrations during the regional survey. As samples were concentrated around gas vents the observed concentrations are significantly higher than those measured in the regional survey. For example during the first detailed survey, CO_2 concentrations of up to 97% and CH_4 values of over 1000 ppm were measured. Radon values (up to 480 Bq/l) also exceeded the amount expected if this radioactive gas were only produced *in situ* via the decay of ^{226}Ra in the local shallow volcanic rocks. Contour maps of these gas species (not shown) highlight two clear circular anomalous zones, one next to a straight creek segment with gas bubbling at its base (fault?) and the other near a geothermal exploration well. Both of these circular anomalies correspond to vent structures that leak significant quantities of CO_2 to the atmosphere. In contrast the second detailed survey, conducted about 1km north of the first in an area defined by electrical tomography anomalies, had slightly lower mean CO_2, CH_4 and Rn values but higher He values (Table 1). Contour maps of CO_2 and He (not shown) give a similar distribution of spotty anomalies aligned parallel to the known NE-SW tectonic elements, with the major anomalies occurring in the area of significant gas vents.

Table 1. Minimum, maximum and mean values for four gas species analysed during the two detailed soil gas surveys (DS1 and DS2).

	CO_2			**CH_4**			**Rn**			**He**		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
DS1	0.05	97.3	9.1	0.26	1076	57.6	12.7	480	127	-540	310	-88
DS2	0.04	97.2	3.1	n.d.	1120	12.0	14.6	313	109	-913	2943	-105

Finally detailed soil gas profiles were conducted across a known gas vent occurring in the area of the second detailed profile to outline relative gas distributions and the size and form of the vent. In this work samples were collected about every 1 m and analysed for a series of different gas species, both in the field and in the laboratory.

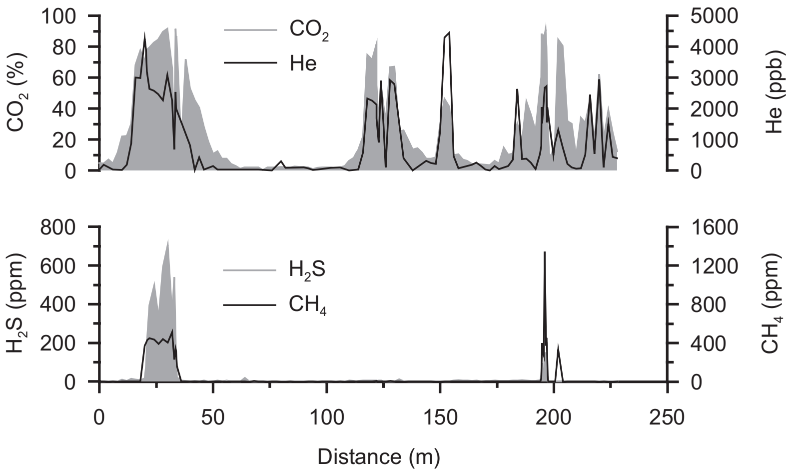

Figure 2. Soil gas concentrations of various species, measured along a profile crossing numerous gas vents in the Latera area.

Figure 2 shows the results for four of these gas types, CO_2, He, H_2S and CH_4. As can clearly be seen in this figure the survey crossed a number of gas vents, however the distribution of the various species is not consistent from one vent to another. For example CO_2 and He are the two gases with the most significant number of anomalies, with both showing a similar spatial and relative concentration distribution. In contrast H_2S and CH_4 are much more spatially restricted, with H_2S showing elevated values in the vent located around 25m while CH_4 is more concentrated in the one at 200m. The different relative distribution of CO_2 / He versus H_2S / CH_4 can be explained in terms of gas abundance and reactivity. For example He is a highly mobile and non-reactive molecule, and thus it is logical that it shows a large number of wide peaks along the entire profile. CO_2, on the other hand, which shows essentially the same distribution, is far more reactive due to its high solubility in water and its involvement in acid-base reactions. The similarity of the reactive CO_2 and the conservative He implies that the high CO_2 flux / concentration (>90%) supplies an excess mass of CO_2 at a rate which is greater than that of dissolution and eventual reaction. In contrast the relatively low concentrations and reactive nature (be it chemical or microbiological) of both H_2S and CH_4 has resulted in the consumption of these gases in the unsaturated zone. Only in the centre of vents, which have sufficiently high flux rates, is it possible for these species to migrate closer to the soil-atmosphere interface, as is observed in the two vents at 25 and 200m.

3.2 Sesta

The Sesta study site is located approximately 260 km to the NW of Rome and about 130 north of the Latera site (described above). In contrast to the Latera caldera, where there is extensive evidence of CO_2 leakage at surface, there are no such manifestations at the Sesta site. Instead the existence of a CO_2 rich gas reservoir at depth was only discovered during deep drilling undertaken for geothermal resource exploration. In terms of CO_2 geological storage it would thus be important to understand the difference between the two sites; in other words why does the Latera reservoir leak whereas the one at Sesta appear to have been sealed for hundreds of thousands of years?

The general area surrounding Sesta is of great interest as a geothermal resource, as it is characterized by one of the highest heat flux rates in Italy. The actual study site occurs within a NNW-SSE trending graben containing a Pliocene clay cover which overlies part of the geothermal field, just to the east of the Larderello geothermal field. Both the eastern and western sectors of the graben are characterized by metamorphic lithologies which are bounded by NNW-SSE and SSW-NNE normal faults. Although delimited by these boundary faults, no active faults and/or fracture systems are observed within the valley. The CO_2 gas cap is hosted within tectonic wedges and confined by a flysch nappe.

Work at Sesta included the same types of gas geochemical surveys which were applied at Latera in an effort to understand if the Sesta site is truly sealed or if it exhibits microseepage from the gas reservoir. Extensive outcrop on the boundaries of the area limited soil gas sampling to the centre of the valley where there was sufficient sedimentary cover; measurements of gas flux were conducted in areas where soil gas samples could not be taken.

A regional soil-gas survey (about 15 samples/km^2) was conducted in the study area, with the main statistical results given in Table 2. The studied gases generally show a uniform distribution and low concentrations which are comparable with other similar Italian basins, although the high CH_4 standard deviation and the strong difference between mean and median for CO_2 and CH_4 highlight the "spot" distribution of some anomalies in the data set. Most of these isolated anomalies, however, can be explained by near surface processes. For example the highest CO_2 and methane values (11% and 890 ppm, respectively) were measured close to a garbage dump and thus are most likely linked to shallow biological degradation of organic matter. Furthermore, the spatial soil gas distribution of the various species does not exhibit any clear structural alignment. This supports the idea that there are no preferential migration pathways, such as faults or fracture networks, in the centre of the valley. Radon, a commonly used fault tracer (e.g. Ciotoli et al., 1998; Ciotoli et al., 1999), has a background value of about 5 Bq/L, which is less than the calculated mean value for Italy (about 20 Bq/L) based on an unpublished database of 15,000 samples constructed by the authors. The most elevated values were observed on the eastern side of valley and are probably linked to the normal bordering graben faults. Finally helium values are almost always less than 200 ppb, with only two significant anomalies (up to 7000 ppb) along the extreme sectors of the valley, again close to the bordering faults.

Table 2. Statistics of some gas species analysed during soil gas surveys at the Sesta study site.

	CH_4	CO_2	O_2	N_2	Rn	He
samples	250	250	250	250	250	250
mean	7.71	0.68	21.18	78.12	5.01	-548.22
median	2.39	0.35	21.39	78.13	2.77	-455.7
min	n.d.	0.04	9.95	57.46	0.37	-2088
max	888.3	11.01	23.36	83.68	58.09	6823.74
quart. inf.	2.07	0.2	20.87	77.06	1.85	-1059.7
quart. sup.	2.82	0.79	21.76	79.21	6.1	-64.44
variance	3427.4	1.35	1.4	4.46	58.85	584893
std. dev.	58.54	1.16	1.18	2.11	7.04	764.78

Gas flux measurements were performed in order to complete the investigation in the areas where outcropping lithological units did not allow for the collection of soil gas samples, as well as to better evaluate the sequestration capacity of the flysch nappe which overlays the CO_2 gas cap. Table 3 compares the main statistical parameters of flux data from various Italian sites (including both Sesta and Latera) located in different geological settings. Although the limited number of measurements at each site does not allow for a true statistical comparison, as expected the volcanic areas (like Latera) have far higher flux rates compared to the sedimentary basins (like Sesta), both because of deep gas production via thermo-metamorphism and the occurrence of permeable fault structures. A good example of this can be seen by comparing the Sesta and Siena data, as the basin-wide averages are very similar, whereas the detailed flux survey values above the Siena Rapolano fault are two orders of magnitude higher (similar to the Latera and Ciampino values). These results highlight the low permeability of the flysch and sediments overlying the gas cap at Sesta and indicate that the site has efficiently sequestered the CO_2 at depth despite the occurrence of normal faults bordering the graben.

Table 3. Statistical comparison of gas flux rates from different sites located in different geological settings throughout Italy.

Geological setting	Site	count	minimum	maximum	median
Sed. basins	Sesta	25	6.0×10^{-9}	7.9×10^{-8}	2.7×10^{-8}
	Siena basin	12	n.d.	5.4×10^{-8}	1.1×10^{-8}
	Siena Rapolano fault	11	1.0×10^{-8}	1.8×10^{-5}	2.6×10^{-6}
Volcanic areas	Latera	25	7.0×10^{-8}	2.0×10^{-5}	9.0×10^{-6}
	Ciampino	5	1.8×10^{-7}	1.3×10^{-5}	3.4×10^{-6}
Tectonic basins	S. Vittorino	8	5.3×10^{-7}	5.7×10^{-5}	2.1×10^{-5}
	Fucino	15	3.0×10^{-9}	9.7×10^{-8}	2.4×10^{-8}

4. INJECTION TEST

An injection test was performed within the NASCENT project which consisted of the injection of a gas mixture into a fault structure and the subsequent monitoring of soil gas and groundwater chemistry in order to outline permeable pathways and flow rates in the subsurface. Such types of gas injection tests have been used by various researchers to better understand the dynamics of gas migration in the shallow environment (Ciotoli et al., in submission; Gascoyne and Wuschke, 1997; Lineham et al., 1996).

The gas injection test was conducted within the area of the Latera study site, at a location which has numerous gas vents and which, based on geophysical surveys and the alignment of the vents, has a fault crossing the site at depth. During this experiment a total of 8000 L of gas (40% Ar, 40% He and 20% CO_2) was injected into a faulted interval between 9 and 12 m below ground surface. Soil gas samples were collected at regular intervals around the injection borehole from a grid of fixed sample points (64) and analysed both in the field and the laboratory for the injected gas species. Ground water samples were also collected from 6 peizometers drilled to 5m depth into the shallow aquifer in order to monitor for breakthrough of the highly soluble CO_2 in the dissolved phase.

Results from the gas injection test highlight the importance of understanding the chemical and physical characteristics of the gases being monitored, as aqueous solubility, gas density and both water- and gas-phase diffusivities play a critical role in the travel times and mass attenuation features of migrating gases. The gas mixture injected at the Latera test site consisted of three rather different species, ranging from the highly insoluble, highly mobile low density helium to the very soluble, reactive and dense gas carbon dioxide, while argon has characteristics which lie between these two extremes. These differences are mirrored in the results obtained during the test, with helium arriving very early at surface within a very small area around the injection well and at high concentrations. In contrast CO_2 arrived much later, had a more diffuse distribution and was observed at much lower relative concentrations than those seen for He. In addition injected helium returned to background values within a very brief period of time, on the order of weeks, whereas the injected CO_2 appears to continue to slowly seep from the system even a month after the experiment had ceased.

A mechanism to explain these results is proposed whereby at early times the more soluble gases are stripped from the gas bubbles, enriching them in helium, and that this gas phase, upon reaching the water table, migrates rapidly through the unsaturated zone to surface due to its low density and high diffusivity. In contrast at later times the groundwater in the bubble flow path becomes progressively more saturated in CO_2, resulting in less transfer to the dissolved phase and more of this gas reaching the water table. Once in the unsaturated zone the more dense CO_2 moves laterally on top of the water table, resulting in the observed lateral dispersion, temporal attenuation and lower concentrations (due to both dilution by soil gas and removal into the aqueous phase) observed in the soil gas surveys. Lateral migration of CO_2 saturated groundwater, and eventual release of this gas to the unsaturated zone via vent activity is another possible mechanism, however this can only explain anomalies observed down gradient from the injection point. In any case, dissolved gas results confirm the importance of CO_2 mass transfer into the aqueous phase, as measured concentrations of dissolved CO_2 in observation piezometers increased by 2 to 3 times background levels in wells located down-gradient from the injection well

5. MONITORING STATION

One way to allay public concern regarding CO_2 storage safety is to develop early warning systems which can monitor gas compositions and concentrations in the near-surface environment. Increased concentrations of CO_2 or other associated gases in these phases, above natural biogenic variations, would then trigger a warning. One such station has recently been developed and deployed in the San Vittorino area of central Italy. Although the monitoring station (jointly funded by the EC NASCENT project and the Civil Protection Agency - Region of Lazio) was originally deployed to monitor for dissolved gas precursors related to CO_2-induced sinkhole formation, it could easily be deployed to monitor soil gas above a CO_2 sequestration site (for example above abandoned wells).

The San Vittorino plain is a triangular-shaped intramontane basin filled with fluvial-lacustrine sediments and local travertine deposits, and is surrounded by mountains formed by carbonate and siliciclastic successions thrusted onto various bedrock lithologies (Centamore and Nisio, 2003). The plain is bordered by normal and/or strike-slip faults and is also cross-cut by other regionally important features. The fault segments that cross the plain are not easy to identify due to the plastic nature of the filling sediments, however evidence of their existence is given by the occurrence of flowing springs, mineralised waters, gas bubbling vents and generally elevated soil gas and gas flux values throughout the valley. It has been the interaction of these deep acidic gases, like CO_2 +/-H_2S, with the spring and ground waters which have resulted in the formation of more than 30 sinkholes in the central and eastern sectors of the plain

The monitoring station uses gas permeable tubing to sample gases dissolved in groundwater via diffusion. As the internal volume of the tube represents a "head space", equilibrium concentrations will be governed by Henry's Constant. The use of gas permeable tubing has been shown to be effective for other gas species (e.g. Jacinthe and Groffman, 2001; Jacinthe and Dick, 1996). The gas permeable tubing is placed in a piezometer (installed above a microgravity minimum in the town of Vasche) and is linked at surface with the monitoring station, which houses CO_2, H_2S and H_2 sensors, a continual power supply and an external data relay system. The in-house developed software system is programmable to sample at different intervals, however a sample time of once every 4 hours was chosen to allow the sampling tube to re-equilibrate with the surrounding water. Recorded data can be down-loaded from the laboratory via modem.

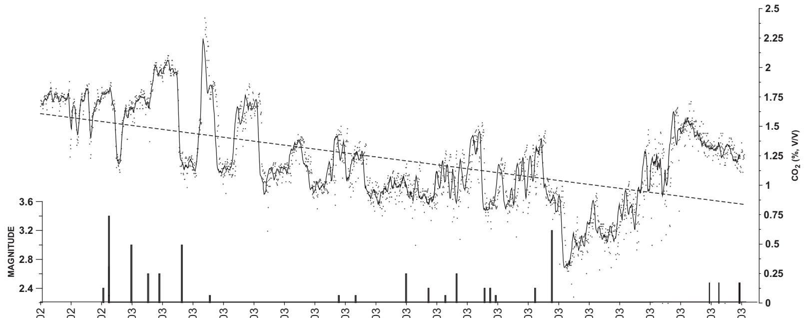

Figure 3. Dissolved CO_2 results from the monitoring station installed in Vasche (after Annunziatellis et al., 2004). Dots indicate individual values while the running average is a black line. The vertical bars are earthquakes near the station registered by the Istituto Nazionale di Geofisica e Vulcanologia in Italy.

The geochemical monitoring station began to collect data on December 20, 2002, and during the intervening period it has collected approximately 2 years worth of dissolved gas data. Some of the data collected during the monitoring period is shown in Figure 3 (note that the values are not dissolved gas concentrations but rather the concentration in the silicone tubing which has equilibrated with the groundwater). The general decreasing trend of the line chart also shows several sharp drops in the signal, which could be linked to different environmental variables (such as water and atmospheric temperatures affecting the sensors) or to the occurrence of earthquakes. The first case cannot be verified because this prototype station was not equipped with temperature sensors. The second hypothesis can be studied by comparing the dissolved gas data with the occurrence of earthquakes in an area surrounding the station site, as shown in the figure. In particular there were about 4 magnitude-3 earthquakes in the region during the monitoring period. The line chart shows abrupt decreases in correspondence with earthquakes which occurred in the Reatini Mts, the Sibillini Mts and at Gran Sasso Mt. There are, however, other CO_2 decreases which cannot be correlated with seismic events in the region and thus there may be multiple processes which contribute to the signal.

6. SUMMARY AND CONCLUSIONS

The present work presents an overview of some results obtained by the authors within the NASCENT project. This EC-funded project examined various sites throughout Europe which can be considered as natural analogues of anthropogenic geological CO_2 storage, due to the accumulation, or leakage at surface, of naturally-produced deep CO_2. The goals of this work can be subdivided into three broad fields: i) understanding why some reservoirs leak while others don't; ii) understanding the possible effects of CO_2 should it leak into the near-surface environment; and iii) using the leaking sites to develop, test and optimise various monitoring technologies.

In regards to the first point, the leaking natural analogue site at Latera provides insight into both macro- and micro-scale gas migration mechanisms, as well as spatial and temporal variations in gas behaviour. This study suggests that: i) gas emanation along "gas bearing" faults is not homogeneously distributed; ii) gas release to the atmosphere is highly localised and spatially restricted; and iii) the near-surface spatial distribution of different deep-origin gases depends on their mobility, reactivity and solubility. In regards to the non-leaking Sesta site, both soil gas and flux values highlight that the clayey cover (which is characterized by recent but sealed faults) prevents gas migration towards surface and that this site has the main features needed for a suitable CO_2 geological storage site (such as clay cover, sealed faults, the lack of seismicity, etc.). A clear comparison of the CO_2 data from various natural analogue study sites is given in Figure 4, with the leaking sites of Latera, Ciampino and San Vittorino showing a markedly different statistical distribution as compared to that for the non-leaking Sesta site.

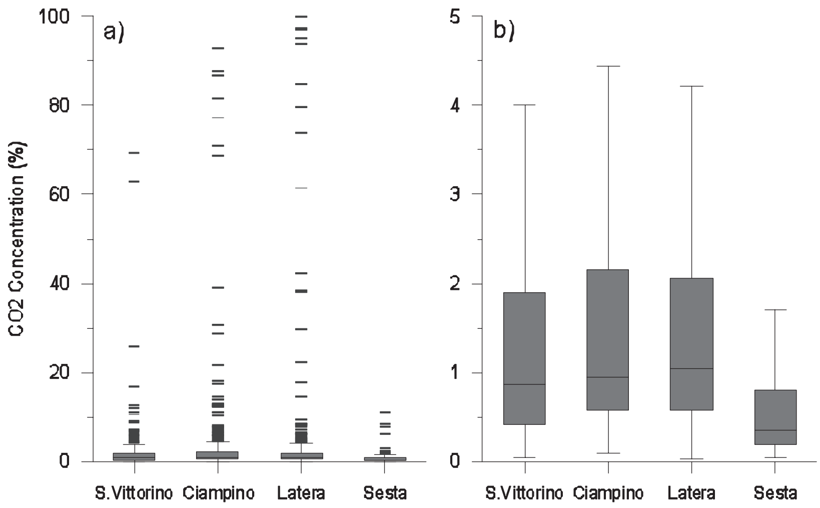

Figure 4. Box plots of soil gas CO_2 data from 4 studied sites. The boxes show the upper and lower quartiles (and median inside the box), the vertical lines show the normally-distributed minimum and maximum while the horizontal lines show outliers. The plot in (a) shows all the data while (b) is the same but without outliers. Note that the three sites showing CO_2 leakage are very similar whereas that the non-leaking Sesta site has significantly lower values.

In regards to the second point, related to near-surface effects of CO_2 leakage, much work was conducted by the authors on this topic however these results were not discussed in detail in this paper. In particular the effect on vegetation (Latera), groundwater composition and sinkhole formation (San Vittorino) and air quality (Ciampino) was observed, however in most cases the effects are highly localized and any risks can be managed with relatively simple measures.

Finally in terms of the third goal, that is the testing of various monitoring techniques on the naturally leaking sites, work during the various soil gas and gas flux surveys have shown that these methods are uniquely adapted to near-surface studies for both site assessments and eventual site monitoring. This was particularly well shown in the gas injection tests, which tested monitoring techniques as well as examined migration mechanisms. Results from the gas injection test also highlighted the importance of understanding the chemical and physical characteristics of the gases being monitored, as aqueous solubility, gas density and both water- and gas-phase diffusivities play a critical role in the travel times and mass attenuation features of migrating gases. This was clearly shown by the highly different breakthrough and migration behaviour of He and CO_2 during the test. Another technique tested during the project was geochemical continuous monitoring stations, which have the potential to monitor for leaking CO_2 in the vicinity of deep injection wells or along known tectonic structures. The development, construction, testing and application of the prototype geochemical station during this work has provided "proof of concept" and has shown that the unit is capable of monitoring dissolved CO_2 in groundwater, sensing variations in concentration and transmitting the data in real-time back to the laboratory for processing and interpretation.

The experience gained during this work on natural analogues in Italy has already been shown to be practical, economical and highly useful during its application to real-life CO_2 geological sequestration sites in Algeria (In Salah EGR project) and Canada (Weyburn EOR project).

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