

STUDY OF NATURAL CO₂ EMISSIONS IN DIFFERENT ITALIAN GEOLOGICAL SCENARIOS

A refinement of natural hazard and risk assessment

N. Voltattorni, G. Caramanna, D. Cinti, G. Galli, L. Pizzino and F. Quattrocchi

Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata n° 605, 00143 Rome, Italy

Abstract: Natural gas emissions represent extremely attractive surrogates for the study of CO₂-effects both on the environment and human life. Three Italian case histories demonstrate the possible co-existence of CO₂ natural emissions and people since Roman times. The Solfatara crater (Phlegraean fields caldera, Southern Italy) is an ancient Roman spa. The area is characterized by intense and diffuse fumarole and hydrothermal activity. Soil gas flux measurements show that the entire area discharges between 1200 and 1500 tons of CO₂ a day. In proximity of Panarea island (Aeolian islands, Southern Italy), a huge submarine volcanic-hydrothermal gas burst occurred in November, 2002. The submarine gas emissions locally modified seawater pH (from 8.0 to 5.0) and Eh (from +80 mV to -200 mV), causing a strong modification of the marine ecosystem. Collected data suggest an intriguing correlation between the gas/water vent location/evolution and the main local and regional faults. CO₂ degassing also characterizes the Telesse area (Southern Italy), one of the most seismically active segments of the southern Apennine belt with the occurrence of five large destructive earthquakes in the last 500 years. Geochemical surveys in this area reveal the presence of high CO₂ content in ground-water. Carbon isotopic analysis of CO₂ reveal its deep origin, probably caused by the presence of a cooling magmatic intrusion inside the carbonate basement. All the above mentioned areas are constantly monitored since they are densely populated. Although natural phenomena are not always predictable, local people have nevertheless learnt to manage and, in some case, exploit these phenomena, suggesting significant human adaptability even in extreme situations.

Key words: natural emissions; carbon dioxide; soil gas; dissolved gas; flux measurement.

1. INTRODUCTION

Natural degassing phenomena can be studied as “natural analogues” in the frame of geological storage and sequestration of anthropogenic CO₂ emissions, especially when the risk of possible leakage at surface is taken into account with potential consequences in the biosphere.

Active and quiescent volcanic areas release high amounts of CO₂ to the atmosphere (Chiodini et al., 1998) from both active craters, as plumes and fumaroles, and along the flanks of volcanic edifices as diffusive soil emanations (Allard et al., 1991a; Baubron et al., 1990).

The two basic processes which are recognised to drive soil gas movement through rocks and sediments are *diffusion* and *advection*.

If transport through a stationary medium take place by diffusion, the steady state diffusive flux Φ_d is proportional to the concentration gradient, $dC/d\lambda$, as expressed by Fick's first law:

$$\Phi_d = -vD(dC/d\lambda) \quad (1)$$

where v and D represent soil porosity (i.e., the fraction of pore volume to total soil volume) and the diffusion coefficient, respectively, and the minus sign indicates that gas moves from points of high concentration towards points of low concentration (or partial pressure). On the contrary, advection involves the movement of matter due to the action of a force, i.e., a pressure gradient $dP/d\lambda$. Advective flow Φ_a is described by the well-known Darcy's law:

$$\Phi_a = (k/\mu)(dP/d\lambda) \quad (2)$$

where k is the specific permeability and μ is the viscosity of the fluid.

Although equation 2 was experimentally derived for the steady flow of liquids in porous media, it has also been extensively used to describe the advective flow of compressible fluids in porous media (Gurrieri and Valenza, 1988). For the sake of correctness, the steady advective flow of compressible fluids is described by comparatively complex, well-known equations (e.g. Scheidegger, 1974). Because of mathematical complexities many workers have decided to study the steady flow of gases assuming that they are incompressible. Although this assumption might seem unreasonable, it is justified when the pressure gradient is comparatively small.

Exhalation is the process that transfers gas from the soil to the atmosphere via the already-described mechanisms of diffusion and advection. Diffusive gas exhalation takes place due to the different

concentrations of that gas in the soil and atmosphere. Advective exhalation exists when the gas in the soil has a higher total pressure than that in the atmospheric (eg. barometric pumping). Exhalation can be measured in terms of flux from the soil, i.e. the quantity of gas per unit area per unit time ($\Phi_{\max} = \text{Kg m}^{-2}\text{s}^{-1}$; $\Phi_{\text{volume}} = \text{m}^3\text{m}^{-2}\text{s}^{-1}$). Generally, mean values for CO₂ exhalation are $3.7 \times 10^{-7} \text{ m}^3\text{m}^{-2}\text{s}^{-1}$ (de Jong and Schappert, 1972) or $0.4 - 4 \times 10^{-7} \text{ m}^3\text{m}^{-2}\text{s}^{-1}$ (Kanemasu et al., 1974).

2. SAMPLING AND ANALYSIS

Many techniques are used to sample soil-gases, waters for dissolved gas determination and gas/water from submarine gas emission points. Samplings were performed using well tested methods (Lombardi & Reimer; 1990; Bertrami et al., 1990; Hutchinson and Livingston, 1993; Matthias et al., 1980).

2.1 Soil-gases

Soil gas samples are collected from shallow point sources. The soil-gas survey is generally carried out in the summer during a period of stable meteorological conditions. A 1m hollow steel probe with a conic point at the bottom and a sampling port on top is inserted to a depth of 0.5m below the ground surface. Two 50 cc samples of soil gas are extracted with a syringe for cleaning the probe, then a soil-gas sample is extracted and stored in an evacuated 25 ml steel cylinder for laboratory analysis (He, H₂, O₂, N₂, CO₂, CH₄ and H₂S) by means of a *Perkin-Elmer AutoSystem XL* gas chromatograph.

Furthermore, soil-gas flux measurements have been performed in situ by means of an accumulation chamber (volume: 50 litres) set on the ground in such a way as to eliminate the input of atmospheric air. Every five minutes a gas sample is extracted from an external septum located on the top of the chamber and analysed in loco using a portable gas chromatograph. These measurements result in an accumulation curve which can be used to calculate soil gas flux.

2.2 Dissolved gases in water

The method used is based on the partitioning equilibrium of gases between liquid and gas phases. It is possible to derive the initial concentrations of the gases dissolved in the liquid phase from concentrations

in the gas phase, using the partitioning coefficients of the different species (Capasso & Inguaggiato, 1998). Samples are collected in glass flasks sealed with gas-tight rubber/teflon plugs. In the laboratory, 10 cc of pure argon are injected into the flask drawing out the equivalent water volume through a needle, thus leaving the apparatus at atmospheric pressure. Since dissolved gases can be under or over saturated in natural water samples it is necessary to restore atmospheric pressure inside the flask before extraction. This is obtained by adding or removing a few ml of water by connecting the flask upside down to a tube filled with water open to the atmosphere. After restoring the sample to standard conditions (25°C, 1 atm) and shaking it for 5 min, a portion of gas is drawn for gas chromatography analysis by means of a *Perkin-Elmer AutoSystem XL* gas chromatograph.

2.3 Submarine fluid sampling

To collect gas samples a plastic funnel (30 cm diameter) is placed (with a 12 kg ballast around the lower ring) on the gas vent. Then the funnel is connected to a glass flask filled with air at a pressure which is greater than the expected hydrostatic pressure to prevent sea water from entering the sample. This system allows one to change flasks underwater in order to collect multiple samples for each vent. The same device is also used to collect gas samples in NaOH-filled flasks. In this case the external section of the flask valve is filled with distilled water to avoid sea water contamination. A traditional glass sampler, filled with water collected close to the vent, is used for dissolved gas. In regards to hot water sampling from underwater springs, the main difficulty is due to the low water flux. In order to avoid seawater contamination, a evacuated glass flask connected to a steel hose is used. Once the hose is fixed in the spring outlet, a 60 cl syringe connected by a 3 way valve, is used to expel the seawater from the hose and then fill the evacuated flask with only the geothermal water. In this case, seawater contamination is as low as reasonably achievable.

3. GEOLOGICAL SETTINGS OF STUDIED AREAS

Three Italian sites are considered here to show different geological scenarios with natural CO₂ gas accumulations and emissions. Both the Panarea (Aeolian islands, Southern Italy) and Solfatara (Phlegraean fields, Southern Italy) areas are characterised by volcanic activity, whilst the Telesse area hosts one of the most seismically active segments of the southern Apennine belt.

3.1 Panarea island (Aeolian islands, Southern Italy)

Panarea Island belongs to the Aeolian Arc, a volcanic structure extending for about 200 km along the north-western side of the Calabro-Peloritano block. This is a fragment of the Hercynian-Alpine orogenic belt (consisting of various types of metamorphic, sedimentary and intrusive rocks) that detached from the Corsica-Sardinia block and migrated south-eastward to its present position during the opening of the Tyrrhenian Sea. The exposed volcanic activity took place entirely during the Quaternary, from about 400 ka to the present (Gillot, 1987). The distribution of volcanoes is strongly controlled by regional fault systems which are oriented E-W, NW-SE and NE-SW. Seismic studies reveal a crust of about 20-25 km beneath the Aeolian arc (Gasparini et al., 1982; Barca and Ventura, 1991, and references therein) which indicates mantle upwelling.

The volcano of Panarea is a cone shaped edifice, rising from a depth of 1700-1200 m below sea level up to 421 m above sea level; its maximum diameter is about 20 km (Gabbianelli et al., 1993). The emergent rocks form the main island of Panarea and a number of islets. The submerged summit of the volcano is characterised by a broad and almost flat surface covering about 50 km² at an average depth of 100-150 m below sea level.

3.2 The Solfatara area (Phlegraean fields, Southern Italy)

The ancient Romans were aware of the Solfatara of Pozzuoli (located near the centre of the Phlegraean caldera) since Imperial times. Strabone (66 B.C. -24 A.C.) gives the most ancient written testimony, indicating it in his work "Strabonis geographica" with the name "*Forum Vulcani*", which means dwelling of the god Vulcano, entrance to Hades. The Solfatara is a sub-circular depression with a 12 km diameter. It originated about 35 ka BP after the eruption of the Campanian Ignimbrite (Rosi et al., 1984). The Phlegraean Fields magmatic system is still active, as the last eruption occurred in 1538 A.D. at Monte Nuovo. Faults affecting the Phlegraean Fields caldera follow two preferred strikes, NW-SE and NE-SW, that also affect the Campanian Plain and the inner sectors of the Apennine belt (Hyppolite et al., 1994; Orsi et al., 1996). The most impressive thermal manifestations (including fumaroles, mud pools and vigorously boiling pools) are located in the Solfatara area. The *Bocca Grande* (Large Mouth) is the name of the main fumarole and it has water vapour temperatures reaching approximately 160°C. Within the mouth, the vapour condensate contains salts such as realgar (AsS), cinnabar (HgS) and arsenic sulphide (As₂S₃) which give a yellow-reddish colour to the surrounding rocks. In the

middle of the Solfatara area a bubbling mud pit (called “La Fangaia”) is made up of rainwater and vapour condensation.

3.2.1 Bradyseism phenomenon in the Solfatara area

From 1969-72 and 1982-84 the inhabitants of the Phlegraean area, and Pozzuoli in particular, were witness to and victims of a phenomenon where the earth's surface rose; within a few months the ground level rose by 3.5 metres. This phenomenon is called *bradyseism*, which is literally a slow movement of the earth's surface as opposed to the fast movement due to an earthquake. Deformation connected with bradyseism is due to chemical and physical variations linked to the evolution of the volcanic system in the Phlegraean Fields; this produces an increase in temperature and pressure in the rock above the magma chamber. The increase in pressure translates into a variation in stresses in the rock which leads to the characteristic lifting of the ground surface. The place which shows the best evidence of Phlegraean bradyseism over the centuries is the *macellum* (a market of Roman period, better known as the *Temple of Serapide*) situated close to the port of Pozzuoli (Fig. 1). On the columns of this building there are holes made by lithodomes (sea mollusks living in coastal areas between high and low tide line) which provide evidence of the variations in ground level relative to sea level from the IV century A.D. onwards.



Figure 1. The “Macellum” (Temple of Serapide) within the Phlegraean Fields: at the left a view during the 1960’s showing that the area was below sea level. At the right, the same site today. Remains of the ancient buildings provide evidence of the ground level variations due to bradyseism thanks to holes made by lithodomes, sea mollusks living between high and low tide line.

3.3 The Telesse area (Southern Italy)

The studied area belongs to the Sannio-Matese zone, one of the most active seismic regions of the southern Apennines, where destructive

earthquakes have occurred several times in the past. At the present, the area is characterised by low-energy sequences ($M_{dmax} = 4.1$) but not much is known about the tectonic structures responsible for such seismicity (Vilardo et al., 2003). The Sannio-Matese area is located in the frontal portion of the Apennine fold and thrust belts, at the junction between the northern and southern subsidiary arcs. At this location different tectonic styles are superimposed as a result of Neogene and Quaternary thrust, strike-slip and extensional tectonics (Di Bucci, 1995; Corrado et al., 1997). Two geological units characterise the Sannio-Matese area:

1. the Molise Unit having highly variable structural trends, ranging from E-W in the south to N-S in the north;
2. the Sannio Unit is interpreted as a rootless thrust sheet originally deposited in a deep basin area located internally alongside the Latium-Abruzzo carbonate platform (Patacca et al., 1992). According to unpublished surface and subsurface data (Corrado et al., 1998) the entire thickness of the Sannio Unit is estimated to be about 3500 m.

Carbonates in this area are intensely fractured and host very important aquifers. They are locally affected by huge CO₂ and H₂S fluxes that play a very important role in defining the degree of water-rock interaction and, consequently, the final water chemistry. These gases rise along well known local and regional faults that cross the area. Moreover, near the town of Telesse, extensive outcropping travertine layers are found, testifying to past geochemical processes acting in the area. Moreover, the Telesse area is characterised by the presence of an ancient spa / hot spring tradition. The sulphur spring formed after the 1349 earthquake causing the mineral water discharge.

4. RESULTS AND DISCUSSION

4.1 Panarea island

In proximity of Panarea island (Aeolian islands, Southern Italy) a huge submarine volcanic-hydrothermal gas burst occurred during November, 2002. The high-pressure gas release created sinkholes with the collapse of the seafloor. During the first months of Panarea “activity”, some vertical logs were performed in the area characterised by gas emissions (Fig. 2) which showed the presence of convective cells containing a mixture of water and gas from the vents. Furthermore, they revealed a modification of sea water pH from 8.0 to 5.0 and Eh from +80 mV to -200 mV, probably due to the presence of H₂S in the emission points. The *STS* data logger permitted

the temperatures of the gas emission points to be measured. The data acquisition interval was one measurement per hour in order to have a correlation with sea tide fluctuations. The gas emission temperatures range from 30 to 90°C, except for the “black point” whose mean value was around 120°C.

More than 100 samples (both water and gas) were collected from November 2002 to December 2004. Analyses were performed in order to determine major and minor elements, trace elements, dissolved gases in water and gases in free phase. Results suggest that the sea water was locally affected by the acidic, reducing and more saline fluids that circulated at high temperatures in the volcanic rocks.

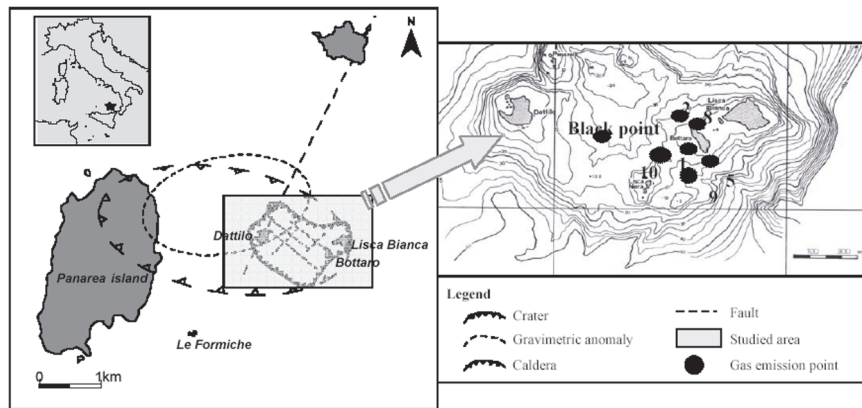


Figure 2. Panarea island location: on the right a detailed map of the studied area where gas emission points have been monitored since November 2002.

Gas samples (Tab.1) are mainly composed of carbon dioxide (98%, v/v) and methane (around 10 ppm) except for the “black point”, whose mean value is around 600 ppm.

Figure 3 shows the direct relationship between temperatures and CH₄ content in the “black point”, suggesting the thermogenic origin of the methane. Slightly elevated helium concentrations (mean value = 11 ppm) were found at every point. He isotopic analyses were performed on 32 samples in order to define its origin, with values from 4.1 to 4.5, suggesting a magmatic origin. Temporary variations of both H₂ and H₂S content have the same trend, inferring fractionation of gases by partial dissolution in water. The observed gaseous and chemical composition of the Panarea emission points is very different from that reported in the literature (Fig. 4), as data collected before November 2nd, 2002 have values typical of hydrothermal fields (represented by N₂), whilst samples collected after the

recent gaseous emission have concentrations typical of volcanic fields (high He concentrations). This data suggests an evolution of the system controlling the Panarea emissions.

Table 1. Mean values of gases emitted at Panarea island.

Gas species	Mean value
CO ₂ (vol. %)	98
CH ₄ (ppm)	10
N ₂ (vol. %)	0.4
He (ppm)	11
H ₂ (ppm)	1100
H ₂ S (vol. %)	2.2

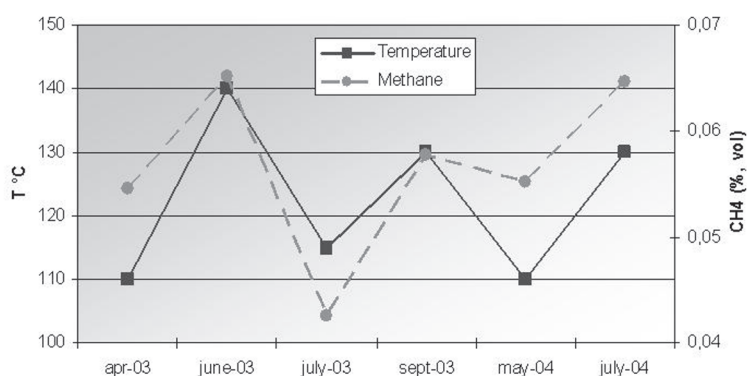


Figure 3. Comparison between methane (% v/v) and temperature variations (°C) at the “black point” (Panarea island). The observed direct relationship infers a thermogenic origin of the methane gas.

4.2 The Solfatara area

The Solfatara area has been characterized by intense and diffuse fumarolic and hydrothermal activity since Roman times. The area was investigated by means of a detailed soil-gas survey in the inter crater sector, during which 32 soil gas flux measurements (1 sample/100 m) were carried out using an accumulation chamber and a portable gas-chromatograph. Φ_{CO_2} is typically 1127.32 gr/m²*d, although the highest flux values were found in the “La fangaia” and near the “Bocca Grande” and “Bocca Nuova” fumaroles. These fumaroles have the highest outlet temperatures (145°-165°C) amongst the several fumaroles present in the area (mean discharge temperature = 100°C). Fumarole effluents have similar chemistry, with H₂O as the main component, followed by CO₂ and H₂S (Chiodini et al., 2001).

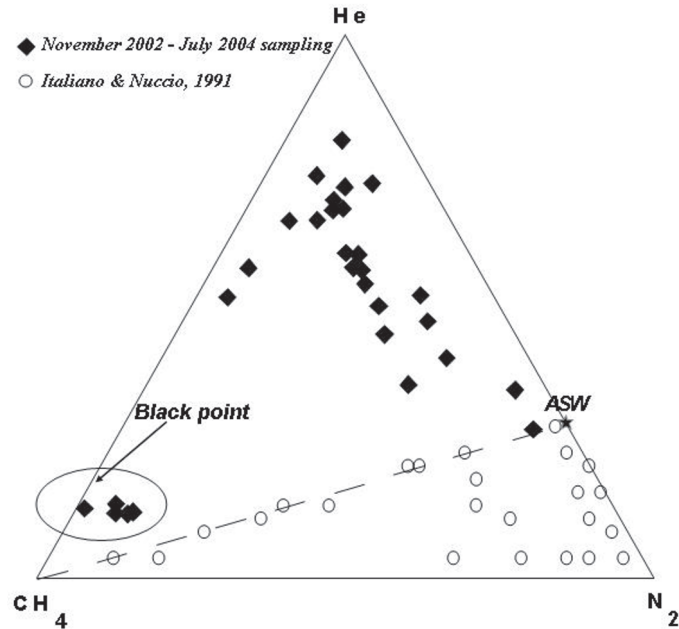


Figure 4. Ternary diagram (N₂-He-CH₄) for gas samples at Panarea island. Data from the literature (white dots, Italiano & Nuccio, 1991) have values typical of hydrothermal fields, whilst samples collected from November 2002 to December 2004 have concentrations typical of volcanic field suggesting an evolution of the system controlling Panarea emissions.

Based on their stable isotopes, the fumarole fluids were interpreted as magmatic fluids which are variably contaminated by metamorphic and meteoric components (Panichi & Volpi, 1999; Allard et al., 1991b). On the basis of outlet temperatures and the content of H₂O, CO₂ and of un-reactive gases (i.e., Ar, N₂ and He) from fumarole fluids it was possible to estimate the flux of steam and thereby the heat flux involved in the diffusive degassing process. Chiodini et al. (2001) calculated that the entire Solfatara area releases 1500 t/d of hydrothermal CO₂ through diffusive degassing. The contour map (Fig. 5) shows an area of about 0.5 km² of high Φ_{CO_2} values representing an important diffuse degassing structure crossed by a NW-SE band of low fluxes. The highest Φ_{CO_2} values overlap with faults and fractures, confirming that the degassing process is strictly related to tectonic structures. In fact, the area is characterised by a regional extensional tectonic feature and by transverse structures considered as transfer faults along which the main regional volcanoes are located (Acocella *et al.*, 1999).

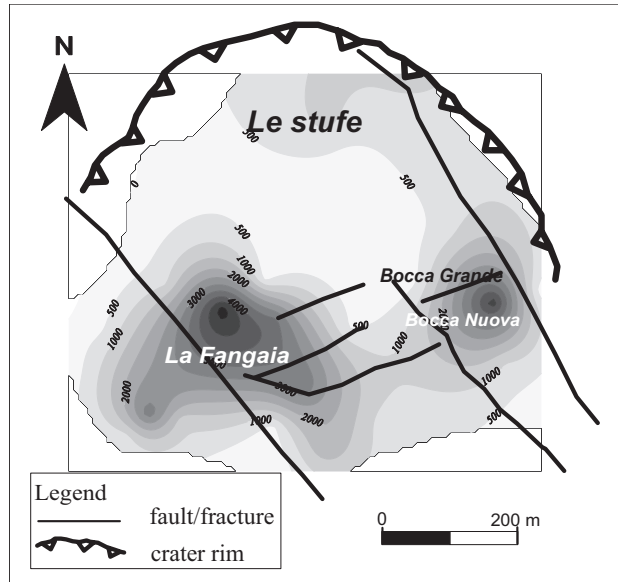


Figure 5. CO₂ flux contour map of the inter crater sector of the Solfatara area. Highest Φ_{CO_2} values overlap faults and fractures confirming that the degassing process is strictly related to tectonic structures.

4.3 The Telesse area

The Telesse area is one of the most seismically active segments of the southern Apennine chain. Several destructive earthquakes ($M = 7$) struck the area and surroundings in the past centuries. The last energetic seismic sequence (2800 events) occurred in October 1997 ($M_{\text{dmax}} 4.1$) a few km away from the Telesse area, during which a first geochemical survey was performed. The survey was repeated in May 1998 during a quiescent period. A total of 82 water samples were collected in order to understand the main water-rock interaction processes and the possible influence of the stress field on water chemistry. Results indicated two main chemical families, Na-HCO₃ and Ca-HCO₃ waters, characterised by different salinities. These types of waters reflect the complexity of the geochemical processes occurring in a geological environment that is made up mainly of outcropping Mesozoic platform carbonates (locally with dolomite), covered by sedimentary layers (clays, marls and sands) and the occurrence of a volcanic complex made up primarily by ignimbrites.

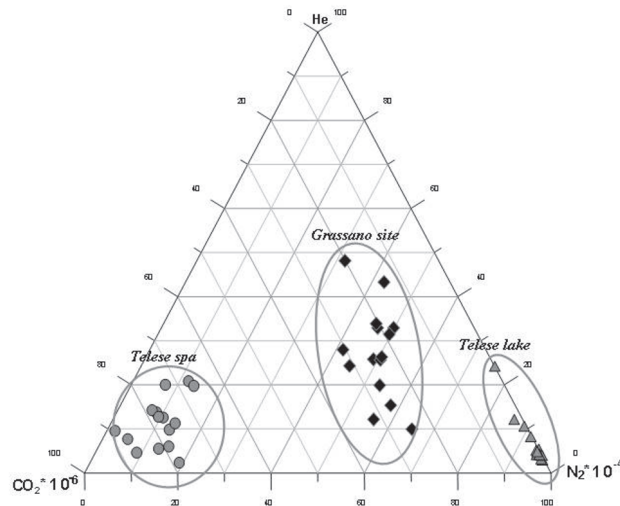


Figure 6. Ternary diagram N_2 -He- CO_2 . The three sampled aquifers have different chemical compositions. It is clearly evident the CO_2 enrichment of the Telesse spa in comparison with the Telesse lake samples (shallow aquifer composition) and those of the Grassano river (representing the intermediate aquifer).

On the basis of these first results, three sites representing three different geochemical environments (that is, three different aquifers, Fig. 6) were chosen for monthly geochemical monitoring:

- the Diana spring (Telesse spa) is a mineralised (2000-2500 $\mu S/cm$), acidic (pH = 6.1) and ipo-thermal (about 20°C, constant all over the year) water having a Ca- HCO_3 chemistry. Water chemical analyses revealed the presence of a high CO_2 content (more than 90%, v/v) in the groundwater. Isotopic analysis of total carbon ($\delta^{13}C = +0.4\text{‰}$) revealed a deep origin probably due to the presence of a cooling magmatic intrusion within the carbonate basement. Helium isotope ratios ($R/Ra = 2$) strongly support this hypothesis. Due to its geochemical features, the Diana spring represents the end-member of the deep aquifer.
- the Grassano spring is located a few kilometres from the town of Telesse. It is a medium-mineral water (800 $\mu S/cm$) with a temperature of 11.5°C, a near-neutral pH and a Ca- HCO_3 chemistry. Its geochemical characteristics are typical of a relatively long residence time in the hydrologic circuit with non negligible water-rock interaction processes with carbonates. The discharge is fed by local meteoric waters that only partially receive the deep inputs. Due to its characteristics and considering the other two analysed springs, the Grassano spring is considered the end-member of the intermediate aquifer.

- the Telese Lake is a small, 17 m deep lake located about 1 km away from the town of Telese; the water has a medium-low value of salinity (TDS = 0.3 g/l), an alkaline pH (8.0-8.5) and a Ca-HCO₃ chemistry. Water temperature, at the surface, is linked to seasonal variations, ranging from 6°C in the winter up to 25°C or more during the summer. All reported chemical features, together with a dissolved gas content very similar to ASW (Air Saturated Water), define this water as a shallow one without deep input. For these reason, this represents the shallowest hydrologic circuit presently discharging in the studied area.

Several studies on the monitoring of gas content in waters for seismic prediction suggest that during phases preceding or following seismic energy release rocks undergo physical-structural variations which favour the mobilization of deep fluids, such as CO₂ and H₂ (Wakita et al., 1985; Honda et al., 1982; Lombardi, 1981). In view of these researches, monthly water sampling in the Telese area and surroundings have the primary goal to detect eventual relationships between seismic activity and chemical/geochemical variations in the aquifers. In figure 7 results from the Diana spring (Telese spa) monitoring (April 2003-October 2004) are reported. The graph clearly highlights the different behaviour of dissolved CO₂ in comparison with dissolved H₂ observed during the sampling.

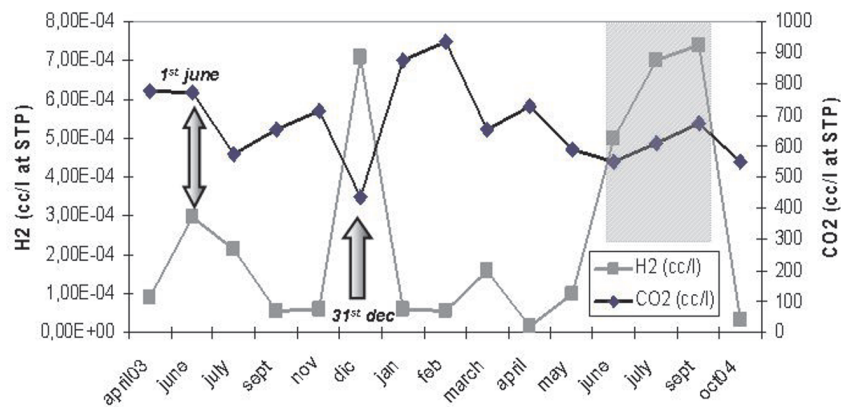


Figure 7. H₂ versus CO₂ content at the Telese spa (Diana spring). It is interesting to note that in correspondence with earthquakes (the two arrows) H₂ and CO₂ contents change. The shaded rectangle indicates a three-month period of small earthquakes during which the H₂ and CO₂ contents undergo a slight increase.

The two arrows in the graph indicate the correspondence between earthquakes and H₂ and CO₂ content trends. The June survey was performed

17 days after an earthquake ($M_d = 4.1$) occurred in the adjacent Molise region, at a distance of about 70 km from Telesse. Another earthquake ($M_d = 4.2$) occurred on December, 16th, 2003 in the same area. A geochemical survey was performed 15 days before this earthquake. During June-September 2004, a sequence of small earthquakes ($M_{max} = 4.1$) in an area just 100 km away from the studied sites took place. During the same period an increase of both dissolved H_2 and CO_2 content was observed (Fig. 7, shaded rectangle). It is worth noting that in the period January-May 2004 no earthquakes with $M \geq 4.0$ occurred within 100 km from the Telesse area (INGV, 2004) and, in the same period, dissolved H_2 has an almost constant trend.

5. CONCLUSIONS

The main purpose of this paper is to show some results from areas characterised by natural accumulations and emissions of CO_2 . These areas represent interesting natural analogues for the study and prediction of the possible consequences of leakage from geological sequestration sites of anthropogenic CO_2 (i.e., the return to surface, potentially causing localised environmental problems).

Three Italian sites, representing different geological scenarios, were described. All these sites are linked to migration towards the surface of significant quantities of carbon dioxide. In particular, two of these sites are densely populated but people have learned to live with CO_2 gas emissions since ancient Roman times and, for this reason, they have even tried to exploit them. Nowadays the above mentioned areas are constantly monitored in order to study the temporal evolution of different phenomena. In particular, the aim of our research is to evaluate and mitigate risks for local populations, taking into account several factors controlling CO_2 emissions and studying the gas behaviour in time and space. To date, the obtained results suggest that gas uprising is generally well localised around restricted areas, often controlled by local tectonics (faults and/or fractures). This implies that, in the frame of geological CO_2 sequestration, it is necessary to carefully assess the presence of pathways (fault and/or fractures) that might allow the migration of CO_2 out of the reservoir.

REFERENCES

- Acocella, V., Salvini, F., Funicello, R., and Faccenna, C., 1999, The role of transfer structures on volcanic activity at Campi Flegrei (Southern Italy), *J. Volcan. Geotherm. Res.*, **91**:123-139.
- Allard, P., Carbonelle, J., Dajlevic, D., Le Bronec, J., Morel, P., Robe, M. C., Maurenas J.M., Faivre-Pierret R., Martin D., Sabroux J.C., and Zettwoog P., 1991a, Eruptive and diffusive emissions of CO₂ from Mount Etna, *Nature*, **351**:387-391.
- Allard, P., Maiorani, A., Tedesco, D., Corceci, G., and Turi, B., 1991b, Isotopic study of the origin of sulphur and carbon in Solfatara fumaroles, Campi Flegrei caldera, *J. Volcanol. Geotherm. Res.*, **48**:139-159.
- Barca, D., and Ventura, G., 1991, Evoluzione vulcano-tettonica dell'isola di Salina (Arcipelago delle Eolie), *Mem. Soc. Geol. Ital.*, **47**:401-415.
- Baubron, J. C., Allard, P., and Toutain, J. P., 1990, Diffusive volcanic emissions of carbon dioxide from Vulcano Island, Italy, *Nature*, **344**:51-53.
- Bertrami, R., Buonasorte, G., Ceccarelli, A., Lombardi, S., Pieri, S., and Scandiffio, G., 1990, Soil Gases in Geothermal Prospecting: Two Case Histories (Sabatini Volcanoes and Alban Hills, Latium, Central Italy), *J. Geoph. Res.*, **9**:21,475-21,481.
- Capasso, G., and Inguaggiato, S., 1998, A simple method for the determination of dissolved gases in natural waters: An application to thermal waters from Vulcano Island, *Applied Geochemistry*, **13**(5):631-642.
- Chiodini, G., Cioni, R., Guidi, M., Raco, B., and Marini, L., 1998, Soil CO₂ flux measurements in volcanic and geothermal areas, *Applied Geochemistry*, **13**(5):543-552.
- Chiodini, G., Frondini, F., Cardellini, C., Granirei, D., Marini, L., and Ventura, G., 2001, CO₂ degassing and energy release at Solfatara volcano, Campi Flegrei, Italy. *J. Geoph. Res.*, **106**(8):16216-16221.
- Corrado, S., Di Bucci, D., Naso, G., and Butler, R. W. H., 1997, Thrusting and strike-slip tectonics in the Alto Molise region (Italy): implications for the Neogene-Quaternary evolution of the Central Apennine Orogenic System, *J. Geol. Soc. London*, **154**:679-688.
- Corrado, S., Di Bucci, D., Naso, G., Giampaolo, C., and Adatte, T., 1998, Application of the organic matter and clay mineral studies to the tectonic history of the Abruzzo-Molise-Sannio area, Central Apennines, Italy, *Tectonophysics*, **285**:167-181.
- de Jong, E., and Schappert, H. J. V., 1972, Calculation of soil respiration and activity from CO₂ profiles in the soil, *Soil Science*, pp. 328-333.
- Di Bucci, D., 1995, Rapporti tra piattaforme carbonatiche e "Alloctono" lungo la media valle del Sangro, *Mem. Soc. Geol. Ital.*, **114**:443-463.
- Gabbianelli, G., Romagnoli, C., Rossi, P.L., and Calanchi, N., 1993, Marine geology of the Panarea-Stromboli area (Aeolian Arcipelago, Southeastern Tyrrhenian Sea). *Acta Volcanol.*, **3**:11-20.
- Gasparini, P., Iannaccone, G., Scandone, P., and Scarpa, R., 1982, The seismotectonic of the Calabrian Arc. *Tectonophysics*, **84**:267-287.
- Gillot, P. Y., 1987, Histoire volcanique des Iles Eoliennes: Arc insulaire ou complexe orogénique anulaire ?, *D. T. IGAL 11*, 35-42.
- Gurrieri, S., and Valenza, M., 1988, Gas transport in natural porous mediums: a method for measuring CO₂ flows from the ground in volcanic and geothermal areas, *Rend. Soc. Ital. Mineral. Petrologia*, **43**:1151-1158.
- Honda, M., Kurita, K., Hamano, Y., and Ozima, M., 1982, Experimental studies of He and Ar degassing during rock fracturing, *Earth Planet. Sci. Lett.*, **51**:206-214.

- Hutchinson, G. L., and Livingston, G. P., 1993, Use of chamber systems to measure trace gas fluxes, *American Society of Agronomy*, special publication, **55**.
- Hypolite, J., Angelier, J., and Roure, F., 1994, A major change revealed by quaternary stress patterns in the Southern Apennines, *Tectonophysics*, **230**:199-210.
- INGV (2004) – Seismological report
- Italiano, F., and Nuccio, P. M., 1991, Geochemical investigations of submarine volcanic exhalations to the east of Panarea, Aeolian Islands, Italy, *J. Volcan. Geoth. Res.*, **46**(1-2):1-185.
- Kanemasu, E. T., Powers, W. L., and Sij, J. W., 1974, Field chamber measurements of CO₂ flux from soil surface, *Soil Science*, **118**(4):233-237.
- Lombardi, S., 1981, Variazione del tenore in elio in alcune manifestazioni sorgive e gassose della valle del Sele nel periodo immediatamente successivo all'evento sismico del 23/11/1980, *Rend. Soc. Geol. Ital.*, **4**.
- Lombardi, S., and Reimer, G. M., 1990, Radon and Helium in soil gases in the Phlegrean fields, central Italy, *Geoph. Res. Let.*, **17**(6):849-852.
- Matthias, A. D., Blackmer, A. M., and Bremner, J. M., 1980, A simple chamber technique for field measurements of emissions of nitrous oxide from soils, *J. Envir. Qual.*, **9**(2): 251-256.
- Orsi, G., De Vita, S., and Di Vito, M., 1996, The restless, resurgent Campi Flegrei nested caldera (Italy): constrains on its evolution and configuration, *J. Volcanol. Geotherm. Res.*, **74**:179-214.
- Panichi, C., and Volpi, G., 1999, Hydrogen, oxygen and carbon isotope ratios of Solfatara fumaroles (Phlegrean Fields, Italy): further insight into source processes, *J. Volcanol. Geotherm. Res.*, **91**:321-328.
- Patacca, E., Scandone, P., Bellatalla, M., Perilli, N., and Santini, U., 1992, The Numidian-sand event in the Southern Apennines, *Mem. Soc. Geol. Padova*, **43**:297-337.
- Rosi, M., and Santacroce, R., 1984, Volcanic hazard assessment in the Phlegrean Fields: a contribution based on stratigraphic and hystorical data, *Bull. Volcanol.*, **47**:359-370.
- Scheidegger, A. E., 1974, The physics of flow through porous media, University of Toronto Press, Toronto, 353p.
- Vilardo, G., Nappi, R., Petti, P., and Ventura, G., 2003, Fault geometries from the space distribution of the 1990-1997 Sannio-Benevento earthquakes: interferences on the active deformation in Southern Apennines, *Tectonophysics*, **363**:259-271.
- Wakita, H., Nakamura, Y., and Sano, Y., 1985, Groundwater radon variations reflecting changes in regional stress field, *Earthq. Predict. Res.*, **3**:545-557.