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Soil gas geochemistry: significance and application in geological prospectings

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1. Introduction

Gas geochemistry has been proven to be a reliable and simple technique to apply, at different scales, to many geological scenarios (Annunziatellis et al., 2003; Lewicki et al., 2003; Baubron et al., 2002; De Gregorio et al., 2002; Ciotoli et al., 1998; Ciotoli et al., 1999; Lombardi et al., 1996; Hickman et al., 1995; Duddridge et al., 1991; Durrance and Gregory, 1988; Eremeev et al., 1973). The importance of fluid geochemistry is rooted in the fact that the Earth is an open system and that fluid-releasing crustal phenomena are the major means for the exchange of matter and energy at different depths. As such, fluid-releasing channels like active faults and fractures are actually a ''window'' on subterranean physical and chemical variations (Ciotoli et al., 2007).

The study of spatial distribution of soil gas anomalies at the surface, can give important and interesting information on the origin and processes involving deep and superficial gas species. This information can be applied and studied in different frameworks, for example:

I) seismic zonation, examining, at the surface, anomalous concentrations of deep gas species that upraise throughout preferential pathways (faults and/or fractures). Soil gas distributions can be directly linked to the evolution of the stress regime and gases migrate preferentially through fractured zones but only along pathways whose permeability has been enhanced by seismic activity and/or through areas of brittle deformation.

II) Environmental protection, such as the monitoring of naturally occurring toxic gases to highlight zones with high health risks for humans. The presence of magmatic chambers can cause an accumulation of gases in the subsurface and local structural features can favour high degassing phenomena. These events are particularly dangerous in populated areas and it is necessary to build risk maps to define the potential health hazard in terms of both short-term and long-term risk.

III) Radionuclide migration, both in the pollution assessment from abandoned uranium mines and in the study of high-level radioactive-waste isolation systems. The main approach is to study the natural migration of radiogenic particles or elements throughout clay formations that are considered an excellent isolation and sealing material due to their ability to immobilize water and other substance over geological timescales. The evaluation of long-term behaviour of clays under normal and extreme conditions is still the main topic in questions relating the role of clays as geological barrier for the permanent isolation of long-lived toxic residues.

Soil gas distribution would be affected by surface features such as pedological, biogenic and meteorological factors: these are supposed to have only a subordinate effect on gas leakage (Hinkle, 1994). However, it is possible to properly interpret soil gas anomalies and recognize influences of surface features studying the association of different gases (having different origin and physical/chemical behaviour), collecting a large number of samples during periods of stable meteorological and soil moisture conditions (e.g., during dry season) and using appropriate statistical treatment of data (experimental variograms to investigate the spatial dependency of gas concentrations).

Soil gas geochemistry involves the study of many gaseous species (radiogenic, trace and diagenetic gases); each of them can give specific information on the conditions that allow their formation, accumulation and/or migration.

Field data can show the usefulness of the soil gas method for detecting, for instance, crustal discontinuities even when faults are buried or cut non-cohesive clastic rocks which makes surface recognition difficult using traditional field methods (Ciotoli et al., 1998; Lombardi et al., 1996; Duddridge et al., 1991; Durrance & Gregory, 1988). These characteristics as well as the rapidity and the low cost of the soil gas survey, make this method a powerful tool for geological investigation which can significantly contribute to hazard assessment and forecasting, especially when continuous monitoring is performed (Klusman, 1993; Reimer, 1990; King et al., 1996; Sugisaki, 1983).

In this chapter, we outline the results from two soil gases: radon, a radiogenic trace gas, and carbon dioxide, which generally acts as carrier for trace gases. We will show data obtained in either prospecting or monitoring case studies.

2. Radon and Carbon Dioxide origin and behaviour

Radon (^{222}Rn) is a rare gas and is probably the gas used the most frequently for mapping and predicting purposes. ^{222}Rn is a naturally occurring radioactive daughter product of the uranium decay chain, with a short half-life (3.8 days). In the geologic environment, it displays a poor intrinsic mobility (Tanner, 1964; Dubois et al., 1995). In diffusive systems, due to its low mobility and its short half-life, radon obviously comes from a short distance below the measuring instrument. Information of a deep origin, however, is expected to be noticed when Rn of a subsurficial origin is extracted by a rising gas/water column. In this latter case, radon being incorporated in the fluid during the last steps of the process, can be used as a tracer, acting as a relative flow meter and velocity meter of the bulk fluid. It gives therefore information about both the steady state conditions and disequilibrium features of a global reservoir, which can be a hydrothermal cell, possibly magma-generated (Pinault & Baubron, 1996). Soil radon activities analyzed in surface conditions depend upon the following main factors: the emanating power of the rock and soil (Morawska & Phillips, 1993), the permeability of the host rock and the flow of the carrying gas (Ball et al., 1991). Generally, radon activities increase with increasing flows (because the gas velocity increases, causing both less time for decay and more extraction). For higher flows, however, dilution of radon by the flux may occur with a subsequent decrease of radon activities measured at the surface.

All these features allow radon to be used as a tool for mapping and determining characteristics of hydrothermal systems (D'Amore et al., 1978; Cox, 1980; Etiope & Lombardi, 1995), for fault detection in volcanic terrains (Crenshaw et al., 1982; Aubert & Baubron, 1988; Baubron et al., 1991), for uranium exploration (Fleischer et al., 1972; Klusman, 1993; Wattananikorn et al., 1995; Charlet et al., 1995) and for groundwater flow characterization (Gascoyne et al., 1993). ^{222}Rn monitoring has long been used for both earthquake (King, 1978; Fleischer & Magro-Campero, 1985; Segovia et al., 1989; Shapiro et al., 1989; Woith et al., 1991) and volcanic prediction purposes (Cox et al., 1980; Del Pezzo et al., 1981; Thomas et al., 1986; Thomas, 1988; Toutain et al., 1992).

Carbon dioxide (CO_2) is the most abundant gas species in hydrothermal to volcanic environments. Kerrick et al. (1995) calculated that non-volcanic CO_2 emissions from high heat flow areas may substantially contribute to the balance of the carbon cycle. Natural discharges of CO_2 have several sources: the mantle, metamorphism of carbonate-bearing rocks, decomposition of organic material and surface biological activity (Irwin & Barnes, 1980). Generally, carbon dioxide in fault zones is a mixture of some of these sources (Sugisaki, 1983). High CO_2 fluxes appear correlated with both high heat flux areas (associated with active and ancient volcanism) and limited areas with deep fracturing (emitting carbon originated from the mantle and from decarbonation processes, with possible mixing of these two sources). Irwin & Barnes (1980) suggested that discharges of CO_2 might indicate areas with high pore pressure at depth, and therefore may serve to identify potential seismic regions. CO_2 is used for fault mapping (Irwin & Barnes, 1980; (Sugisaki et al., 1980; Sugisaki, 1983; Baubron et al., 1990, 1991) as well as for both seismic and volcanic monitoring (Shapiro et al., 1982; Toutain et al., 1992; Rahn et al., 1996).

3. Sampling and analytical procedures

Soil gas surveys can be performed at both regional (e.g., sampling grid: 1 sample/km^2) and local scale (detailed sampling grid including profiles and/or transects) on the basis of the goal of the research. The surveys should be performed during summer or dry periods to avoid climatic factors which may affect soil gas values (Hinkle, 1994).

Shallow soil gas samples are obtained using a 1 m stainless steel probe fitted with a brass valve: this system enables soil gas to be collected and stored in metallic containers (with a vacuum 10^{-2} atm) for laboratory analysis or to be pumped for on-site Rn analysis.

Radon determination is accomplished in the field with an EDA Instrument RDA-200 Radon Detector.

Generally, the studied gases include major (N_2, O_2, CO_2) and trace (^{4}He, H_2) gases and light hydrocarbons (C_1 to C_4). The determination of helium is performed with a Varian Instrument Mass 4 spectrometer. N_2, O_2, CO_2 and light hydrocarbons concentrations are analyzed using a Fison Instrument GC-8000 Series gas-chromatograph. The used detectors are: Thermal Conductivity Detector (TCD) for N_2, O_2 and CO_2 in order to achieve sensitivity up to percentage and Flame Ionization Detector (FID) for light hydrocarbons with a sensitivity of an order of 0.2 ppm.

A specific technique has been developed to collect submarine samples (Caramanna et al., 2005) in proximity of gas vents. In order to collect free/dry gas samples, a plastic funnel is inverted (30 cm diameter with 12 kg ballast around the lower ring) and placed precisely on the gas vent to be sampled. All of the samplers are stored in a plastic box that is carried underwater by the divers. The funnel is connected, through a silicon hose, to a Pyrex glass flask with twin valves. This flask is pre-filled with air at a pressure above that of the hydrostatic pressure expected at the sampling depth in order to stop seawater from entering the sampler. Afterwards, collected gas samples are analysed at the laboratory.

4. Results

Results from different geological scenarios are presented highlighting the usefulness of the method in geochemical exploration. In particular, three different topics (seismic zonation, toxic emanation and radionuclide migration) will be treated showing two examples of studies for each of them in order to give a general idea of the soil gas geochemistry applications.

4.1 Seismic zonation

Earthquakes constitute a severe source of human disasters all around the world. Consequently, short-term considerations, through the search for precursory signals, have received great attention in the last several decades. Among the techniques used for the search of precursors, geochemistry has provided some high-quality signals, since the 1960's, mainly as the result of instrumental developments. Focusing interest on geochemical anomalies linked to seismo-tectonic activity is not an unexpected development, owing to the multiple evidence of a genetic link existing between fluid flows and faulting processes (Hickman et al., 1995).

The Colpasquale area is located in the central Italian region of Marche that was devastated by a sequence of shallow earthquakes over a three month-long period (September-December, 1997). The occurrence of this catastrophic event as well as the long duration of the "seismic sequence", presented a unique opportunity to apply a study of gas migration to a zone undergoing active displacement. Soil gas surveys were performed one day, one week, one year and two years after the main shock (Ms 5.6) in this area (Lombardi & Voltattorni, 2010).

Figure 1 shows box plots used to display and compare the distribution characteristics of the Rn and CO_2 soil gases during the different surveys. The graphs indicate that the median values of radon activity (Fig. 1a) are not temporally constant, thus displaying the complex character of this gas whose leakage can vary as a function of many factors including, in particular, the variation in the stress regime. The highest median value (50.8 Bq/l) occurred during the second 1997 survey and increases again in 1999 after a very low 1998 median value. The great variability of mean values during years suggest that gas microseeps can be influenced by many factors, such as fault permeability, fracture width, an increase/decrease of grain surface and porosity, as well as grain comminution by coseismic cracks that produce active surface area and circulation pathways (Holub & Brady, 1981). Median value of CO_2 (Fig. 1b) is quite constant during the first three surveys while doubles during the last campaign.

The use of variogram surface maps has the potential to define phenomena affecting gas distribution along a specific direction (fault-related anisotropy effect). Figure 2 shows the radon variogram surface maps. During the first two surveys the distributions are isotropic, suggesting that there is no preferential direction along which the degassing phenomena occur. A slight anisotropy is evident during the third campaign (Fig. 2c), but only in the last survey is it possible to observe the maximum spatial data continuity (Fig. 2d) along a major NW-SE anisotropy axis. This orientation parallels the direction of the Apennine belt along which the main faults and earthquakes are distributed (Cocco et al., 2000).

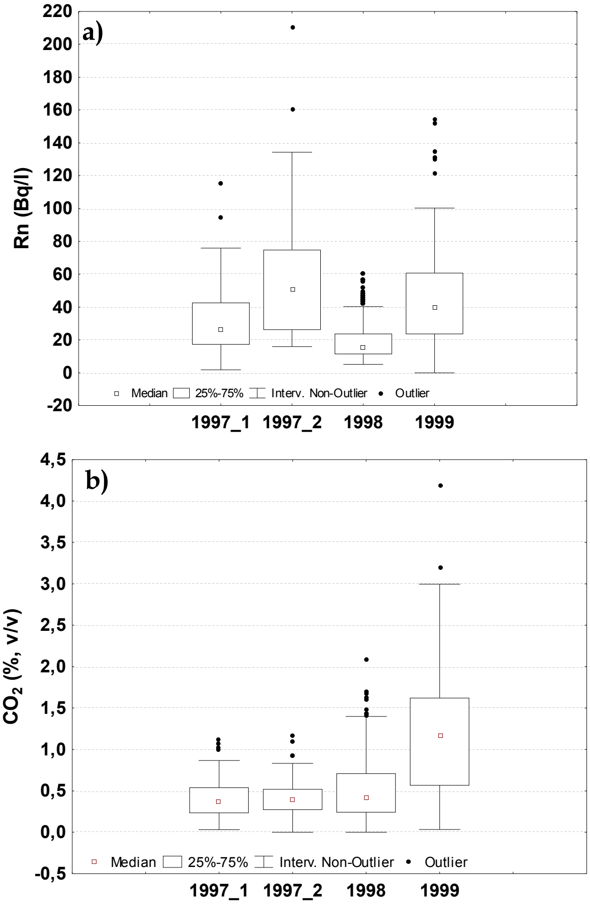

Fig. 1. Box plots of the different soil gas species (Rn and CO_2) during the four surveys at the Colpasquale area (Marche region). The plot a) highlights that Rn concentrations are not temporally constant, but rather the leakages of this gas can vary as a function of many factors, such as the variation of local stress regime.

These results suggest an "evolution" of the radon distribution, starting with an initial radon leak immediately after the first seismic event. This initial phase could have been caused by sudden degassing soon after the earthquake as the result of the opening of numerous fractures, resulting in widespread anomalies and the basic "flooding" of the local soil gas with radon. Once the earthquakes ceased some of the structures began to close and become less permeable to gas flow, allowing the system to slowly return to a state of equilibrium by dissipating the high radon concentrations into the atmosphere. However, where fractures remained open at depth, such as within inferred faults, they provided a steady but reduced flux of radon to the surface.

The CO_2 variogram surface maps (Fig. 3) also show spatial variability over the three years. The anisotropy seems to rotate clockwise from a mostly E-W direction in the first survey to a NE-SW direction in September 1999. The variogram maps imply that the shallow gas distribution may be linked to the variation of the stress regime, as the final NE-SW anisotropy is in accordance with the process of an extensional stress regime of the region (Amato et al, 1998).

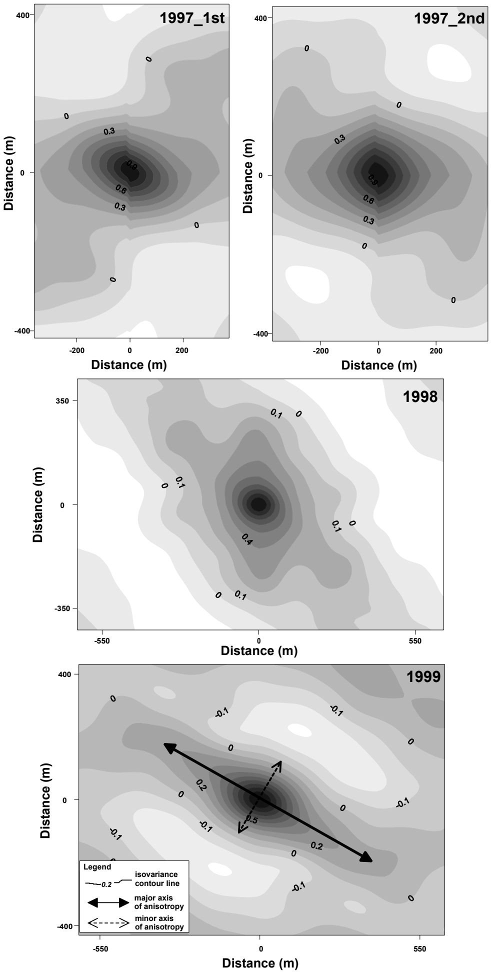

Fig. 2. Variogram surface maps of radon data from the Colpasquale area (Marche region). The first two surveys show an isotropic distribution, meaning that there is no evident preferential anomaly orientation. A slight anisotropy is evident during the third campaign, but only in the last survey it is possible to observe the maximum spatial data continuity with a major anisotropy axis oriented NW-SE.

The Fucino Basin (central Italy) is another studied area characterized by known and inferred structural discontinuities. The Fucino basin (about 250 square kilometers) is an intramontane tectonic depression located in peninsular Italy within the Apennine chain. The basin is affected by a complex fault network (Nijman, 1971; Giraudi, 1989; Blumetti et al., 1993; Galadini & Messina, 1994) due to an intense Quaternary activity whose most evident geomorphic expression are high mountain fronts. The geometry of these faults and the kinematic indicators, mainly normal or oblique slip, confirm that extensional tectonics has been mainly responsible of the evolution of the basin (Blumetti et al., 1988, 1993; Galadini & Messina, 1994)

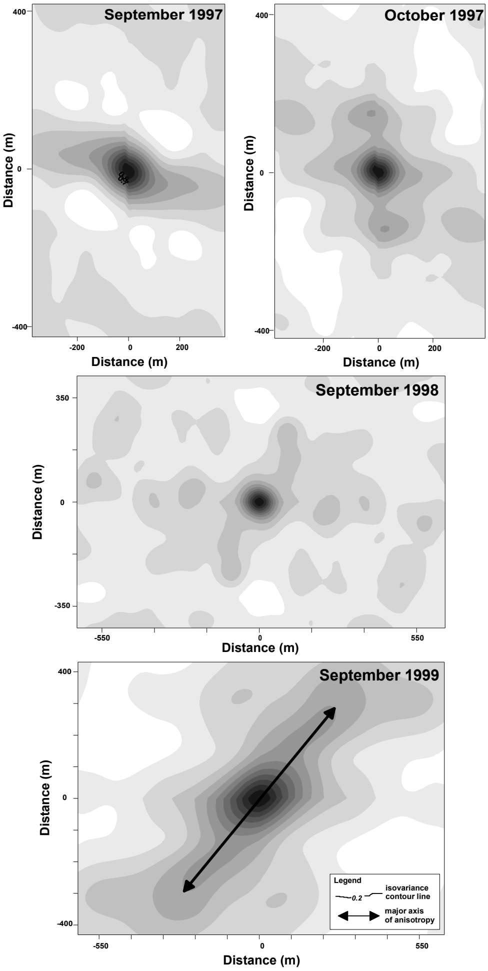

Fig. 3. Variogram surface maps of CO_2 data from the Colpasquale area (Marche region). The maps show a variability of spatial data continuity over the three years. The anisotropy seems to rotate clockwise from a mostly E-W direction at the first survey to a NE-SW direction in September 1999.

Soil gas surveys were performed in two stages: a regional sampling was carried out over the Fucino plain with a density of 4 -6 samples/km^2 (548 samples) and three transects were carried out at a more detailed scale (sample density of 10-20 samples/km^2 for transects 1 and 2, and 80-100 samples/km^2 for transect 3), crossing evident or inferred structural features in order to achieve a better definition of soil gas distribution.

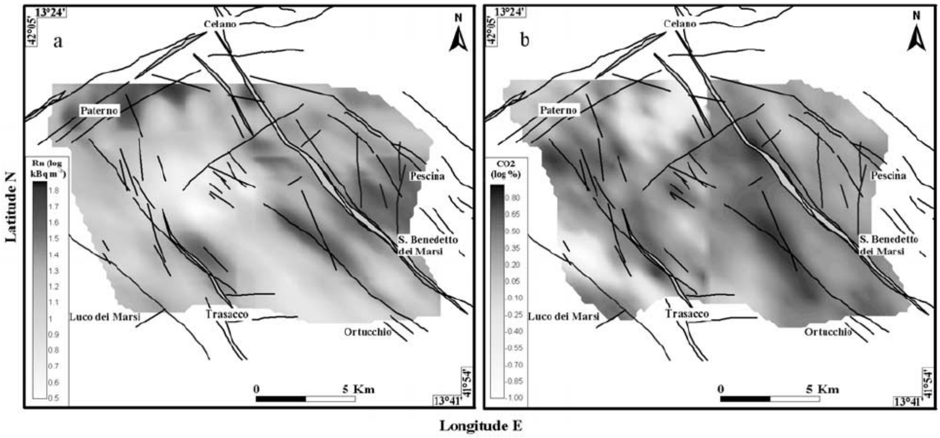

Fig. 4. Contour maps of (a) Rn and (b) CO_2 in the Fucino Plain. Radon and carbon dioxide anomalies well fit with the trend of known structural features both in the eastern and western sectors.

Results obtained from the regional survey show that radon and carbon dioxide anomalies (Figure 4) fit well with the trend of known structural features both in the eastern and western sectors, mimicking the general NW-SE fault orientation of the area.

Higher Rn and CO_2 concentrations characterize the eastern sector of the Fucino Plain where the most active/recently activated faults (OF and SBGMF) occur. The shape of the anomalies confirms the highly anisotropic behaviour and shows the spatial domain of the faults affecting the radon distribution. In the western sector, radon distributions define the southern and the northern segments of the known Trasacco Fault (TF), in agreement with structural observations (Ciotoli et al., 1998). It is quite clear that the anomalies are smeared laterally, confirming the rotation of the anisotropy axis toward the E-W direction. In this sector this phenomenon is probably linked to a more complex fault geometry (wide fracturing) associated with a shallow structural high of carbonate substratum. Furthermore, in the north-western sector of the plain very high radon anomalies clearly define the WSW-ENE ACF, as well as some associated minor Apenninic faults oriented toward the centre of the plain. The CO_2 contour map shows low values with respect to the eastern sector, but an anomalous distribution similar to that of radon. The anomalies are located in correspondence with the TF and with the minor Apenninic faults in the northwester sector of the plain. Minor CO_2 anomalies are located in the centre of the plain where fault-induced liquefaction was recognized during the 1915 Avezzano earthquake, and along a WSW-ENE buried fault.

The results from the three transects yielded anomalies with different features, reflecting the different gas-bearing properties of the eastern seismogenic faults related to the 1915 earthquake (Mb = 7.0) and the hidden structural features occurring in the western side of the plain (Ciotoli et al., 2007). All the achieved results show that gases migrate preferentially through zones of brittle deformation, by advective processes as suggested by the relatively high rate of migration needed to obtain anomalies of short-lived ^{222}Rn in the soil pores.

4.2 Toxic emanation

The sudden and catastrophic, or slow and continuous, release at surface of naturally occurring toxic gases like CO_2 and Rn poses a serious health risk to people living in geologically active regions. In general this problem receives little attention from local governments, although public concern is raised periodically when anomalous toxic gas concentrations suddenly kill humans or livestock.

An area in proximity of Panarea Island (Aeolian Islands, southern Italy) was interested by a huge submarine volcanic-hydrothermal gas burst during November, 2002. The submarine gas emissions chemically modified seawater causing a strong modification of the marine ecosystem and the death of mainly benthonic life forms and serious damage to the sea-grass Posidonia oceanic (Voltattorni et al., 2009).

Gases have been collected from the seafloor at variable depths (depending on gas emission point depth) and the chemical compositions of the submarine gas emissions have displayed a complex combination of temporal and spatial variability from November 2002 to December 2006. The temperatures of leaking fluids are variable at the different gas emission points (Fig. 5): highest temperature measurements refer to Black point ranging between 110 °C and 137 °C, excepting the first measurement (a few days after the gas burst, on November, 13, 2002) being 30 °C. Lower temperatures (mean value: 86.7 °C) have been measured at the Sink point and at Vent 8 (mean value: 52.11 °C). According to Capaccioni et al. (2007), a possible explanation for the temperature variability at the different gas emission points is related to an inferred magmatic system centred on or closer to Black point and whose diameter probably does not exceed a few hundred meters. Vents 1 and 2 have recorded the lowest values (mean values, respectively: 39.75 and 33.8 °C). Being located at the margins of the inferred magmatic system, the latter vents have probably been affected by thermal cooling in the declining stage, because of a rapid inflow of cold seawater from the surroundings.

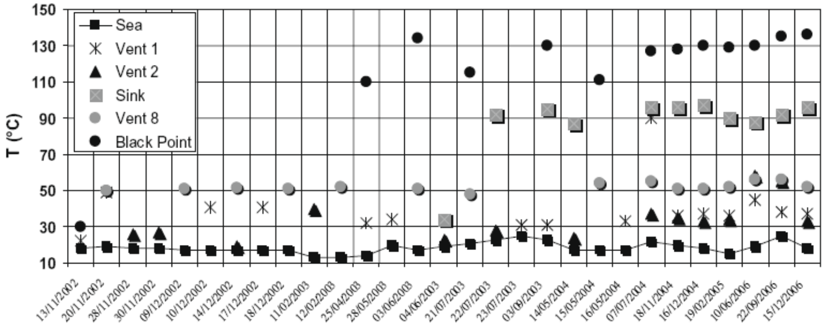

Fig. 5. *T* measurements at Panarea vents. Fluids from vents are very hot (especially from Sink and Black point with temperatures >90 °C) but due to their low flow, they do not affect temperatures of the surrounding seawater.

All of the collected gases are CO_2-dominant (the content varies from a minimum of 83.64 vol. % to a maximum of 98.43 vol. %). Fig. 6 shows a comparison of the CO_2 values from the five monitored vents through a statistical distribution (box plots). The CO_2 leakage varies at the different vents being higher at the Black point and lowest at the Sink point. However, median values are very similar for each vent suggesting a common degassing input linked to local tectonic features. In fact, all the gas emission points are located along N–S, E–W and NE–SW oriented active faults controlling the Aeolian Volcanic District. The main consequence of the presence of high levels of CO_2 in the water chemistry is a generic acidification of the sea with a reduction in pH. This phenomenon affected both the macro and the micro biota. Regarding the macro life-forms in particular, extensive damage to the benthic life-forms was observed; this damage was mainly to the calcareous-shell organisms. Even though the damage to the benthic life-forms seems to be permanent, there is a general healing of the ecosystem with the return of some species of fish. Another organism that was seriously affected by the presence of carbon dioxide is the "Posidonia oceanica" sea-grass. Once the Posidonia was dead, the available substratum was colonized by other species such as more resistant algae. Of the studied micro life-forms, the viral abundance was affected by the presence of the gas vents with a decrease close to the carbon dioxide plumes. From these results it is possible to hypothesize that viruses can be less tolerant than prokaryotes to the carbon dioxide chemistry and this can have consequences on the biota equilibrium in the areas affected by increased levels of CO_2 (Manini et al., 2008).

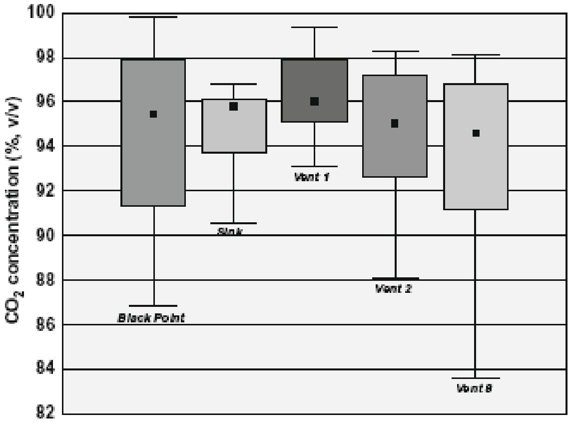

Fig. 6. Box plots of soil gas CO_2 data from the Panarea vents. The median values are very similar for each vent suggesting a common degassing input linked to local tectonics.

Another example of toxic emanation study was performed in the Albani Hills area (a volcano located about 20 km southeast of Rome and extending over an area of about 1500 km) where strong areally diffuse and localised spot degassing processes occur (Annunziatellis et al., 2003). The main structural features which cause the high degassing phenomena are buried highs in the carbonate basement which act as gas traps.

Data were processed in order to build risk maps and highlight areas having a potential health hazard in terms of the short-term risk caused by elevated CO_2 concentrations and the long-term risk caused by high radon concentrations (Beaubien et al., 2003).

Figs. 7 and 8 show the contour maps of radon and carbon dioxide concentrations in soil gas calculated using the kriging method and spherical variograms model estimation. In the surveyed area, the distribution of anomalous radon values (>60 kBq/m^3) shows a maximum anisotropy orientation (N340°–350°), which parallels that of the Apennine mountains. This can be seen both in the western and the eastern sectors along the Appia road (where aligned effervescent water springs occur). Point anomalies occur around the Consorzio Vigna Fiorita (from 75 to 250 kBq/m^3, 1.8–2.4 in log scale), as well as near the village of Cava dei Selci (>100 kBq/m^3) where the major gas release occurs. Background values (i.e. in situ production) occur in the central sector of the area.

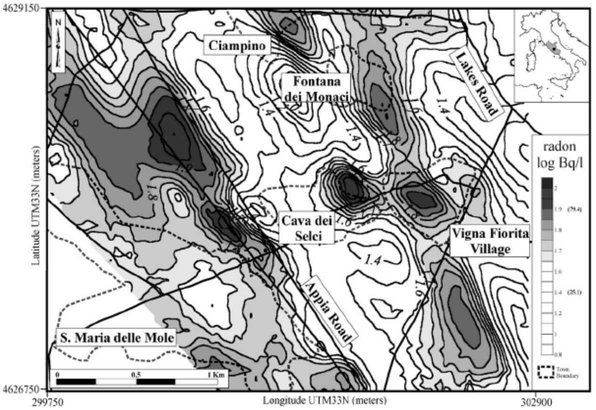

Fig. 7. Map of the radon distribution in soil gas. The radon anomalous values (>60 Bq/l, 1.7 in log scale) shows clear linear trends parallel to the Apennine mountains. The anomalies are located in the western sector where an alignment of sparkling water springs also occur, and in the eastern sector.

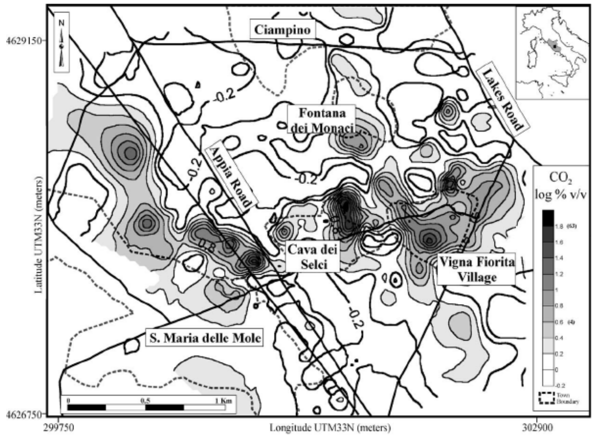

Fig. 8. Map of the carbon dioxide distribution in soil gas. Carbon dioxide concentrations also show a mild anisotropy along a NW–SE major axis, similar to that of radon. Most of the anomalous concentrations (up to 80%, 1.9 in log scale) occur as spots in the eastern sector.

The distribution of radon anomalies in the Ciampino–Marino districts marks the presence of high permeability channels (faults and fractures) along which, due to the action of a carrier gas (such as CO_2), the short-lived Rn is able to migrate quickly and produce soil gas anomalies. Furthermore, the orientation of the anomalies accords with the trend of known structural features, mimicking the general NW–SE trend of the Ciampino high (Di Filippo & Toro, 1995). The anomalies are spatially continuous along the major NW–SE axis, and their width of about 1 km emphasises the spatial domain of the faults which border the Ciampino high structure.

The soil gas CO_2 results (Fig. 8) show a pattern that is similar to that in the radon contour map. Most of the anomalous concentrations (up to 80%, 1.9 in log scale) occur as spots in the eastern sector (Cava dei Selci area and the urbanised area of the Consorzio Vigna Fiorita). The high CO_2 levels in the ground are therefore probably associated with a low enthalpy geothermal system, either metamorphic reactions involving the carbonate substratum or magma degassing, corresponding to faults associated with the Ciampino high.

Generally, the high radon concentration in soils causes high radon concentration indoor: as reported in the literature (Reimer & Gundersen, 1989), indoor radon and soil gas radon show a linear correlation coefficient of 0.77. For this reason, indoor radon measurements (30 samples) were made, using a Genitron Instruments AlphaGuard Radon monitor in random selected private and public dwellings and cellars located in the surveyed area (Cava dei Selci and S. Maria delle Mole villages). Fig. 9 shows a comparison between mean indoor radon values calculated for cellars, ground and first floors and soil gas concentrations. The mean values calculated for the three monitored levels highlight the expected trend, in which cellars show the highest values (in certain sites, measured indoor radon values are extremely high up to 25 kBq/m^3). It is worth noting that the mean soil gas concentration corresponding to the cellar measurements is not the highest. This confirms that enclosed spaces in contact with the ground are more affected by radon and/or toxic gas accumulations.

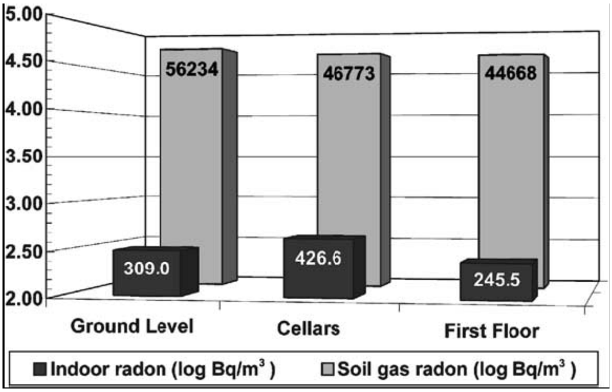

Fig. 9. The bar chart shows the comparison between the radon indoor mean values at different levels (cellars, ground levels and first floor) with the radon concentrations measured in the soil gas samples at the same sites. Numbers in the bars indicate the radon values in Bq/m^3. The figure highlights that cellars show the highest radon values (up to 25,000 Bq/m^3).

4.3 Radionuclide migration

Two different examples of the study of radionuclide migration will be discussed. The first one regards the study of soil gas distributions in clays altered by heating, based on findings at Orciatico site of natural analogue of nuclear waste disposal. The second example is related to the presence of an abandoned uranium mine in proximity of the main natural water resource of Kyrgyzstan (central Asia).

The physical properties of thermally altered clays of the Orciatico area (Tuscany, Central Italy) were studied as argillaceous formations could act as geological barriers to radionuclide migration in high-level radioactive-waste isolation systems. Though available data do not allow exact evaluations of depth, many features of the Orciatico igneous body (widespread glass, highly vesicular peripheral facies etc.) point to a shallow emplacement, comparable with that reasonably forecast for a repository. Not even exact definitions of the temperature of magma at the moment of emplacement are feasible. Only some evaluations can be proposed: from its distinctly femic composition temperatures over 800 °C may be assumed for the alkalitrachytic magma intrusion (Leoni et al., 1984; Hueckel & Pellegrini, 2002). These values are much higher than those expected around a radiowaste container (up to 300°C, according to Dayal & Wilke, 1982); therefore, as to the thermal aspects the Orciatico magmatic body and its metamorphic aureole must be regarded as an extreme condition model of a radiowaste repository and probably it can be mainly used to demonstrate a worst case. The study was performed through detailed soil gas surveys in order to define the gas permeability of the clay unit (Voltattorni et al., 2010). A total of 1086 soil gas samples was collected in the Orciatico area. A first survey was performed collecting 486 samples along a regular grid near the village of Orciatico with a sampling density of about 500 samples/km^2. After that, monthly surveys (from April to September 1998) were performed to monitor possible variations of soil gas concentration due to weather conditions.

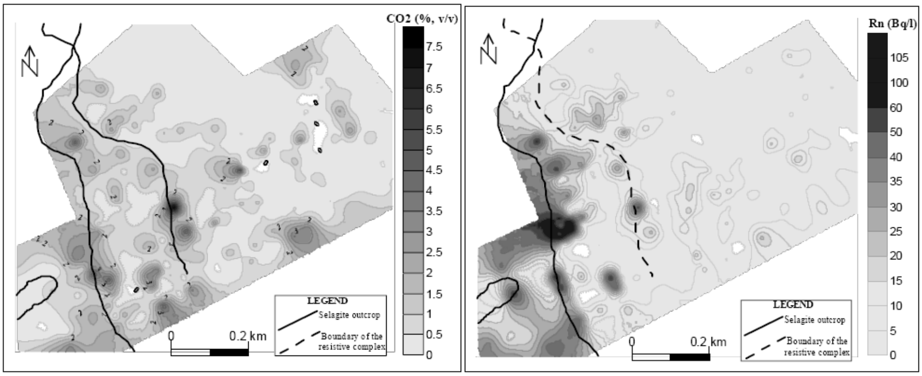

Fig. 10. Carbon dioxide (to the right) and radon (to the left) distributions in soil gases. Anomalous values (CO_2 >2 %,v/v, Rn >25 Bq/l) are in correspondence of the boundary of the resistive complex supposed on geoelectrical results.

The radon, as well as the CO_2 contour line maps, figure 10, show that highest values (^{222}Rn> 25 Bq/l, CO_2>2 %,v/v) occur in the south-western part of the studied area (characterized by the presence of the igneous body outcrop named Selagite) and along a narrow belt, with direction NNW-SSE, where metamorphosed clays (named Termantite) are present.

Furthermore, anomalous values occur in unaltered clays especially in correspondence of the boundary of the resistive complex supposed on previous geoelectrical results (Voltattorni et al., 2010). All over the north-eastern sector, in non metamorphosed clays, radon and carbon dioxide values are very similar to background values reported in literature (Rn: 10-15 Bq/ l, CO_2: 0.5 %,v/v).

As radon and carbon dioxide values seem to decrease gradually from Selagite outcrop towards un-metamorphosed clays, soil gas data set were projected along one longitudinal lines coinciding with a performed geoelectrical profile. Figure 11 shows polynomial regression (3rd degree) of radon and carbon dioxide values plotted against the distance from a reference point. Graphs highlight a slight decreasing trend of radon soil gas values (continuous line) towards the NE, from Selagite outcrop until un-metamorphosed clays.

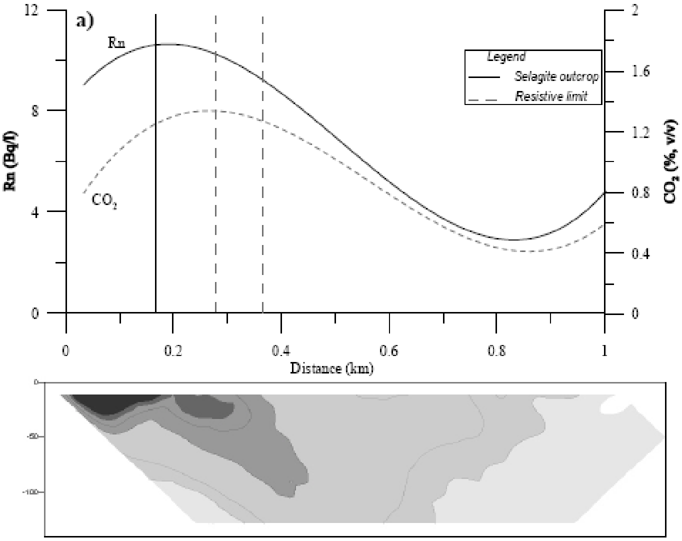

Fig. 11. Comparison between polynomial regression (3° degree) map and geoelectrical profile. Radon graph (continuous line) highlights a general slightly decreasing trend of soil gas values towards the NE, from Selagite outcrop until un-metamorphosed clays. The same behaviour is well evident also for CO_2 polynomial regression (dashed line). Values slightly rise towards un-metamorphosed clays, indicating the presence of structural discontinuities not visible at the surface.

The same behaviour is well evident also for CO_2 polynomial regression (dashed line): the overlapping peaks in the radon-carbon dioxide plots should confirm that the soil gas distribution is linked to clay alteration degree. In fact, highest CO_2 and Rn values were found between Selagite outcrop and the first resistive limit, in a narrow belt characterized by a high alteration degree and, probably, by an intense shallow fracturing (Gregory & Durrance, 1985). On the other hand, after the second resistive limit, where clays did not undergo the effects of the intrusive body, radon and carbon dioxide values are in agreement with the mean values reported in literature excepting in the last 200m of the profile where values slightly increase again.

The results of this study provided specific information about soil gas permeability on the Orciatico clay units characterized by different degrees of thermal alteration. This research represents the first study performed in thermally and mechanically altered clays and results demonstrated that the method gives interesting information also in clays that apparently did not undergo to mineral and geotechnical variations. Radon and carbon dioxide soil gas anomalies are mostly concentrated in zones where the Selagite and thermally altered clays are present. Soil gas distributions are interpreted as being due to intense shallow fracturing of clays along the inferred Selagite boundary: the volcanic intrusion caused thermo-hydro-chemical and thermo-hydro-mechanical stress and contact metamorphism in the clay. Far from Selagite, clays apparently prevent the rising of gases. In fact, small soil gas anomalies were found over the estimated intact Pliocenic clays having permeability due to structural discontinuities not visible at the surface. This study allowed to highlight the role of soil gas technique for the identification of secondary permeability in a clay sequence: clay can strongly modify its characteristics (i.e., reduction of the properties of isolation and sealing material) when affected by even very low thermal alteration although this effect is not visible through traditional investigative methods. The results of this study suggest a review of the role of clays as geological barrier for the permanent isolation of long-lived toxic residues in the radioactive-waste isolation framework.

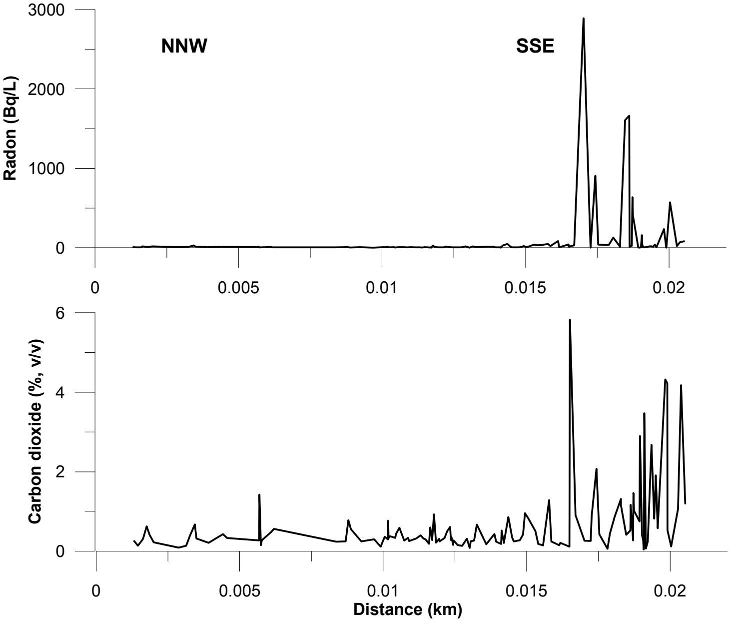

Fig. 12. Radon and carbon dioxide profiles at Djilubulak valley (Kyrgyzstan, central Asia). Graphs highlight a slightly decreasing trend of radon and carbon dioxide soil gas values towards the north, from the waste until the lake.

A different study of radionuclide migration was performed in the Djilubulak ephemeral stream valley on the southern shore of Issyk-Kul (Kyrgyzstan, central Asia), one of the largest and most pristine lakes in the world (Gavshin et al., 2002). The tail storages from the past mining may pose a pollution hazard to the lake water and sediments. A chain of six protective pools interconnected by drain pipes descend from the abandoned mine and processing plant down the Djilubulak stream valley. To assess the effectiveness of these catch pools and the scale of pollution risk, a soil gas survey was performed from the abandoned mine to the shore of the lake (Giralt et al., 2003; Voltattorni et al., 2004).

In the river bed the soil gas survey was done performing measurements following both profiles perpendicular to the river flow and random distribution. The profiles were carried out approximately every 200 m. In each profile, the measurements were made roughly every 30-40 m. A total of 130 soil gas samples were collected sampling at the lower part of the river valley (close to the lake shore), along the river valley and at the waste.

The highest radon values (>40 Bq/ l) occur in the south-eastern part of the studied area characterised by the presence of the waste. All over the northern sector radon values are very similar to background values reported in literature (10-15 Bq/ l). The CO_2 soil gas distribution shows a greater concentration of anomalous values (> 3%) all over the mine and the waste area. Hypotheses about biogenic and/or thermogenic origin of this gas require isotope analysis. In spite of this, it is reasonable suppose that mine ruins and coal remains influenced soil gas distribution as highest values are present all over the waste and there is a good correspondence between high radon and carbon dioxide values. Fig 12 shows two profiles along which results were projected considering a longitudinal line intersecting the valley. Graphs highlight a slightly decreasing trend of radon and carbon dioxide soil gas values towards the north, from the waste until the lake. The overlapping peaks in the Rn and CO_2 plots imply that the soil gas distribution is linked to the presence of radioactive material in the waste. In fact, highest CO_2 and Rn values were found in the same area. On the other hand, outside the "contaminated" area, where soil did not undergo the effects of the mine activities, radon and carbon dioxide values are in agreement with the mean values reported in literature (Voltattorni et al., 2004).

Soil gas results, therefore, suggest that there has not been a significant down-stream migration of radiogenic particles or elements, either via mass transport during flooding events or via groundwater movement. However, it is worth noting that in case of a catastrophic event such as an intensive flash flood, the deposits of Kadji-Sai could be eroded and distributed in the Djilubulak valley and may reach the shores of Issyk-Kul Lake (Gavshin et al., 2002). These contaminants would then produce high local levels of radioactivity in any area they reach. In the worst case scenario, the exposure rates in the Djilubulak valley and at its confluence with Issyk-Kul Lake may reach values which exceed not only safe exposure rates for general public but even long-term occupational exposure limits. The total amount of radioactive deposits currently at the site would not pose danger to the entire Issyk-Kul Lake and areas further than 10–15 km from the site.

5. Conclusion

The limitation of soil gas investigations lies in weaker crustal gas concentrations in cases of thick sedimentary cover, and in high level of atmospheric dilution in soils (Baubron et al., 2002). However, on the basis of the many achieved results, it can be said that soil gas prospection constitutes a powerful tool to identify complex phenomena occurring within the crust.

The comprehensive approach followed in this study has provided insights on the spatial influence of tectonic discontinuities and geology on gas migration toward the surface. Soil gas measurements, performed at different scales, involved two gaseous species with very different geochemical behaviour. Soil gas surveys yielded different features of the anomalies, reflecting the different gas bearing these properties of the pathways along which gases can migrate.

The association of the two proposed gas species, radon and carbon dioxide, is considered fundamental in the study of gas migration as CO_2 often acts as carrier in transporting the radon trace gas: this mechanism for surface soil gas anomalies is due to advection as suggested by relatively high rate of migration needed to obtain anomalies of short-life ^{222}Rn in the soil pores.

As soil gas distribution can be affected by some phenomena related to the climatic factors, soil moisture and gas behaviour (mobility, solubility and reactivity), a multivariate study including a large number of gaseous species has been considered.

However, independent from gas origin, all the results show that gases migrate preferentially through zones of brittle deformation and enhanced permeability. In order to quantify the spatial influence of fault geometry and geochemical properties on the distribution of soil gases, the geostatistical approach (i.e., variograms) is necessary.

Because of the very high variability of gas concentrations at the surface, soil gas prospection appears necessary in order to select potential optimum sites for surveillance to identify, for example, regional changes of strain fields or variations in toxic emanation. Due to the complex relationship between geology and local phenomena, a network of geochemical stations would be much more useful.

It is hoped that the present study has brought attention to the problems associated with natural gas migration and that there is more awareness of how the soil gas method can be used in these situations, both to plan land-use zoning or to resolve health problems in existing residential areas dealing with the danger of natural toxic gases. In the case of the former, areas defined as high risk can be zoned for agricultural or parkland use and not for residential development, while for the latter modifications can be made on 'high-risk' existing homes or monitoring stations can be installed to improve safety.

Communication of these results to the local government can result in heightened awareness and the initiation of some preventive programmes, such as the development of a continuous monitoring station.

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