Hazardous gas emissions from the flanks of the quiescent Colli Albani volcano (Rome, Italy)

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Abstract

Gas hazard was evaluated in the three most important cold gas emission zones on the flanks of the quiescent Colli Albani volcano. These zones are located above structural highs of the buried carbonate basement which represents the main regional aquifer and the main reservoir for gas rising from depth. All extensional faults affecting the limestone reservoir represent leaking pathways along which gas rises to the surface and locally accumulates in shallow permeable horizons forming pressurized pockets that may produce gas blowout when reached by wells. The gas, mainly composed by CO_2 (>90 vol.%), contains appreciable quantities of H_2S (0.35-6 vol.%), and both represent a potentially high local hazard. Both gases are denser than air and accumulate near ground where they may reach hazardous concentrations, and actually lethal accidents frequently occur to animals watering at local ponds. In order to evaluate the rate of degassing and the related hazard, CO_2 and H_2S diffuse soil flux surveys have been repeatedly carried out by accumulation chamber. The viscous gas flux of some important discrete emissions has been also evaluated and the CO_2 and H_2S air concentration measured by portable devises and by Tunable Diode Laser profiles. The minimum potential lethal concentration of the two gases (250 ppm for H_2S and 8 vol.% for CO_2) is 320 times higher for CO_2, whereas the CO_2/H_2S concentration ratio in the emitted natural gas is significantly lower (15-159). This explains why H_2S reaches hazardous, even lethal, concentrations more frequently than CO_2. A relevant hazard exists for both gases in the depressed zones (channels, excavations) particularly in the non-windy early hours of the day.

1. Introduction

The Tyrrhenian margin of Central and Southern Italy is a volcanic-geothermal area characterized by a thinned continental crust (<25 km), a high heat flow (>80 mWm^2) (Baldi et al., 1992; Della Vedova et al., 1984; Gambardella et al., 2004), by the presence of Quaternary alkali-potassic volcanoes (Mattei et al., 2010) and a strong degassing of endogenous CO_2 from high pressure sources at depth (Chiodini et al., 1995, 2004). After the famous active volcanoes of Campania (Vesuvius, Campi Flegrei, Ischia), Colli Albani (CA), located just SE of Rome, is the most recent of the potassic volcanoes of Central Italy as its eruptive activity, begun about 600 ka ago, continued likely up to Holocene (5.8 ka). In addition geological and archaeological evidence supports the repeated occurrence, up to Roman epoch, of lahars generated by water overflow from Albano crater lake (Funiciello et al., 2010 and references therein). Here, in the 4th Century b.C., Romans carried out the first volcanic risk prevention work of mankind, excavating a drainage tunnel to keep the lake water level below the crater rim (Ghini, 1999; Funiciello et al., 2002, 2003, 2010).

Although a controversy exists on the age of the most recent eruption of CA (see the discussion in Carapezza et al., 2010a), there is unanimous agreement that the volcano be considered dormant and not extinct as in any case the time elapsed since the last eruption does not overrun the average duration of its quiescent periods. In addition the volcano summit area, hosting the most recent craters, is affected by recurrent shallow seismic swarms and by a significant vertical uplift, phenomena that look very similar to those usually occurring on active volcanoes (Carapezza et al., 2010a and references therein). Also the likely magmatic origin of the widespread gas emissions of CA (Carapezza and Tarchini, 2007) supports its present quiescent condition.

Carbon dioxide is the most abundant CA endogenous gas (93-99%). CO_2 rising from depth dissolves and accumulates into the main regional aquifer hosted in buried Mesozoic limestones and into shallower aquifers hosted either in Neogene sediments or in the superficial volcanic rocks (Capelli and Mazza, 2005; Carapezza and Tarchini, 2007). There are no high temperature fumaroles or thermal springs at CA, their lack being explained with the hydrogeological setting of the volcanic complex, which favours a strong infiltration of cold meteoric water that obscures any conductive or convective heat flux from depth (Carapezza and Tarchini, 2007). All extensional faults connecting the buried aquifers with the surface represent preferential pathways for the gas to escape, and in fact CA contains many manifestations with cold dry gas emissions (mostly CO_2 with minor H_2S, N_2, CH_4) from discrete vents and zones with huge diffuse soil fluxes (Chiodini and Frondini, 2001; Carapezza et al., 2005; Carapezza and Tarchini, 2007). Most of these gas manifestations are located above structural highs (horsts limited by faults) of the buried dense carbonate basement which correspond to positive Bouguer gravity anomalies (Fig. 1). As the gas is denser than air, it tends to accumulate near the ground, in morphological depressions, channels or house basements, where CO_2 and/or H_2S may reach hazardous concentration if not dispersed by wind. Many lethal accidents have actually occurred to animals but also to a human (Carapezza et al., 2003; Carapezza and Tarchini, 2007). Another hazard is related to the presence of pressurized gas pockets at shallow depth (10-230 m) confined beneath an impervious cover (clayey lahar deposits, altered tephra), that have caused several dangerous gas blowouts when reached by wells (Carapezza and Tarchini, 2007; Carapezza et al., 2010a, 2010b).

In this paper we present the results of a detailed geochemical study of the natural CO_2 and H_2S degassing of CA, aimed at assessing the related hazard. In all the main gas emission sites, the diffuse CO_2 and H_2S soil flux has been measured and also the viscous flux has been evaluated on some discrete degassing vents. The air concentration of the two gases has been measured with two different techniques. In all manifestations, the gas has been sampled and its chemical and isotopic composition analyzed.

2. Geochemistry and origin of the endogenous gas emission

Chemical and isotopic analyses of CA endogenous gas, representative of the main manifestations studied in this paper (Cava dei Selci, Solforata di Pomezia, Tor Caldara) are reported in Table 1. Carbon dioxide is always the main component with a concentration up to 99 vol.% and N_2 and H_2S show rather wide variations (0.18-6.08 vol.% and 0.35-6.3 vol.% respectively). Methane has a low concentration compared with that of the high-temperature (T) geothermal fluids of Central Italy (Tuscany). This indicates that an abiotic origin of CH_4 by high-T conversion of CO_2 (Minissale at al., 1997) does not occur in the CA deep carbonate reservoir because of its relatively low temperature (100-150 °C; Carapezza and Tarchini, 2007). The CA methane, which is slightly higher in Tor Caldara gas (Table 1 and Fig. 2a), has a likely low-T organic origin. In the ternary diagram of the main components (Fig. 2a), because of their low CH_4 content, the CA gases are aligned along the CO_2-N_2 side, as in most gas manifestations of the Tyrrhenian margin of Central Italy (Minissale et al., 1997). In the triangular diagram CO_2-N_2-H_2S (Fig. 2b) most samples show a limited though appreciable variation of the CO_2/H_2S ratio with a strong variation of the N_2 content, with the exception of Tor Caldara-Lavinio gas whose H_2S content is significantly higher. The variation of the H_2S content likely reflects a variable extent of its oxidation to SO_4^{-2}during interaction with the water of aquifers encountered by the rising gas, and actually sulphurous water springs are found in all the CA gas manifestations (Giggenbach et al., 1988). In the triangular diagram N_2-He-Ar (Fig. 2c) CA gases, particularly those of Cava dei Selci, show a variable degree of contamination with air or air-saturated water (ASW) of a primary deep gas. It has to be noted that Giggenbach (1991) considered the gases plotting near the N_2 corner as representative of andesitic volcanoes of actively subducting zones. In Central Italy cold gas emissions, the not atmospheric N_2 has instead a likely crustal origin from metasedimentary rocks hosting the deep aquifers (Minissale at al., 1997). The diagrams of Figures. 2a and 2c suggest that CA gases could result from the addition of variable quantities of crustal N_2 to a deep mantle gas.

The carbon isotopic composition ($\delta^{13}C$) of CO_2 has a rather wide variation range (-3.5 to 1.39 ‰ vs. PBD) which prevents a clear identification of its source. An origin of the CO_2 of the Central Italy gas manifestations from the Mesozoic carbonates has been suggested by Panichi and Tongiorgi (1976) and Minissale et al. (1997). More convincingly, Chiodini et al. (2000) have shown the presence in the western side of the Apennine chain, including the Tyrrhenian volcanic zones, of a common deep CO_2 source. This deep CO_2 has a $\delta^{13}C$ of about -3 ‰ which is compatible with the carbon isotopic composition of a CO_2 deriving from a crustally contaminated mantle, but is not compatible with a derivation from metamorphic decarbonation ($\delta^{13}C_{CO2}$ > 2 ‰).

A useful contribution to the gas origin is provided by its helium isotopic composition, the $^3He/^4He$ ratio (R) expressed with respect to the same ratio in air (Ra). The R/Ra of CA gas ranges from 0.89 to 1.90 (Table 1) and although much lower than in the "typical mantle" (R/Ra≈ 8.0; Marty and Jambon, 1987) it is very near and even slightly higher than the R/Ra found in the fluid inclusions of phenocrysts of CA volcanic rocks (Martelli et al., 2004). Helium isotopic composition therefore suggests a likely origin of CA gas from a deep magma source affected by crustal contamination during its primary generation in a subduction process (Carapezza and Tarchini, 2007).

3. Diffuse and viscous fluxes of CO_2 and H_2S and air concentration

3.1. Methodology

Air concentration of CO_2 and H_2S has been measured at variable height from the ground either on single points by portable Dräger X-AM 7000 and by Tunable Diode Laser (TDL) profiles of variable length, height and duration. The used Dräger has a IR sensor with 0-100 vol.% range for CO_2, whereas three different electrolytic cells have been used for H_2S with an upper detection limit of respectively 50, 100 and 500 ppm. The TDL (Schiff et al., 1994; Tittel et al., 2006; Weber et al., 2006) measures every few seconds the average air concentration of CO_2 and H_2S on the profile length, and simultaneously the wind direction and speed are recorded by a sonic anemometer. The diffuse soil flux of CO_2 and H_2S has been measured by two portable accumulation chambers (a.c.) (Chiodini et al., 1998; Carapezza and Granieri, 2004), each with a net internal volume of 3000 cm^3, placed on dry soil, carefully avoiding any evident viscous degassing spots. The a.c. were equipped with a LI-820 infrared detector (0–2 vol.%) for CO_2 and with a TOX-05 detector for H_2S (0-20 ppm). In the 2007 survey at Cava dei Selci, H_2S fluxes have been estimated by measuring the H_2S concentration inside the chamber with a Jerome® 631-X gold film sensor (0.003-50 ppm) after a known time interval. The CO_2 and H_2S soil flux data were processed following the GSA method (Chiodini et al., 1998; Cardellini et al., 2003) using the graphical procedure by Sinclair (1974) and estimating the mean flux value and its 90% confidence interval by means of Sichel's t estimator (David, 1977). A sequential Gaussian simulation approach (sGs, Deutsch and Journel, 1998; Cardellini et al., 2003) was also used with 100 simulations for each flux map. In vegetated environments the background for CO_2 soil flux depends on the extent of soil respiration (Kucera and Kirkham, 1971) and only flux values above background have been considered to have an endogenous source. The biological natural sources of H_2S are the decay of organic sulphur and the activity of sulphate-reducing bacteria (Riemenschneider et al., 2005). Background of H_2S soil flux is very low (10^{-8}-10^{-6} kg/m^2 day at Solforata according to Voltaggio and Spadoni, 2009) so all the measured flux values (minimum = 0.01 g/m^2day) have been attributed to an endogenous inorganic source. Viscous gas flux from discrete vents, most of which occur in water ponds (e.g. Solforata), has been estimated by some new experimental devises, including a floating platform (140x140x30cm) and plastic buckets placed above the degassing vents and measuring the gas flow rate across known pipe sections by volumetric gas counters. Soil Rn and Tn concentration has been measured by Durridge RAD7 through a probe inserted in the soil at 30 cm depth. Rn is the average of the last two of a number (generally five) of measurement cycles, continued until a stable value is reached. Accuracy is ±2 %, depending on environmental factors. Chemical and isotopic analyses of the collected gas samples have been made in the laboratories of INGV-Palermo and of IGG-CNR, Pisa.

3.2. Cava dei Selci

Located on the north-western flank of CA about 20 km from the center of Rome (Fig. 1), Cava dei Selci is a densely inhabited zone characterized by a permanent gas emission mostly from sites where the low permeability surface cover made of lahar deposits from Albano crater lake, was removed by excavations or crossed by wells (Carapezza et al., 2003, 2007). An increase of the degassing rate has been reported in relation to the CA seismicity (Quattrocchi and Venanzi, 1989; Chiodini and Frondini, 2001; Funiciello et al., 2002) and lethal accidents by gas inhalation have occurred to a human and to dozens of animals including cows and sheep (Carapezza et al., 2003). The main gas manifestation occurs within an old stone quarry where excavation removed the low permeability surface deposits and encountered a shallow aquifer. The quarry was partly filled by loose material from nearby excavations and a depression formed, which for many years hosted a seasonal pond of stagnant water with many rising gas bubbles. Anomalous degassing occurs also from the soil near to old uncemented shallow water wells (Carapezza et al., 2007).

3.2.1. Diffuse soil degassing of CO_2 and H_2S

Ten years of observation (Carapezza et al., 2010a and references therein) indicate that Cava dei Selci is a zone of permanent anomalous degassing, though with a strong variation of the total diffuse CO_2 soil flux from the target area (6350 m^2) from 25 to 3-4 ton/day. Unfortunately part of the target area has been affected in October 2009 by the building of a road which modified the soil permeability preventing a reliable comparison of old and new gas flux measures. The main emissive zone has been fenced, but small animals (cats, birds) are still frequently found dead within the depression. The last six surveys of the target area were made in the period March 2009-January 2011. The diffuse CO_2 soil flux ranged from 4.1 to 9.9 ton/day corresponding to medium-low values compared to the maxima of 25 and 20 ton/day recorded in May 2000 and July 2007 respectively. In February 2007 also the diffuse H_2S soil flux was measured for the first time from the target area finding a total of 84 kg/day (10.4 ton/day of CO_2 flux). In July 2009 a wider surface (8200 m^2) was investigated for CO_2 and H_2S flux (Fig. 4). It extends southward up to the zone near houses affected in May 2008 by accidental gas blowout from very shallow geognostic boreholes (see Fig. 3 and Carapezza et al., 2010a, 2010b). The total flux was estimated to 12.5 ton/day for CO_2 and 36 kg/day for H_2S (Table 2), the latter being nearly half of the 2007 H_2S release from a nearly equivalent surface.

3.2.2. Continuous automatic monitoring of the CO_2 soil flux

In December 2003 an automatic station was installed at Cava dei Selci outside the depression but near to its south-eastern limit (Fig. 3), to monitor hourly the CO_2 soil flux by a. c., together with some environmental parameters which may affect it (atmospheric pressure, humidity and temperature of soil and air, wind direction and speed; Carapezza et al., 2008b and references therein). The station operated until mid June 2008, with some interruptions due to battery malfunctioning or to sensor and hardware maintenance.

The CO_2 soil flux (Table 3) varied of over two orders of magnitude, from ten to several thousands of g/m^{2}day and important variations were recorded also in the climatic conditions, with soil temperature and humidity ranging from 2 to 29 °C and from 17.5 to 100 % respectively. Data have been statistically processed in order to recognize the CO_2 flux anomalies produced by endogenous phenomena by filtering the effects due to environmental variations, by a Principal Component Regression with a forward-stepwise method (Vandeginste et al., 1998). Firstly, environmental data have been substituted, through a Principal Component Analysis, with independent artificial variables (factors) maintaining the highest possible variance of the original environmental data set. Then a forward-stepwise regression has been made between CO_2 flux and factors, so to identity those factors which, in the lowest number, may explain the maximum flux variability. The regression indicates that 17.2 % of the CO_2 flux variance can be explained by variations of environmental parameters, a relatively low value compared with those found at similar automatic stations on active volcanoes, such as Stromboli (29.4 and 68.2 %, Carapezza et al., 2008b) and Vulcano (34 %, Carapezza et al., 2011). The CO_2 soil flux appears positively correlated with the temperature of air and soil and negatively with air and soil humidity, whereas the strong wind effect observed at Stromboli and Vulcano (Carapezza et al., 2008b, 2011) has not been found at Cava dei Selci.

In Fig. 5A the measured CO_2 soil flux is compared with that obtained by the environmental model and in Fig. 5B the time variation of the standardized residuals (ST) is reported. ST is the difference between the measured flux value and the computed environmental contribution and therefore it identifies the flux variations due to endogenous causes. Several periods of strong endogenous degassing with ST exceeding 2σ are recognized as in summer 2007, however so far no clear correlation has been found with geological phenomena, such as earthquakes, although no relevant anomalous seismicity occurred at Colli Albani during the observation period.

3.2.3. Air concentration of CO_2 and H_2S

The exposure limits for human health of CO_2 and H_2S air volume concentration, established for working environments (NIOSH, 1981; WHO, 1987) are the following:

- TWA – Time Weighted Average, 8 hours: CO_2 = 0.5 % H_2S = 10 ppm
- STEL – Short Term Exposure Limit, 15 minutes, CO_2 = 3 % H_2S = 15 ppm.

The potentially lethal air concentration threshold is 8 % for CO_2 and 250 ppm for H_2S (Carapezza et al., 2011 and references therein). Chronic exposure to H_2S may cause serious health effect on the eyes of humans and animals, the exposure to even very low H_2S concentration (≥ 25 ppb) causing eye irritation (Lambert et al., 2006).

The first measurements at Cava dei Selci (Carapezza et al., 2003) revealed hazardous air concentration of both gases. The H_2S air concentration has been monitored since December 2003 for over six years with hourly measures by a Dräger Polytron 7000 electrochemical cell placed at 150 cm height at the automatic

CO_2 soil flux station (location in Fig. 3). Only 59 measures (0.16 % of the total) exceeded the STEL and in two cases the instrumental detection limit of 50 ppm was reached. In October 2005 CO_2 air concentration was measured by a Dräger portable IR detector on 92 of the fixed points of the CO_2 soil flux target area. The measures were made at 25 cm from the ground and were repeated also at 50 and 100 cm height when a non-zero value had been recorded at the lower elevation. Near the ground at 15 cm height, CO_2 locally exceeded the lethal threshold, with a maximum of 10.8 % and at 50 and 100 cm height, maximum concentrations exceeded STEL and TWA respectively. On 22 May 2007, the use of gun power permitted to observe the gas dispersion from the depression toward houses (Fig. 6).

The CO_2 and H_2S air concentration has then been measured by TDL profiles in February and May 2007 and again in July 2009. The profile length, height, duration and results are reported in Table 4 and their location is shown in Figure 3. The maximum air concentration has been recorded in the first hours of the day when wind ceases and the gas, denser than air, accumulates near ground (Fig. 7). It is interesting to note that H_2S exceeds frequently the lethal concentration threshold at 20 cm above the ground (e.g. 378 and 508 ppm maxima recorded over respectively 52 m and 25 m length in profiles 6 and 10, Table 4, Fig. 7). The average CO_2 air concentration along the TDL profile length remained always lower than STEL (Table 4); however it reached hazardous values in limited sectors of the profiles, as shown by continuous measures by Dräger X-AM 7000 made at different heights on the most emissive point of the TDL profile 10 (Fig. 8). The lethal CO_2 concentration of 8 % was exceeded both at 10 cm above the soil (for two hours, with a maximum of 20 %) and at 40 cm (for 15 minutes, with a maximum of 9.5 %) and STEL was exceeded also at 150 cm height (max. 4.2 %). The concentration drop at 7:00 am is due to the rising of wind, which unfortunately frequently disperses the gas towards the nearby houses as shown by the use of gas tracers (Fig. 6). Table 5 shows the persistence of hazardous H_2S air concentration, up to lethal values, recorded at some TDL profiles. The Dräger measurements show also a decrease of the CO_2/H_2S air concentration ratio with elevation (from 691 at 40 cm height to 353 at 150 cm height) likely reflecting the different densities of the two gases.

3.3. Solforata di Pomezia

Solforata di Pomezia (hereafter Solforata) is a zone historically known for its gas emission and the resurgence of sulphurous waters. The gas manifestation is located in the NE portion of the Pliocene – Pleistocene "Ardea transfer basin", a NE-SW elongated tectonic depression controlled by normal faults (Faccenna et al., 1994). This structure formed above a structural high of the buried carbonate basement (positive gravimetric anomaly, see S in Fig. 1) elongated in the same direction and extending from the Tyrrhenian coast toward the Albano crater lake. The area is affected by a significant uplift (1.3 mm/yr) suggesting the presence at depth of a pressurized gas source (Tolomei et al., 2003). The morphology of the zone has been deeply modified by old sulphur mining excavations, with the formation of several artificial small lakes and seasonal ponds. All the area is affected by diffuse degassing, but the main gas emission occurs from the westernmost small lake and a nearby artificial channel. Many gas bubbles can be seen rising from the water, aligned NNE, NE and ENE (Carapezza et al., 2005). The surface not covered by water is characterized by the presence of dozens of CO_2 and H_2S cold discharges, i.e. small vents marked by the absence of any vegetation around and by the presence of fine coatings and crusts of sulphur and sulphates (Voltaggio and Spadoni, 2009). A main NNE-SSW direction of the gas feeding fractures is confirmed by the alignment of the dry gas vents (Voltaggio and Spadoni, 2009) and by CO_2 soil flux profiles (Carapezza et al., 2005). As at Cava dei Selci, the lowering of the water table by overexploitation in the last years caused a seasonal reduction of the surface of the small lakes and ponds. In August 2003 some of them temporarily disappeared and many spectacular small craters and mud volcanoes, produced by the gas emissions, could be observed on the largely dried muddy surface (Carapezza et al., 2005).

3.3.1. Diffuse and viscous degassing of CO_2 and H_2S

In August 1996 the diffuse CO_2 soil flux from Solforata was first estimated by Chiodini and Frondini (2001) by 110 a.c. measures over a 55,000 m^2 surface, finding a total flux of 46 ton/day. A significantly higher value (61.2 ton/day) was found in the summer 2003 by Carapezza et al. (2005) by 200 a.c. measures over 30,000 m^2 (average CO_2 flux = 963 g/m^2 day; maximum flux value = 36,000 g/m^2day). A H_2S flux of about 5 ton/day was indirectly estimated in 1997–1998 by Voltaggio et al. (2001) by measuring the Rn/H_2S ratio in the gas and estimating the Rn flux. This value was later considered too high by the same main author (see Voltaggio and Spadoni, 2009) who, using a different technique, estimated in 2007 the total H_2S flux from Solforata to 1.2 ton/day, most of which (0.96 ton/day) occurs in the form of viscous emissions from the lake and the artificial channel.

Hereafter we present the results of a new and wider CO_2 and H_2S soil flux survey carried out in May 2007. A surface of 229,000 m^2, much wider than those previously surveyed, has been investigated by 356 a.c. measures. By log probability plots of the CO_2 and H_2S flux values (Fig. 9), the log-normal populations have been recognized, which were used to estimate the total fluxes (Table 2). The background flux value for CO_2 has been established at 9.4 g/m^2day. Most of investigated area (167,170 m^2, 73 % of the total) gave CO_2 soil fluxes above the background with a total flux of 88.6 ton/day, whereas a non-zero H_2S flux was found in only 33.6 % (77,000 m^2) of the investigated area (83 measures out of 356), with a total flux estimated at 1.12 ton/day (Table 2). The wider extent of the investigated surface permitted the recognition of new sectors of high CO_2 diffuse degassing, in addition to the ENE-WSW anomalies of the area around the western small lake where the anomalous H_2S flux measures concentrate (Fig. 9). The rate of CO_2 release from the same degassing area was much lower in May 2007 than in summer 2003, with a decrease of the average CO_2 soil flux from 936 to 371 g/m^2day and of the maximum flux value from 36,000 to 9437 g/m^2day.

In May 2007 the viscous flux of CO_2 and H_2S was measured on a number of discrete gas emissions, visible as degassing vents in the artificial channel and as trains of bubbles rising to the surface in the lake. A total of 30 measures were made, 21 on the lake with the floating platform and 9 in the channel with the bucket (Fig. 10). The measured gas flow rate ranged from 0.7 to 62 l/min (Table 6) and on the basis of the cumulative probability plot of Figure 11, 6 low-rate (<4 l/min), 16 medium-rate (4-27 l/min) and 8 high-rate emissions (27-62 l/min) were identified. By a visual comparison with the gas bubbling rate (bubble dimensions and rising velocity) of the measured emissions, 39 additional medium-rate emissions were recognized (32 in the lake and 7 in the channel) and the relative average of measured flow rates (20.23 and 10.27 l/min respectively) was attributed to each of them. Very many low rate emissions were also observed; they were estimated to be at least 400 in the lake and 94 were counted in the channel. To each of them the average measured flow rate (1.25 l/min) was arbitrarily attributed. Using the 2007 gas analysis of Table 1 a total viscous flux of 5.32 ton/day for CO_2 and 0.053 ton/day for H_2S has been estimated with actually measured values of 1.8 ton/day for CO_2 and 0.018 ton/day for H_2S (Table 6). The total flux (diffuse plus viscous) estimated in May 2007 was 94.5 ton/day for CO_2 and 1.14 ton/day for H_2S, a value close to the 1.21 ton/day estimate of spring 2007 by Voltaggio and Spadoni (2009).

3.3.2 Air concentration of CO_2 and H_2S by TDL measures

Seven TDL profiles were carried out in February and May 2007 at Solforata (see Fig. 9 for location) to measure the CO_2 and H_2S air concentration on the western lake surface and in the nearby channel. Results are shown in Table 4. The maximum concentration of CO_2 (5102 ppm) has been measured in the 52.4 m long profile no. 1 over the lake. Particularly interesting are the results of profile no. 7 run for 19 hours over the channel which contains several small gas bubbling vents and where dead animals frequently lay. It is clear from Figure12 that the gas air concentration depends on the wind velocity, the maxima (3384 ppm of CO_2 and 343 ppm of H_2S) being recorded in the first hours of the day when wind ceases blowing. For about one hour the H_2S concentration remained at hazardous (>100 ppm) or lethal (>250 ppm) values. As the values reported in Table 4 represent average concentrations measured along the TDL profile length (118 m in profile no. 7) it is clear that in some smaller sectors of the channel, H_2S air concentration (and possibly also that of CO_2) likely reached and long maintained higher immediately lethal values.

3.4. Tor Caldara

The gas manifestation of Tor Caldara (T in Fig. 1) is within a regional natural park located near the Tyrrhenian coast, on a NE-SW oriented structural high of the buried carbonate basement (gravimetric positive anomaly) directed toward the Albano crater lake which is at about 24 km distance. The sulphur deposits of the zone have been cultivated for centuries, leaving two excavated depressions (Miniera Grande and Miniera Piccola) where the main gas emissions are presently found together with some sulphurous water springs (Ventriglia, 1990).

3.4.1. Diffuse soil degassing of CO_2 and H_2S

The first CO_2 soil flux survey by a.c. in the Miniera Grande (MG) zone was carried out on 23-25 August 2005, just after the M = 4.7 Anzio earthquake of 22 August 2005, with epicenter near to Tor Caldara (Fig. 13). The total CO_2 soil flux was estimated to 11.5 ton/day from 77,000 m^2 of anomalous degassing surface (Table 2). A new soil gas flux survey was carried out on July 2009 at MG (Table 2). Data in Table 2 show the strong decrease of CO_2 diffuse degassing recorded at MG in July 2009, with total flux decreasing from 115 to 1.53 ton/m^2day and the mean flux of the most degassing population from 1830 to 167 g/m^2day. Strong degassing persisted in the easternmost part of the MG (Fig. 13), zone characterized by the presence of many aligned degassing vents having the form of small mamilliform knolls with a clayey altered surface with sulphur and sulphate incrustations and formed above and around degassing fractures.

In July 2009 also the H_2S soil flux was measured by a.c. at MG, finding a range from 0.01 to 14.5 g/m^{2}day. Most measures (67.2 %) were below the lower detection limit of 0.01 g/m^{2}day and the related flux map could not be obtained. A spatial coincidence was observed between CO_2 and H_2S soil flux anomalies of MG with the NW-SE alignment of degassing vents (Fig. 14). At MP only a few points had CO_2 soil flux above background, with maxima of 1707 and 2 g/m^{2}day for CO_2 and H_2S respectively.

3.4.2. Air concentration of CO_2 and H_2S

The CO_2 and H_2S air concentrations were measured on July 2009 at MG and MP by two TDL profiles placed at 25 cm from the ground above the most evident degassing zones, i.e. the aligned vents at MG and the gas bubbling points from small ponds of thermal acid water at MP (pH = 5.37-5.5, T = 27.9-28.7 °C) (Fig. 14). The highest concentrations found during respectively 2 hours and 70 minutes of recording were 684 and 957 ppm for CO_2 and 10 and 14 ppm for H_2S (Table 4). We recall that these values represent the maximum average concentrations measured along the profiles length (41 and 15 m respectively) and therefore they can hide higher gas concentrations above single emission points. For this reason the CO_2 and H_2S air concentration has been measured also by a portable Dräger X-am 7000 placed at 15 cm height above the most emissive vents. A total of 67 measures were made, with approximately 1 m spacing: 46 along the trace of TDL profile 1, 17 along TDL profile 2 and 4 in the zone between the two. In 21 points the H_2S air concentration reached the upper detection limit of the devise (500 ppm) which represents an immediately lethal value (Fig. 15). In the points with the maximum H_2S concentration ($\geq$ 500 ppm), the CO_2 concentration was extremely variable, from the normal air value of 330 ppm to lethal values (5 points with $CO_2 >$ 8 vol.% up to 58 vol.%).

4. Radon soil concentration

Radon (^{222}Rn) is a radioactive gas that may be emitted from any rock containing radium (^{226}Ra). It has a short half – life (3.82 days) that precludes a slow transport over large distances. Therefore it is believed to be generated in near surface rocks rich in uranium and radium (Nero, 1992) or transported upward by viscous fluxes of CO_2 along leaking fractures (Ball et al., 1991). As the potassic volcanic rocks of CA are rich in uranium and radium (115–220 Bq/Kg according to Voltaggio et al., 2001) there is likely an ubiquitous source of Rn at shallow depth. To the other hand, in the previous chapters we have shown that CA contains several actively CO_2 degassing structures, which may act as Rn carriers to the surface. Actually a very high daily flux of Rn (4.4 x 10^{10} Bq from 1800 m^2 of degassing surface) has been estimated at Solforata (Voltaggio et al., 2001) and Tuccimei and Soligo (2007) found Rn fluxes of 1.7–23.4 Bq/m^2 min in the Cava dei Selci target area and showed also that high CO_2 fluxes may lead to underestimate Rn. As Rn is a very hazardous gas which may cause lung cancer if long breathed above given indoor air concentration threshold (400 and 200 Bq/m^3 respectively for old and new buildings, ECC recommendation of 21 february 1990) we thought useful to carry out some new soil Rn measurements in the CA investigated zones. Results are reported in Table 7, together with previously published data. Soil Rn shows very high variations and only at Cava dei Selci – Santa Maria delle Mole and Solforata it exceeds 50 kBqm^{-3} (the high risk limit for the European Commission, Dubois, 2005). It seems from these data that the maximum Rn hazard of CA should be found in the proximity of viscous gas emissions, where Rn is directly emitted into atmosphere.

5. Conclusions

A significant gas hazard occurs in each of the three investigated Colli Albani zones characterized by huge cold emissions of endogenous gas. The main gas component is CO_2 which reaches up to 99 vol.% of the total (Table 1). The second potentially hazardous gas is H_2S, whose content in the natural gas emission ranges from ~1 to 6 %. All the main gas emissions, either by diffuse and viscous transport, occur in depressed zones formed by excavations for stone quarrying or sulphur mining purposes, which removed the surface impervious cover made of lahar deposits or of altered tephra, allowing the gas rising from depth to escape to the surface (Carapezza et al., 2003, 2005). In the zones near to gas manifestations not affected by excavations, the impervious surface deposits, or the presence of impermeable layers at shallow depth favour the gas accumulation in permeable horizons causing dangerous blowouts when reached by wells. In fact, besides the recently occurred gas blowouts (Carapezza et al., 2010a, 2010b) anomalous CO_2 soil emissions are observed in the proximity of many old wells drilled near the gas manifestations, as at Cava dei Selci and Santa Maria delle Mole (Carapezza et al., 2005, 2007) and at Lavinio, near Tor Caldara.

Most of the water ponds of the morphologically depressed zones contain cold fumaroles and discrete gas emissions (e.g. Cava dei Selci depression and channel, Solforata channel and MG and MP excavations at Tor Caldara) where carcasses of animals of various sizes (wild pigs, foxes, cats, birds) are frequently found. They have been killed by the gas accumulated at the water surface, where they were drinking, a fate identical to that of the cows and sheep dead at Cava dei Selci water pool (Carapezza et al., 2003). Carbon dioxide has long been considered the killer gas of these accidents, but now our data show that hydrogen sulphide is the most hazardous endogenous gas emitted at CA, and likely at other gas manifestations of Central Italy geothermal-volcanic areas (Barberi et al., 2007). This depends on the difference of the minimum potential lethal concentration of the two gases (250 ppm for H_2S and 8 vol.% for CO_2) that is 320 times higher for CO_2, whereas the concentration ratio between CO_2 and H_2S in the emitted natural gas of CA ranges from 15 to 159, the minimum values being found at Tor Caldara whose gas has the highest H_2S content (5-6%). As a matter of fact, our data on gas concentration in air, either by punctual Dräger measures or by TDL profiles, show that H_2S reaches lethal concentrations more frequently than CO_2, although also the latter can exceed 8 vol.%. In any case our data indicate that hazardous concentrations are reached in absence of wind usually in the early hours of the day.

In addition, it has to be considered that H_2S has serious health effects on people even at nonlethal concentrations (Kilburn, 1993; Lambert et al., 2006). The maximum value for H_2S in 24 hours recommended by WHO (1987) is 150 $\mu g/m^3$ (i.e. ~ 0.1 ppm) and our data show that this level is largely surpassed in all studied environments.

The CO_2/H_2S ratio in the gas emissions ranges from 49 to 159 at Cava dei Selci (the lowest value corresponding to a 1981 analysis with 2% of H_2S, a concentration never found anymore); from 64 to 92 at Solforata and from 15 to 20 at Tor Caldara (see Table 1). It is difficult to compare these values with the CO_2/H_2S ratio in air measured by TDL profiles, because they relate to average concentration along profiles of 15-169 m length. Maximum CO_2 and H_2S recorded by TDL profiles are much lower than the respective concentration in the nearest gas emissions (compare Tables 1 and 3). However, from the scrutiny of TDL it emerges that the average CO_2/H_2S ratios approach the values of the corresponding emission, with the notable exception of Tor Caldara, where CO_2/H_2S TDL averages are nearly one order of magnitude higher.

The lowest values of CO_2/H_2S in TDL profiles correspond to H_2S maxima and in general H_2S air concentration shows a wider variation range with respect to CO_2, which reflects the different stability in air of the two gases, particularly H_2S oxidation.

The shape of the anomalies in the gas soil flux maps of CA indicates that in all the investigated areas, gas is released to the surface through a network of fractures and faults having the direction of the underlying carbonate horst, although some transversal gas leaking fractures have been observed at Tor Caldara. These data confirm the validity of soil gas flux surveys to identify active faults and evaluate the rock permeability at depth (see Chiodini et al., 2007). In the zones, as Cava dei Selci, where CO_2 soil flux has been regularly investigated for several years on fixed grid of points, large variation of the degassing rate with time has been observed. This seems to depend by various factors, such as the temporal proximity to permeability increasing local seismic events and the variation of the water table level caused mostly by seasonal variations of the water exploitation at the largely urbanized periphery of the volcano. In any cases, data indicate that, after a strong gas releasing period temporarily following the most recent 1989-1990 CA seismic swarm (Amato et al., 1984) and a subsequent phase of degassing decrease, the gas pressure at depth seems to re-increase in the last years, possibly by reduction of fracture permeability by hydrothermal self-sealing at depth. It will be important to repeat the geochemical surveys presented in this paper at the occasion of the next CA seismic crisis, as a significant increase of the gas emission rate and the related hazard has to be expected, as shown also by Tor Caldara flux data.

Only at Cava dei Selci there is a densely inhabited zone in the proximity of the gas manifestation (Fig. 3). Here gas hazard (CO_2, H_2S, Rn) is very high, and some of these houses had to be evacuated in February 2010 because CO_2 and H_2S indoor concentration approached lethal values in ground floors and basements (Carapezza et al., 2010c). A detailed risk assessment of this zone, based on indoor air gas concentration monitoring, is presently under progress at the request of local Authorities.

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Figure captions

Fig. 1. Bouguer gravity anomaly map of Colli Albani (after Di Filippo and Toro, 1995) with location of the main endogenous gas manifestations studied in this paper (stars): C= Cava dei Selci, S= Solforata, T= Tor Caldara. Black squares are the wells from where an accidental gas blowout occurred (see Carapezza et al., 2010a). The signs + and – indicate positive and negative gravity anomalies respectively.

Fig. 2. CO_2-N_2-CH_4 (a), CO_2-N_2-H_2S (b) and N_2-He-Ar (c) plots of the Colli Albani gas emissions. Squares: Cava dei Selci; circles: Solforata di Pomezia; crosses: Tor Caldara-Lavinio; asterisks: wells; ASW: air saturated water. Data after Table 1.

Fig. 3. Location of the sites of Cava dei Selci where geochemical measurements have been carried out. The shallow boreholes where the 2008 accidental gas emission occurred (Carapezza et al., 2010a, 2010b) are indicated. The limits of the surface investigated for soil gas flux in July 2009 (a) and of the target area (b) are shown.

Fig. 4. Log probability plots and CO_2 and H_2S soil flux maps for Cava dei Selci July 2009 survey.

Fig. 5. A. Time variation of the CO_2 soil flux recorded by the Cava dei Selci automatic station compared with the results of the Principal Component Regression (see text). B. Time variation of the Standard Residuals and of the total CO_2 flux from the target area.

Fig. 6. Gas dispersion from the Cava dei Selci depression toward houses (picture taken on May 22, 2007 at dawn).

Fig. 7. Temporal variation of H_2S and CO_2 average air concentration measured at Cava dei Selci by TDL night profiles 6 and 10 (see Table 4) and of horizontal wind speed. The lethal concentration threshold for H_2S and the CO_2 and H_2S TWA and STEL are indicated.

Fig. 8. Time variation of the CO_2 air concentration at 10, 40 and 150 cm from the ground, measured by Dräger during the night of 10-11 July 2009 above the most gas emissive point of TDL profile 10.

Fig. 9. Log probability plots and CO_2 and H_2S soil flux maps for Solforata May 2007 survey. The location of TDL profiles is shown with black lines and numbers as reported in Table 4.

Fig. 10. High: The floating platform (pond) and Low: the plastic bucket (channel) used for viscous gas flux measurements at Solforata.

Fig. 11. Probability plot of viscous gas flux measurements at Solforata with indication of the low, medium and high flow-rate populations.

Fig. 12. Time variation of CO_2 and H_2S average air concentration and wind speed recorded in the Solforata channel by TDL profile 7 (see Table 4) in the night of 15 May 2007.

Fig. 13. Tor Caldara. Log probability plots and CO_2 soil flux maps for Miniera Grande surveys of August 2005 and July 2009. The location of the main degassing sites of Tor Caldara is shown in A) where MG is Miniera Grande and MP is Miniera Piccola. The position of the TDL profile no 1 is marked with a black line.

Fig. 14. Tor Caldara. Above: the aligned degassing vents with sulphur and sulphates incrustations of Miniera Grande. Below: the thermal degassing pond of Miniera Piccola with sulphurous water. The soil-Rn measurement devise and the TDL tripods (below) can be seen.

Fig. 15. Air concentration of CO_2 and H_2S measured on July 2009 at 15 cm above degassing points of Tor Caldara. LT indicates the lethal thresholds for H_2S (250 ppm) and CO_2 (8 vol.%). 500 ppm is the upper detection limit for H_2S. The normal CO_2 air concentration (330 ppm) is indicated.

Table 1. Chemical and isotopic analyses of the Colli Albani main gas emissions

Locality Date	Ref.	CO_2 vol.%	H_2S vol.%	CH_4 ppm	N_2 vol.%	H_2 ppm	He ppm	CO ppm	Ar vol.%	O_2 vol.%	$\delta^{13}C$-CO_2 ‰vs.PBD	$^3He/^4He$ R/Ra
Cava dei Selci												
14/11/1981	A	97.5	2	400	0.33	3	3	n.a.	n.a.	n.a.	1.2	n.a.
1981	A	93.7	0.35	480	5.25	<0.001	3	n.a.	0.066	0.55	0.9	n.a.
1996-1997	C	97.33	0.67	440	0.82	2.3	4	n.a.	0.015	0.253	0.91	1.54
1996	D	98.6	0.94	480	0.41	0.9	2.5	n.a.	0.0037	0.003	n.a.	n.a.
1996	D	98.8	0.89	480	0.27	0.9	2.3	n.a.	0.00022	0.0004	n.a.	n.a.
22/9/1999	E	98.5	0.8	460	1.5	n.a.	<0.0002	0.1	n.a.	n.a.	1	n.a.
13/3/2000	E	99.8	0.8	420	0.18	n.a.	3	n.a.	n.a.	n.a.	1.39	1.46
2/6/2000	E	99.8	1	470	0.3	n.a.	<0.0002	n.a.	n.a.	n.a.	n.a.	n.a.
10/3/2004	F	98.92	1.2	390	0.47	n.a.	2.2	n.a.	n.a.	n.d.	n.a.	1.38
21/9/2004	F	96.35	0.52	410	2.9	n.a.	2.4	0.7	n.a.	0.6	n.a.	1.4
29/7/2005	G	98.54	0.8	420	0.5	n.d.	1.9	n.d	0.066[a]	0.05	0.75	1.34
6/2/2007	I	98.58	0.93	452	0.39	n.d.	1.97	0.52	0.063	<0.004	0.783	1.44
30/6/2008	I	98.61	0.62	451	0.64	n.d.	2.44	<0.1	0.104	n.d.	1.18	1.45
29/3/2010	I	98.64	0.9	450	0.31	n.a.	2.3	n.a.	n.a.	0.037	0.87	1.42
Valle Cupella well												
18/10/2003	H	98.25	0.5	440	0.87	7	1.56	n.d.	n.a.	n.a.	1.3	1.9
S.M.Mole well												
23/5/2006	I	94.49	0.0005*	2528	5.92	71.28	43.4	0.055	0.015	0.00103	-0.53	0.89
Maciocco2 well	I	98.55	0.35	490	0.64	n.d.	2.6	n.a.	n.a.	0.073	0.85	1.37
Maciocco 36 well												
S4 27/6/2008	I	98.47	1.10	574	1.048	<0.0015	2.52	0.1	0.104	n.d.	1.12	1.41
S2 30/6/2008	I	92.77	0.35	606	0.80	0.020	2.62	0.1	0.153	n.d.	1.03	1.51
Solforata di Pomezia												
1981-1982	A	97.6	1.07	150	1.28	<0.001	9	n.a.	0.003	<0.001	-3.5	0.95
-	B	97.6	1.4	800	0.8	n.d.	5	n.a.	n.a.	0.19	n.a.	n.a.
-	B	97.6	1.4	500	0.78	3	3	n.a.	n.a.	0.21	n.a.	n.a.
-	B	97.6	1.4	90	0.97	0.4	7.5	n.a.	n.a.	0.024	n.a.	n.a.
-	B	96.0	1.5	150	2.1	7	15	n.a.	n.a.	0.37	n.a.	n.a.
-	B	96.0	1.5	150	2.1	n.d.	15	n.a.	n.a.	0.37	n.a.	n.a.
-	B	96.0	1.5	210	2.37	3	18	n.a.	n.a.	0.087	n.a.	n.a.
1996	D	97.9	1.14	120	0.93	0.6	9	n.a.	0.00036	0.0024	n.a.	n.a.
1996	D	98.0	1.06	110	0.93	0.1	9.3	n.a.	0.00054	0.0004	n.a.	n.a.
16/3/2000	F	99.2	n.a.	110	0.8	n.d.	5.3	n.d.	n.a.	0	1.23	0.95
21/9/2004	F	98.91	1.13*	90	0.87	n.d.	8.1	n.d.	n.a.	0	n.a.	0.94
8/2/2007	I	92.7	1.20	114	6.08	<7	7.43	0.48	0.014	<0.005	1.05	0.91
Tor Caldara-Lavinio												
Lavinio 1981-1982	A	94.2	4.65	1500	0.98	<0.001	2	n.a.	0.005	n.d.	-0.5	n.a.
Lavinio -	B	93.3	6.3	200	0.34	3	0.5	n.a.	n.a.	0.04	n.a.	n.a.
Lavinio -	B	93.3	6.3	240	0.35	2	0.7	n.a.	n.a.	0.025	n.a.	n.a.
Lavinio -	B	93.3	6.3	510	0.34	0.9	1.3	n.a.	n.a.	0.012	n.a.	n.a.
Tor Caldara 10/7/2009	I	92.8	6.0	1200	1.01	<5	n.a.	0.6	(with O_2)	0.08	n.a.	n.a.
Tor Caldara 10/7/2009	I	93.7	5.0	1300	1.11	<5	n.a.	0.6	(with O_2)	0.08	n.a.	n.a.

n.a. = not analysed; n.d. = below detection limit: *measured on the field with Dräger X-am 7000. Data after: [A]Giggenbach et al. (1988); [B]Principe et al. (1994); [C]Minissale et al. (1997); [D]Chiodini and Frondini (2001); [E]Carapezza et al. (2003); [F]Carapezza et al. (2005); [G]Barberi et al. (2007); [H]Carapezza and Tarchini (2007); [I]This paper.

Table 2. Diffuse CO_2 and H_2S soil flux at Colli Albani

Populations	Frequency %	Area m^2	Mean flux (LL-UL) g/m^2day	Total flux (LL-UL) ton/day
CO_2 flux Cava dei Selci, July 2009 (159 measures over 8200 m^2)				
A	77	6314	1933 (1407-2935)	12.5 (9.1-18.9)
B	23	1886	147 (113-216)	
H_2S flux Cava dei Selci, July 2009 (75 measures over 6400 m^2)				
A	39	2496	14.4 (6.7-74.9)	0.036 (0.017-0.187)
B	61	3904	0.026 (0.0023-0.03)	
CO_2 flux Solforata di Pomezia, May 2007 (356 measures over 229,000 m^2)				
A	16	36,640	2048 (1440-3367)	89.2 (64.5-141.4)
B	57	130,530	104 (86-132)	
C	27	61,830	9.4 (7.7-12)	
H_2S flux Solforata di Pomezia, May 2007 (83 measures over 77,000 m^2)				
A	24	18,480	60 (38-128)	1.12 (0.7-2.4)
B	76	58,520	0.06 (0.05-0.07)	
CO_2 flux Tor Caldara, August 2005 (28 measures over 15,700 m^2)				
A	38	5966	1830 (1352-3117)	11.5 (8.4-19.6)
B	62	9734	56 (39-104)	
CO_2 flux Tor Caldara, July 2009 (61 measures over 11,400 m^2)				
A	80	9120	167 (94-426)	1.53 (0.9-3.9)
B	20	2280	1.7 (1.2-2.9)	

LL = lower limit and UL = upper limit identify the 90% confidence interval

Table 3. Descriptive statistics of automatically detected CO_2 flux and environmental parameters

Measured values

Parameter		Meas. No.	Avg.	Min.	Max.	Std. Dev.
CO_2 flux	g/m^2day	30003	366.6	10.1	4286	277.4
Air T	°C	34282	14.5	-6.3	43.4	8.3
Air hum.	%	34318	74.8	2.0	98.7	21.0
Air P	hPa	29832	997.5	948.4	1020.8	7.1
Soil T	°C	25200	16.1	1.9	28.6	6.4
Soil hum.	%	31551	50.0	17.5	100.0	16.3
Wind dir.	°N	34428	154.7	0.0	358.7	95.3
Wind speed	m/s	34428	0.9	0.0	9.7	1.1

Correlation matrix

	CO_2 flux g/m^2day	Air T °C	Air hum. %	Air P hPa	Soil T °C	Soil hum. %	Wind dir. °N	Wind speed m/s
CO_2 flux	1.00	0.34	-0.28	0.09	0.22	-0.31	0.11	0.04
Air T	0.34	1.00	-0.76	-0.03	0.82	-0.62	0.31	0.29
Air hum.	-0.28	-0.76	1.00	0.03	-0.46	0.50	-0.34	-0.43
Air P	0.09	-0.03	0.03	1.00	0.00	-0.09	-0.06	-0.27
Soil T	0.22	0.82	-0.46	0.00	1.00	-0.71	0.09	0.00
Soil hum.	-0.31	-0.62	0.50	-0.09	-0.71	1.00	-0.07	-0.03
Wind dir.	0.11	0.31	-0.34	-0.06	0.09	-0.07	1.00	0.25
Wind speed	0.04	0.29	-0.43	-0.27	0.00	-0.03	0.25	1.00

Table 4. CO_2 and H_2S air concentration measured by TDL profiles at Colli Albani

Profile no.	**Date**	**Location**	**Length m**	**Height cm**	**Duration min**	**CO_2 concentration ppm**			**H_2S concentration ppm**		
Cava dei Selci						**min.**	**avg.**	**max.**	**min.**	**avg.**	**max.**
1	Feb. 2007	Depression	64.6	20	90	464	779	1709	0.43	5.56	7.96
2	Feb. 2007	Near fence	43	20	34	457	627	1392	0.41	2.83	11
3	Feb. 2007	Channel	43.4	20	43	1142	2632	6230	9.03	30.81	122
3 bis.	Feb. 2007	Channel	44.2	20	104	558	750	1290	1.2	3.9	8.9
4	Feb. 2007	Near houses	50	25	60	355	468	649	0.1	0.6	5.2
5	Feb. 2007	Via A. Paris	34.2	25	24	468	527	557	0.3	1.6	10.4
6	May 2007	Depression	52	20	1140	n.d.	n.d.	n.d.	0.5	13.9	378
7	May 2007	Street	107	25	23	n.d.	n.d.	n.d.	0.1	1	2.3
8	May 2007	S. of depression	32	25	40	n.d.	n.d.	n.d.	0.7	7	20.5
9	May 2007	Depression	45.3	20	249	192.5	4002	11,115	n.d.	n.d.	n.d.
10	July 2009	Depression	25	20	746	757	7279	29,770	0.7	52	508
Solforata di Pomezia											
1	Feb. 2007	Lake	52.4	25	70	437	862	5102	0	4.7	42.4
2	Feb. 2007	Channel day	168.6	25	190	467	611	1005	1.8	4.6	11.9
3	Feb. 2007	Lake	98.8	25	60	509	830	1450	0	5.0	10.4
4	Feb. 2007	Channel night	99	25	85	625	1982	2751	3.9	24.4	65.6
5	May 2007	Lake	68.4	20	130	139	880	3026	0.2	5	25.8
6	May 2007	Lake	58.8	20	95	n.d.	n.d.	n.d.	3.1	8.3	22.6
7	May 2007	Channel over night	118	25	1140	160	506	3384	0.2	5.1	342.6
Tor Caldara											
1	July 2009	Miniera Grande	41	25	120	291.2	481.9	684.1	0.8	3.6	9.9
2	July 2009	Miniera Piccola	15	25	70	721.4	829.8	956.9	1.1	6.3	13.8

Table 5. Persistence of H_2S air concentration in TDL profiles at Cava dei Selci and related health effects

Concentration ppm	0-10	10-15	15-100	100-250	>250
Effects	TWA	STEL	Pharyngitis Bronchitis Conjunctivitis	Irritation of upper respiratory tract	Pulmonary oedema with risk of death
Profile 6 Duration minutes	280	290	450	70	35
Profile 10 Duration minutes	170	99	325	106	38

Table. 6. Estimation of CO_2 and H_2S viscous fluxes from Solforata

Flow rate l/min	Meas. vents no.	Avg. l/m	Total m^3/day	Tot. estim. vent no.	Avg. l/m	Total m^3/day	Meas. ΦCO_2 kg/day	Tot. estim. ΦCO_2 kg/day	Meas. ΦH_2S kg/day	Tot. estim. ΦH_2S kg/day
Lake										
0.7 - 4	0	-	-	400	1.25	718.10	-	1329.36	-	13.26
4 - 27	13	20.23	518.98	45	20.23	1310.90	960.74	2426.76	9.59	24.21
27- 62	8	45.05	378.71	8	45.05	518.98	701.08	960.75	6.99	9.59
Total	*21*			*453*			*1661.82*	*4716.87*	*16.55*	*47.03*
Channel	Meas. vents no.	l/m avg.	m^3/day tot	Tot. estim. vents	l/m avg.	Tot. m^3day	kg/day	kg/day	kg/day	kg/day
0.7 - 4	6	1.25	10.77	100	1.25	179.52	19.94	332.33	0.20	3.32
4 - 27	3	10.27	44.35	10	10.27	147.89	82.10	273.78	0.82	2.73
27- 62	0	-	-	0	-	-	-	-	-	-
Total	*9*			*110*			*102.04*	*606.11*	*1.02*	*6.,05*
						Total	*1763.86*	*5322.11*	*17.57*	*53.08*

The total estimated vent number includes measured and visually estimated emissions

Table 7. Radon concentration in Colli Albani soils

Locality	Soil depth m	Measurements no.	Rn concentration range $kBqm^{-3}$			Data source
			Min	Max	Mean	
Cava dei Selci-SMM	0.7-1.0	243	1.48	367.78	52.03	Beaubien et al., 2003
Cava dei Selci depression	0.3	11	1.45	69.7	32.9	This paper
Cava dei Selci house gardens	0.8	4	21.45	97.55	58.09	This paper
VF-VC	0.3	3	0.88	4.38	2.83	This paper
SMM	0.3	2	6.32	118.0	62.16	This paper
Tor Caldara	0.5		0.1	12.9	4.09	Voltattorni et al., 2009
Tor Caldara	0.3	5	0.05	2.77	1.03	This paper
Lavinio	0.3	7	0.12	5.36	2.11	This paper

SMM = Santa Maria delle Mole, west of Cava dei Selci VF-VC = Vigna Fiorita-Valle Cupella anomalous degassing sites near Cava dei Selci (see Carapezza et al., 2005; Carapezza and Tarchini, 2007); Lavinio is the inhabited zone nearest to Tor Caldara.

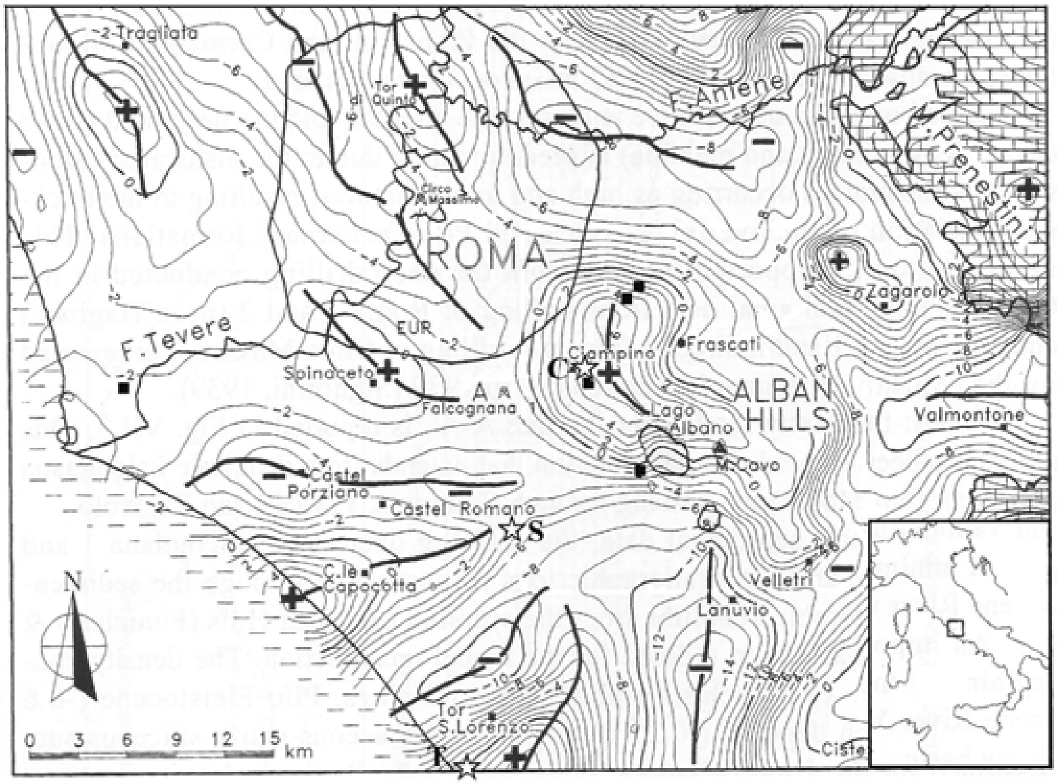

Tragliata
Tor di Quinto
Circo Massimo
ROMA
F. Aniene
F. Prenestini
Zagarolo
Frascati
Ciampino
C
EUR
F. Tevere
Spinaceto
A
Falcognana 1
Lago Albano
ALBAN HILLS
Valmontone
M. Cavo
Castel Porziano
Castel Romano
S
Velletri
C.le Capocotta
Lanuvio
Tor S.Lorenzo
T
Ciste
N
0 3 6 9 12 15 km

Fig. 1

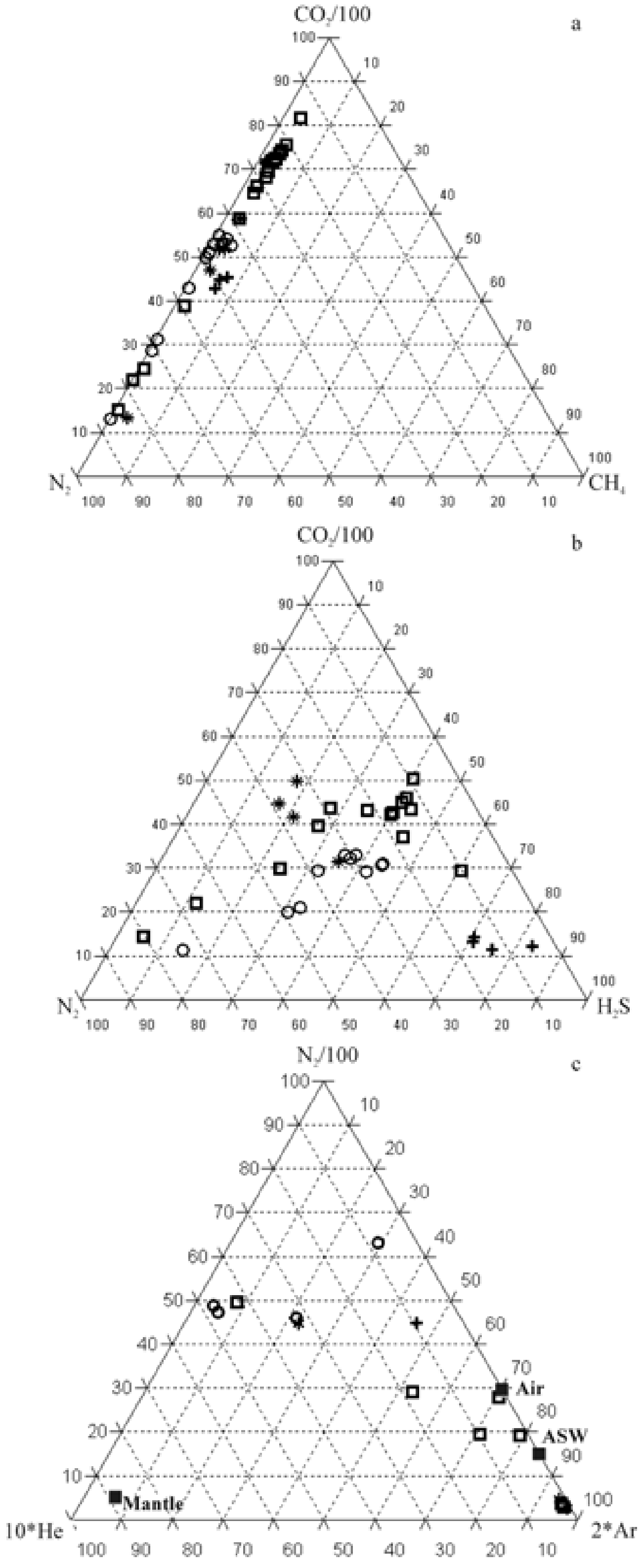


Fig.2

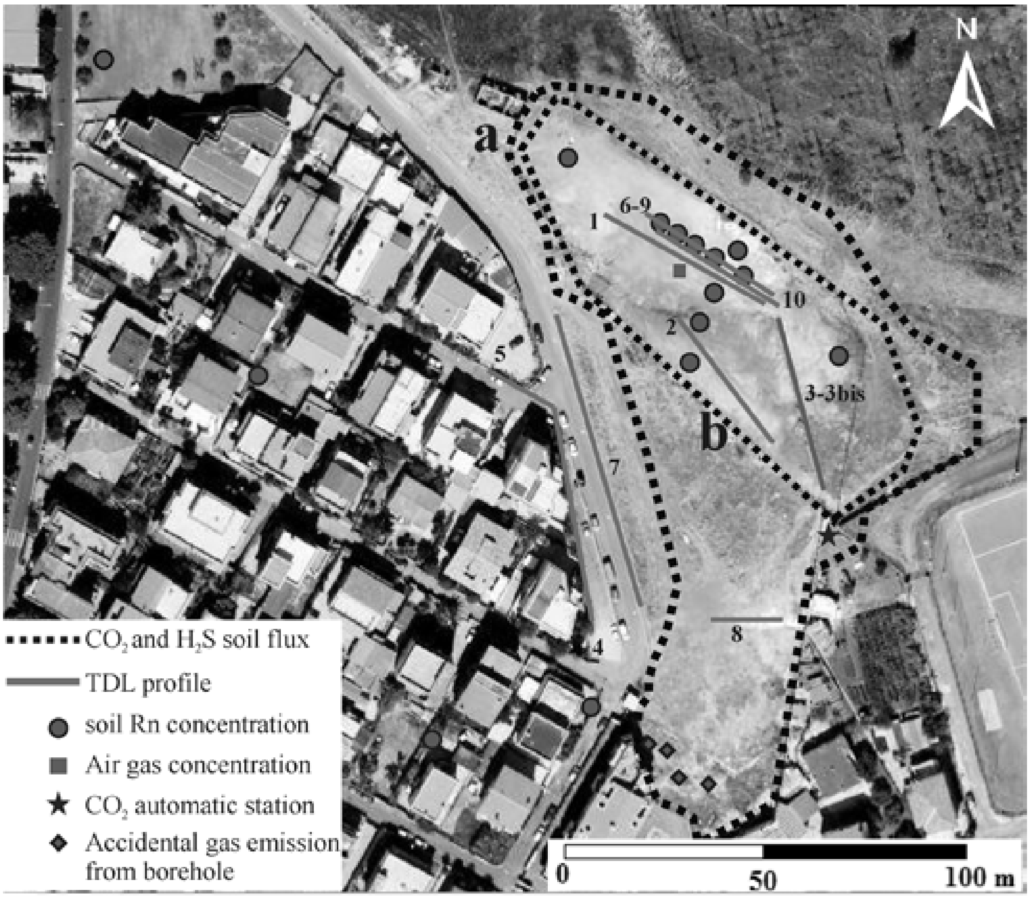

N
a
b
1
6-9
10
2
3-3bis
5
7
8
4
CO$_2$ and H$_2$S soil flux
TDL profile
soil Rn concentration
Air gas concentration
CO$_2$ automatic station
Accidental gas emission from borehole
0
50
100 m

Fig. 3

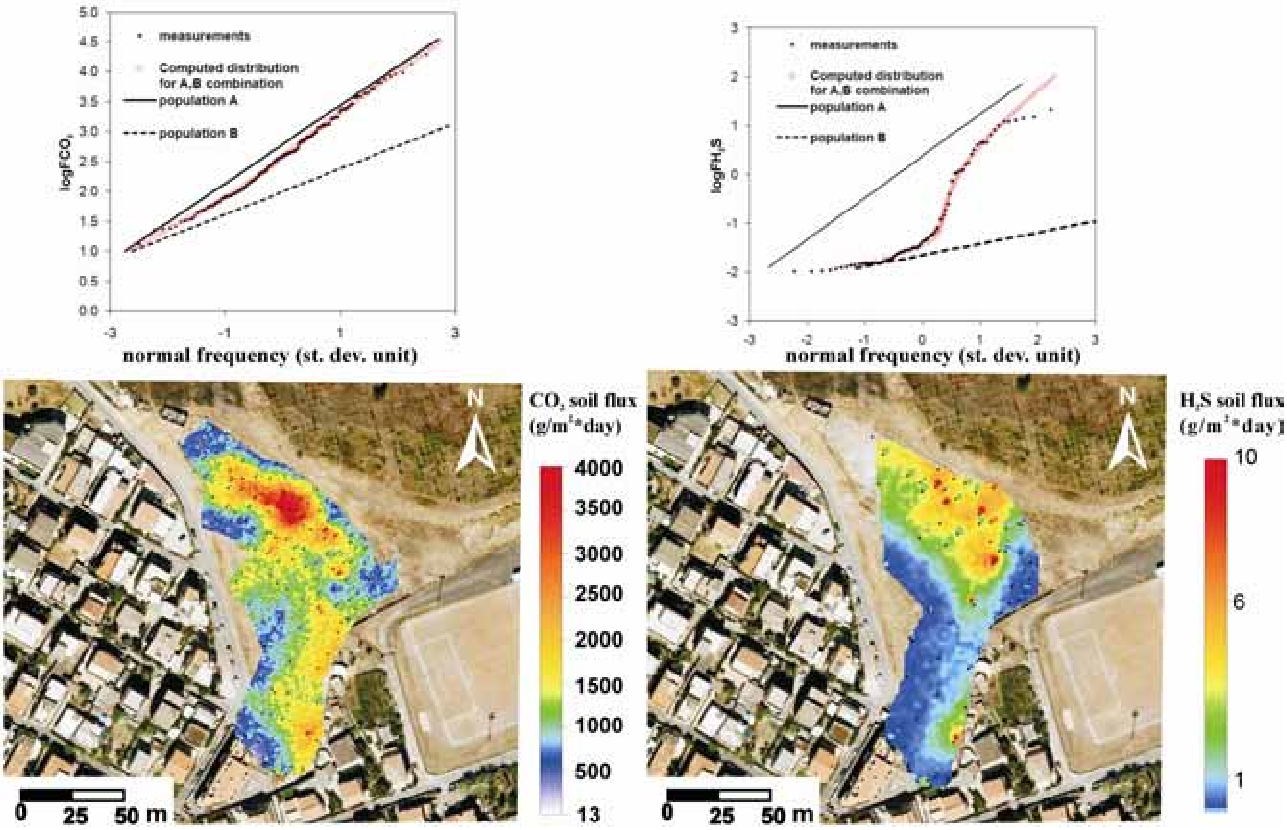

measurements
Computed distribution for A,B combination
population A
population B
logFCO$_2$
normal frequency (st. dev. unit)
logFH$_2$S
normal frequency (st. dev. unit)
CO$_2$ soil flux (g/m^2*day)
4000
3500
3000
2500
2000
1500
1000
500
13
H$_2$S soil flux (g/m^2*day)
10
6
1
N
0
25
50 m

Fig. 4

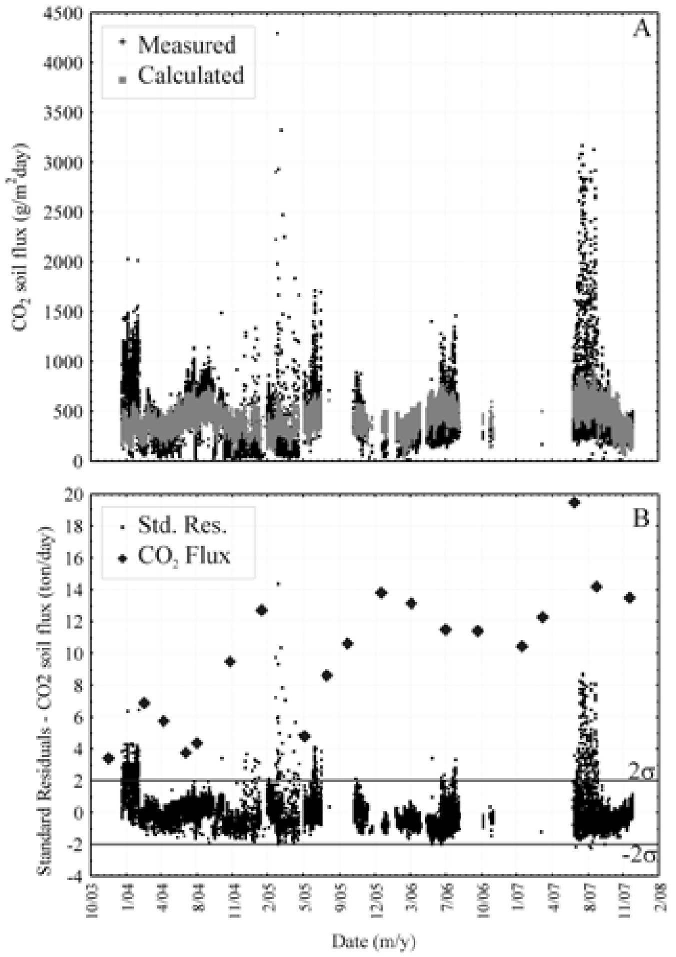

A
Measured
Calculated
CO2 soil flux (g/m2day)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
B
Std. Res.
CO2 Flux
Standard Residuals - CO2 soil flux (ton/day)
20
18
16
14
12
10
8
6
4
2
0
-2
-4
2σ
-2σ
10/03
1/04
4/04
8/04
11/04
2/05
5/05
9/05
12/05
3/06
7/06
10/06
1/07
4/07
8/07
11/07
2/08
Date (m/y)

Fig. 5


N

Fig. 6

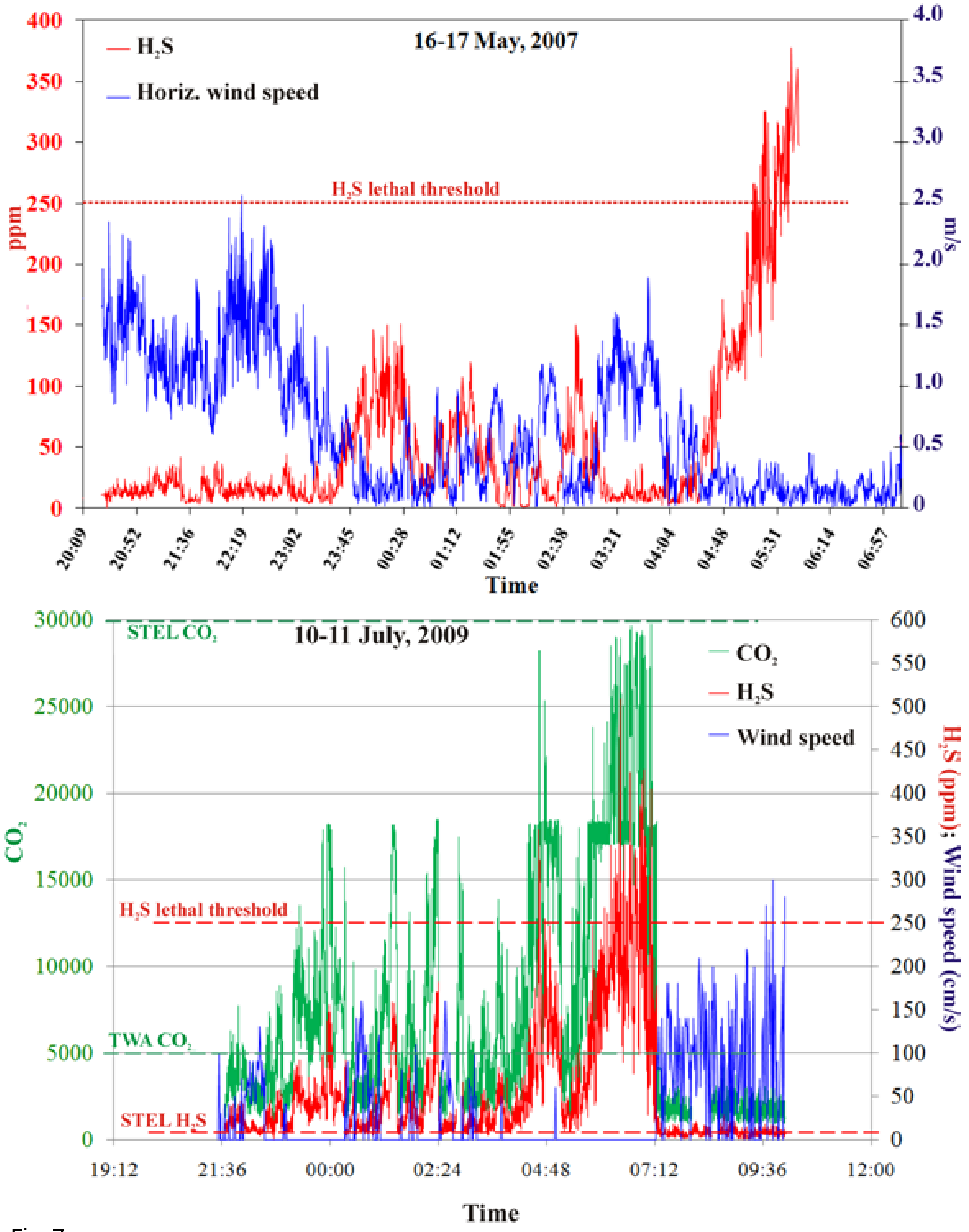

16-17 May, 2007
H$_2$S
Horiz. wind speed
H$_2$S lethal threshold
ppm
m/s
400
350
300
250
200
150
100
50
0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
20:09
20:52
21:36
22:19
23:02
23:45
00:28
01:12
01:55
02:38
03:21
04:04
04:48
05:31
06:14
06:57
Time
10-11 July, 2009
STEL CO$_2$
CO$_2$
H$_2$S
Wind speed
H$_2$S lethal threshold
TWA CO$_2$
STEL H$_2$S
CO$_2$
H$_2$S (ppm); Wind speed (cm/s)
30000
25000
20000
15000
10000
5000
0
600
550
500
450
400
350
300
250
200
150
100
50
0
19:12
21:36
00:00
02:24
04:48
07:12
09:36
12:00
Time

Fig. 7

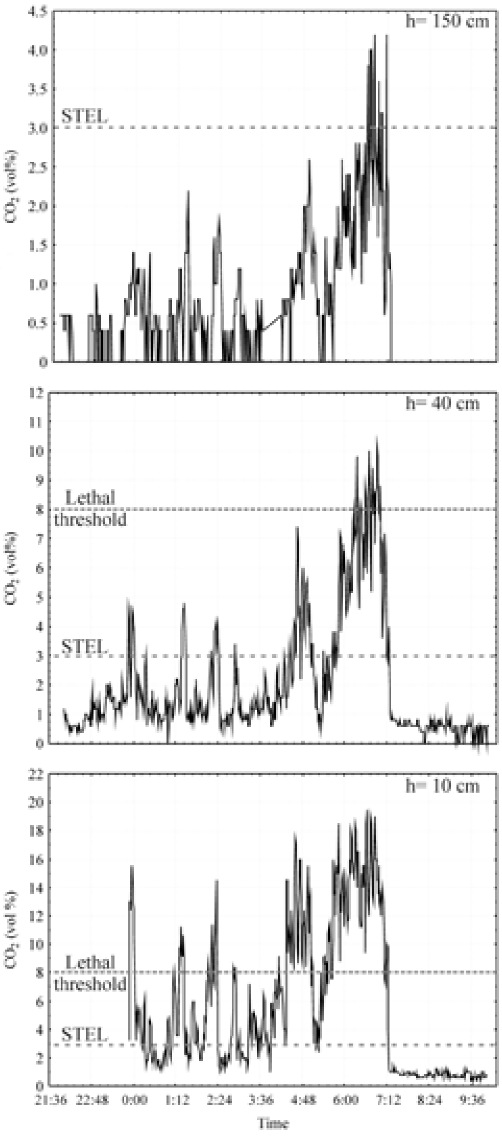
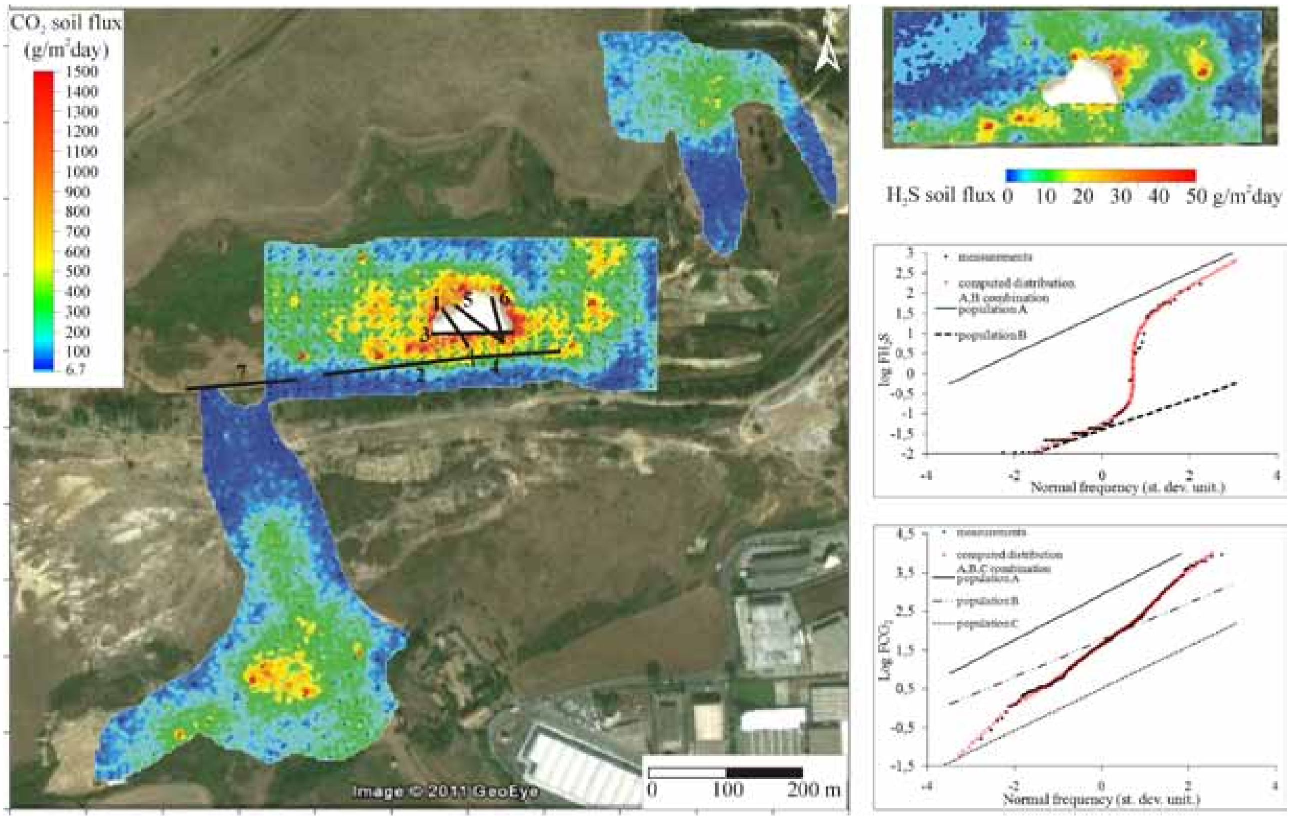

h= 150 cm
STEL
CO$_2$ (vol%)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
h= 40 cm
Lethal threshold
STEL
CO$_2$ (vol%)
0
1
2
3
4
5
6
7
8
9
10
11
12
h= 10 cm
Lethal threshold
STEL
CO$_2$ (vol %)
0
2
4
6
8
10
12
14
16
18
20
22
21:36
22:48
0:00
1:12
2:24
3:36
4:48
6:00
7:12
8:24
9:36
Time

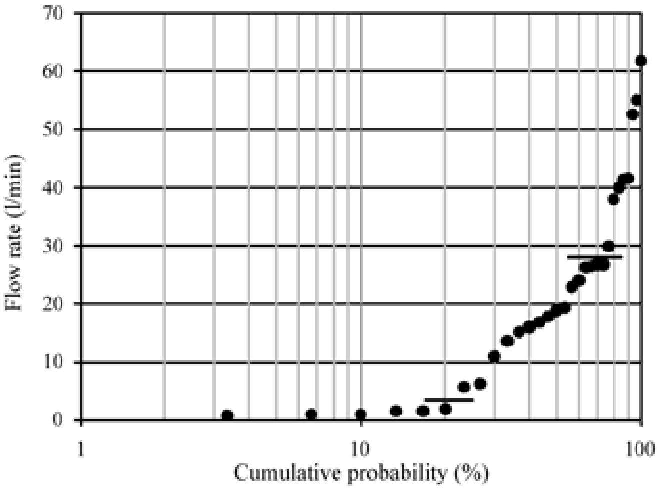
Fig. 8



CO$_2$ soil flux (g/m^{2}day)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
6.7
1
2
3
4
5
6
7
Image © 2011 GeoEye
0
100
200 m
H$_2$S soil flux 0 10 20 30 40 50 g/m^{2}day
measurements
computed distribution A,B combination
population A
population B
log FH$_2$S
Normal frequency (st. dev. unit.)
measurements
computed distribution A,B,C combination
population A
population B
population C
Log FCO$_2$
Normal frequency (st. dev. unit.)

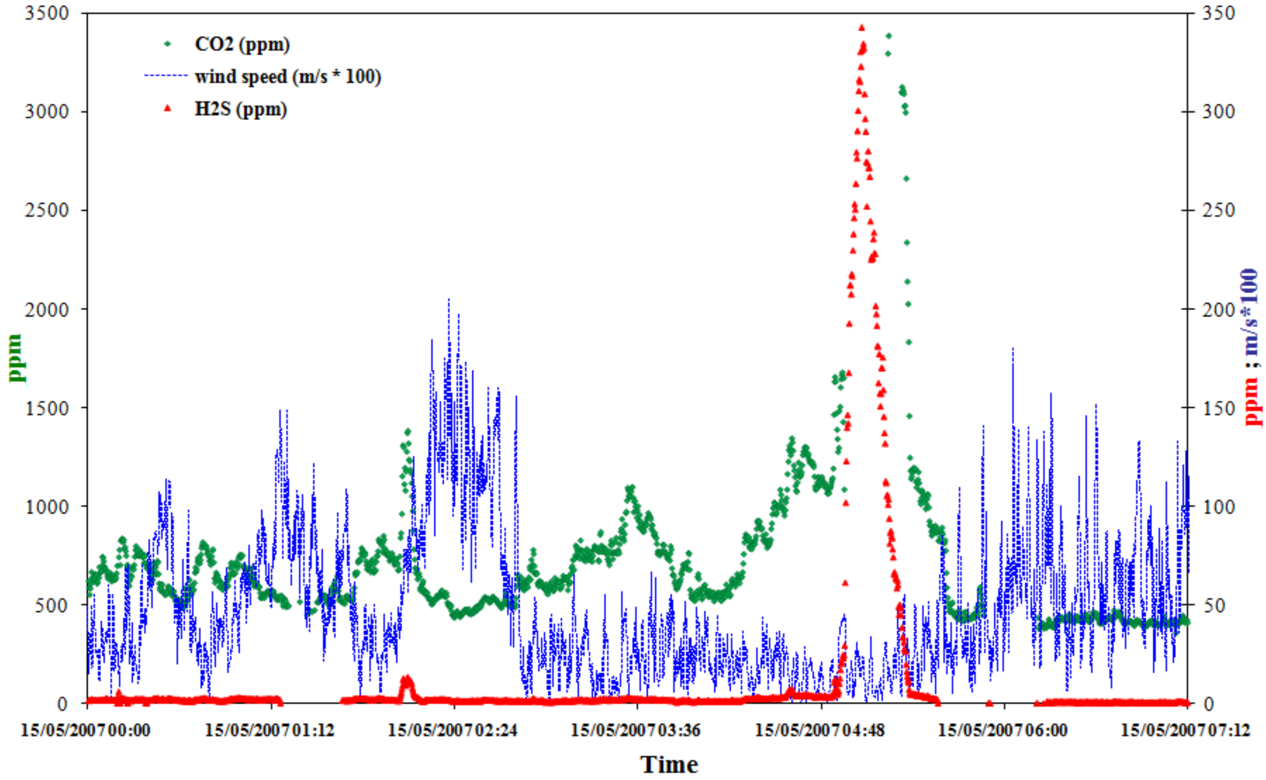
Fig. 9

Fig. 10



Flow rate (l/min)
70
60
50
40
30
20
10
0
1
10
100
Cumulative probability (%)

Fig. 11



CO2 (ppm)
wind speed (m/s * 100)
H2S (ppm)
ppm
ppm ; m/s*100
3500
3000
2500
2000
1500
1000
500
0
350
300
250
200
150
100
50
0
15/05/2007 00:00
15/05/2007 01:12
15/05/2007 02:24
15/05/2007 03:36
15/05/2007 04:48
15/05/2007 06:00
15/05/2007 07:12
Time

Fig. 12

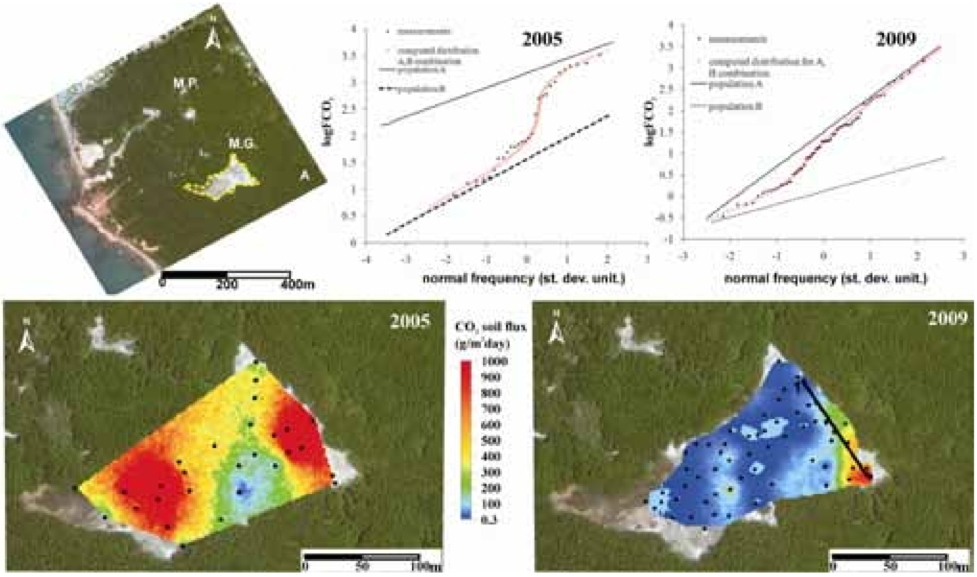
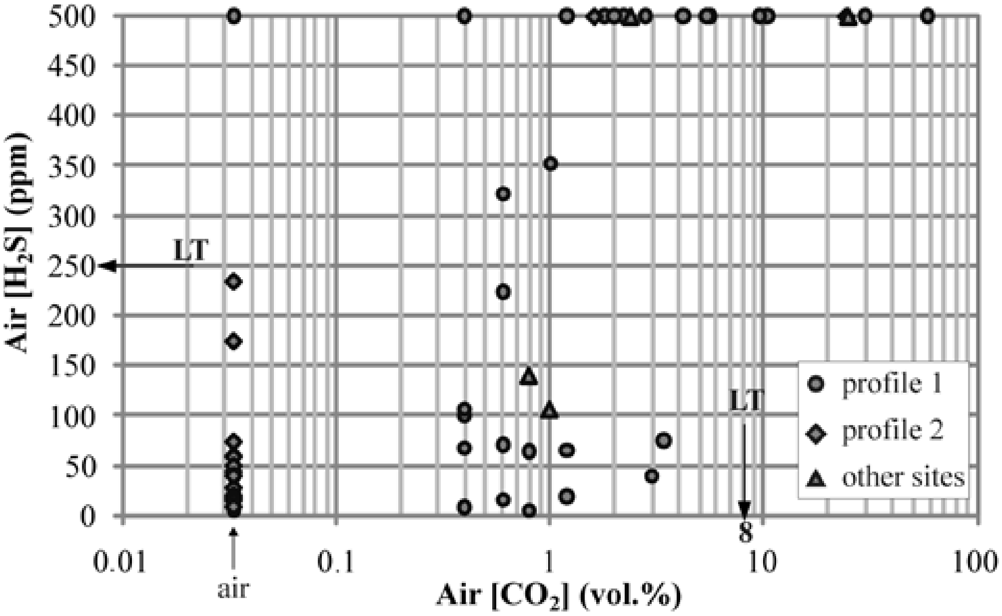

N
M.P.
M.G.
A
0
200
400m
2005
measurements
computed distribution A,B combination
population A
population B
logFCO$_2$
normal frequency (st. dev. unit.)
2009
measurements
computed distribution for A, B combination
population A
population B
logFCO$_2$
normal frequency (st. dev. unit.)
2005
CO$_2$ soil flux (g/m^{2}day)
1000
900
800
700
600
500
400
300
200
100
0.3
2009
0
50
100m
0
50
100m

Fig. 13

Fig. 14



Air [H$_2$S] (ppm)
500
450
400
350
300
250
200
150
100
50
0
LT
LT
8
0.01
0.1
1
10
100
air
Air [CO$_2$] (vol.%)
● profile 1
◆ profile 2
▲ other sites

Fig. 15