

## FEASIBILITY OF HIGH-FREQUENCY MICRO-GASCHROMATOGRAPHY SOIL GAS MONITORING REVEALED AT LA SOLFATARA (CAMPI FLEGREI, ITALY)

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Solfatara crater is a tuff cone located in the central part of Campi Flegrei caldera (Campania, Southern Italy) (Fig. 1). The most recent unrests (1970-1972; 1982-1984) were centered in the caldera inner part, exactly below Solfatara zone (Barberi *et al.*, 1984; 1989; Orsi *et al.*, 1996). After the last bradyseismic event (1982-1984) upwards ground movement slightly decreased, but since 2000 a new increase was recorded, likely linked with new magmatic fluids input into the hydrothermal system, which caused both fluid-pressure increment in the system and chemical-physical macroscopic changes in fumarolic activity (Chiodini *et al.*, 2008, 2010; 2012). Moreover, Orsi *et al.* (2004) include Solfatara crater in the most prone area for new vent opening.

In our work we studied soil gas reactions in near-surface soil, aiming at assessing the feasibility of a novel geochemical monitoring methodology. We performed two CO<sub>2</sub> and H<sub>2</sub>S soil diffuse degassing surveys with the accumulation chamber and soil concentration measurements of CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, He at 0.5 m depth over a target area of 50 points. Soil gas samples were also collected at different depths (0.3, 0.5, 0.8, 1 m) at 7 points out of the previous 50. The presented study permitted to highlight the main gas reactions taking place in near-surface soil, and showed up the feasibility of a new monitoring technique, high-frequency micro-gaschromatography, which could be settled in more easily accessible sites and under less aggressive environmental conditions than those found close to Solfatara fumaroles.

**Diffuse soil degassing assessment.** During February and April 2014, soil flux surveys were performed at Solfatara with an accumulation chamber equipped with a Li-820 infrared detector (0-2 vol. %) for CO<sub>2</sub> and with TOX-05 detector for H<sub>2</sub>S (0-20 ppm) (Carapezza *et al.*, 2011). Measurements were acquired over a fixed grid of 50 points 5 m spaced. Both maps were processed using ordinary kriging in ArcGis.

**CO<sub>2</sub> flux survey.** The decadal monitoring of CO<sub>2</sub>, in active and quiescent volcanoes, and at Campi Flegrei as well, plays an important role in volcanic surveillance. Besides fumarolic degassing, widespread gas diffusion from soil is affected by the presence of faults and fracture systems. CO<sub>2</sub> anomalies-trend therefore outlines the presence of faults and fractures, which represent the most prone way for magmatic/hydrothermal fluids to reach the surface (Granieri *et al.*, 2010). Soil CO<sub>2</sub> flux map shows that the main faults within Solfatara crater have a NW-SE direction and an associated NE-SW trend, and that the principal CO<sub>2</sub> anomalies are located in the inner area and in the zone of high-temperature fumaroles (e.g. Bocca Nuova T= 160 °C) in agreement with those indicated by Todesco *et al.* (2003), Chiodini *et al.* (2010) and Granieri *et al.* (2010).

We estimated the total diffuse CO<sub>2</sub> soil flux rate to 101.2 tonnes/day. A value very similar to the one estimated by Tassi *et al.* (2013), 79 tons/day, during the nearest in time published survey.

**H<sub>2</sub>S flux survey.** According to Giggenbach (1980), H<sub>2</sub>S fugacity in hydrothermal environments is controlled by pyrite coexisting with an unspecified aluminium-silicate. H<sub>2</sub>S dominates in low-temperature fumaroles and solfataras, where discharges arise from deep hydrothermal systems (Giggenbach, 1980). Since decades, fumarolic gas emissions were sampled and analyzed in order to monitor the hydrothermal system activity, and H<sub>2</sub>S concentration in Solfatara fumaroles spanned 0.5 to 1.5 vol.% (Caliro, *et al.*, 2007; Chiodini *et al.*, 2008; Tassi *et al.*, 2013).

In this work we surveyed the H<sub>2</sub>S diffuse soil flux for the first time at Solfatara, using the same technique for CO<sub>2</sub> (Fig. 1). The H<sub>2</sub>S flux map (minima from green to yellow colors;

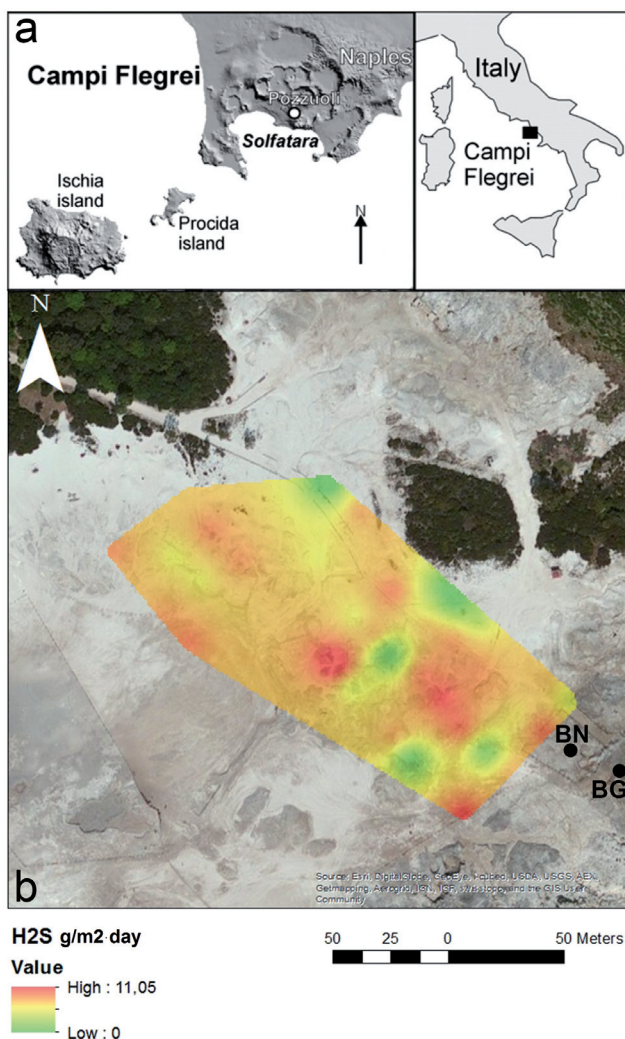


Fig. 1 – a) Hillshade DEM of Campi Flegrei caldera and location of Solfatara crater (mod. after Caliro *et al.* 2007). b)  $\text{H}_2\text{S}$  soil flux map at Solfatara of this work.

the fixed grid, point out that  $\text{CO}_2$  is the predominant species, with percentages spanning 73 to 99 vol. % depending on air contamination, while  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  soil concentrations often are even higher than in H-T fumaroles (up to the 50 % more).  $\text{H}_2$  spans 2 to 2900 ppm, and it shows a clear positive correlation with soil temperature.  $\text{H}_2\text{S}$  maxima and minima are anticorrelated with those of the other gases. The latter species ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , He) do not show a perfect match in maxima and minima distribution (Fig. 2): as uprising gases, a mixture of magmatic fluids flashing hydrothermal liquid to vapour (Caliro *et al.*, 2007), interact with air-saturated waters in shallow low T (< 100 °C) levels, and diffuse through rock volumes of different permeability, explaining the differences in the observed soil gas concentrations. Nevertheless, also other phenomena need to be involved in generating short-scale variations in soil gases: in fact,  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  are enriched in some samples compared to fumarolic composition.

We, therefore, sampled soil gases at different depths in 7 of the previous 50 points, in order to investigate very shallow phenomena governing gas reactions. Figs. 3a and 3b clearly show

maxima from yellow to red colors) shows large variability at small spatial scale. Zones with high values are evidenced not only in the SE sector near Bocca Grande and Bocca Nuova fumarolic vents (BG and BN), but also in the central and western investigated sector. Short-scale variations are commonly associated to micro-fracturing systems of the soil that occur even in apparently homogeneous ground. Also, the spatial variation of the flux is enhanced by the contiguous presence of hydrothermally altered and sealed terrain, low-permeability or less fractured zones (Granieri *et al.*, 2010). But short-scale variations can also depend on fluid interacting with very shallow soil levels, as we will discuss further.

The total soil flux estimated for this first  $\text{H}_2\text{S}$  survey sums up to 0.4 tonnes/day from an area of 0.2  $\text{km}^2$ .

**In-soil gas assessment.** Soil gas were sampled and T were measured at 0.5 m depth over the same 50 point grid of soil flux surveys. Furthermore, we sampled soil gas at different depths (0.3, 0.5, 0.8, 1 m) at seven sites chosen amongst the previous 50, in order to identify processes governing gas reactions at very shallow levels. Dry gas concentrations were measured with Agilent 490 Micro GC Analyzer.

Data acquired at 0.5 m depth over

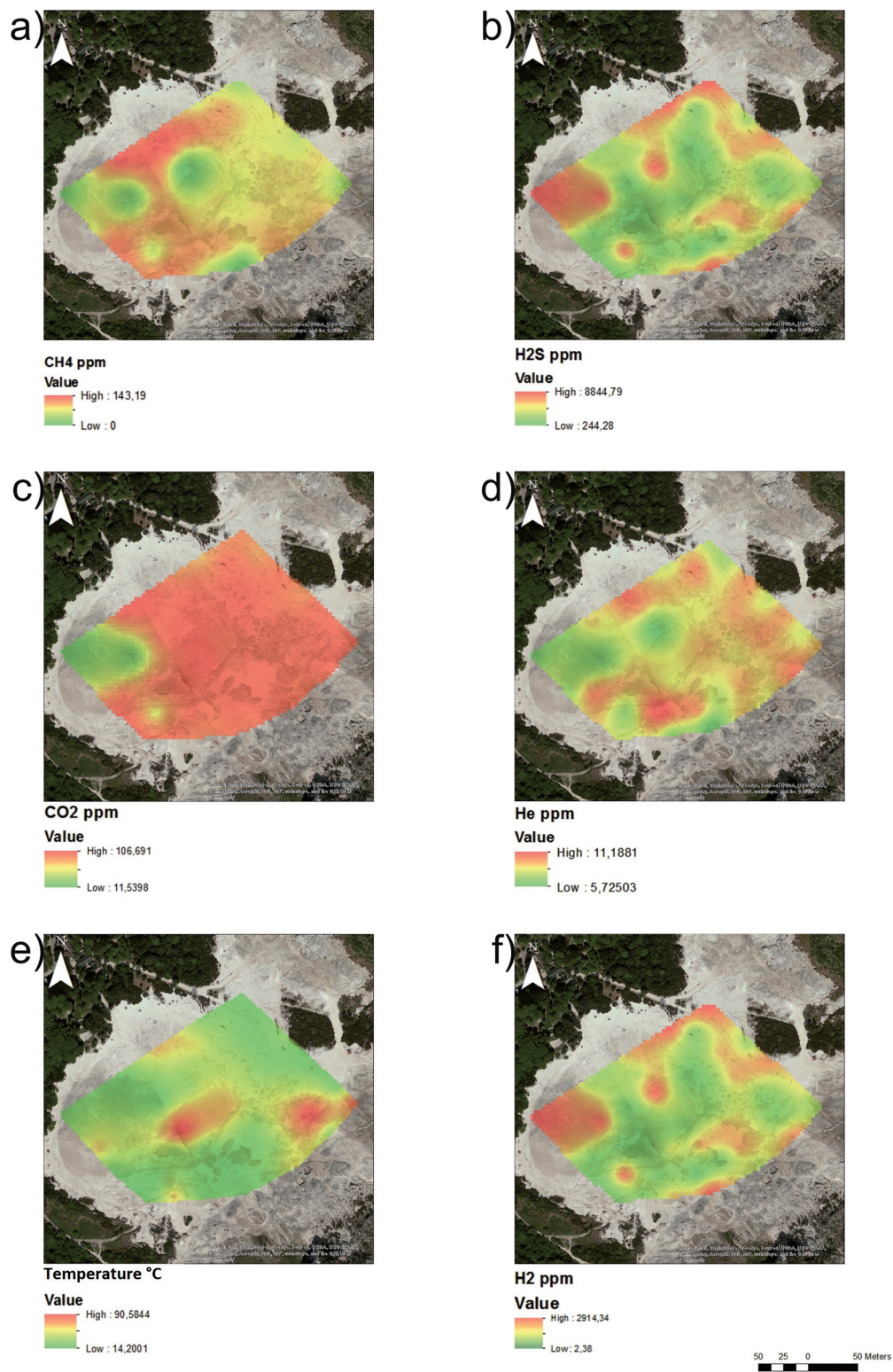


Fig. 2 – Solfatara area concentration maps of: a) CH<sub>4</sub>; b) H<sub>2</sub>S; c) CO<sub>2</sub>; d) He; e) temperature; f) H<sub>2</sub>.



that CH<sub>4</sub> and H<sub>2</sub>S concentrations are way higher in some soil samples than in fumaroles, and that [H<sub>2</sub>] is always positively correlated with T. Furthermore, sampling data show that a decrease of H<sub>2</sub> matches an increase of H<sub>2</sub>S and CH<sub>4</sub> due to T increasing with depth (Figs. 3a and 3b).

On these evidences something has to be hypothesized causing either preferential enrichment of CH<sub>4</sub>, H<sub>2</sub>S or variations in gases equilibrium processes. One possible explanation is the preferential CO<sub>2</sub> removal in surface acid muddy water pools. Another could be that near surface gases condense with neutral pH causing CO<sub>2</sub> dissolution, and thus enrichment in other species. If this cannot be excluded, the quick re-equilibrium of some reactions involving the analysed chemical species seems more noteworthy. We consider, then, two possible reactions for CH<sub>4</sub> and H<sub>2</sub>S genesis and enrichment:



Molar ratios in Eq. 1 justify the observed quick [H<sub>2</sub>] decrease and the less significant (CH<sub>4</sub>) increase with decreasing depth. The linear relation in Fig. 3a shows that reaction 1 occurs quickly and at shallow depth during gas rise, because we observed significant H<sub>2</sub> and CH<sub>4</sub> variations at different depths in the first meter of the soil.

To justify H<sub>2</sub>S enrichment, gas equilibria in sulphur species cannot be considered because H<sub>2</sub>S is the only gas species in the Solfatara volcanic/hydrothermal gas (Chiodini *et al.*, 2001). As previously described, Giggenbach (1980) and Caliro *et al.* (2007) stated that fH<sub>2</sub>S in hydrothermal system is mainly controlled by pyrite coexisting with unspecified allumo-silicate. We can similarly speculate H<sub>2</sub>S enrichment in the shallow Solfatara soil by hydrolysis with sulphide minerals:



All our soil samples show temperature values lower than 100°C and inverse relationship with H<sub>2</sub>S concentrations; this could reflect a variation in thermodynamic conditions compared to the hot fumarolic fluids. In our vertical profile sampling, an increase in H<sub>2</sub>S is very marked and this evidence suggests that the process happens close to the surface. Reaction 2 can be related with emission temperatures, gas flow, soil humidity (condensate) and fH<sub>2</sub>. In fact, when there are high flow/temperature conditions, Eq. 2 can be slowed or even inhibited by a “carrier effect” of the fumarolic gas which likely prevents gas-rock interaction of H<sub>2</sub> or doesn’t allow changes in redox conditions.

As we have previously showed, variations in fH<sub>2</sub> modifies equilibria in Solfatara gas species. Soil (CO), analyzed only in vertical samplings, is affected by reactions in near surface levels too. In Fig. 3d (CO) is plotted as a function of temperature. Samples at T close to 90/100 °C show a CO concentration enrichment, relatively to fumarolic composition (up to 9 ppm against 3.2 ppm in Bocca Grande fumarole). Following Giggenbach (1987), we can linearly combine redox reactions (1) and (3):



To obtain Eq. 4 which explains [CO] increase in the soil:



The previously discussed (CH<sub>4</sub>) increase, framed in a re-equilibration system of all gas species described by Eqs. 1, 2 and 4, leads to a contemporaneous increase in (CO). The observed CO decrease in some soil samples at T < 80 °C is likely related to dilution into the soil with air, resulting also in a T decrease.

**Conclusions.** Previous authors proposed a conceptual geochemical model for Solfatara system, which describes the mixing process between the magmatic component and the hydrothermal one at depth, ruling out the emitted fluid composition and variations into the crater.

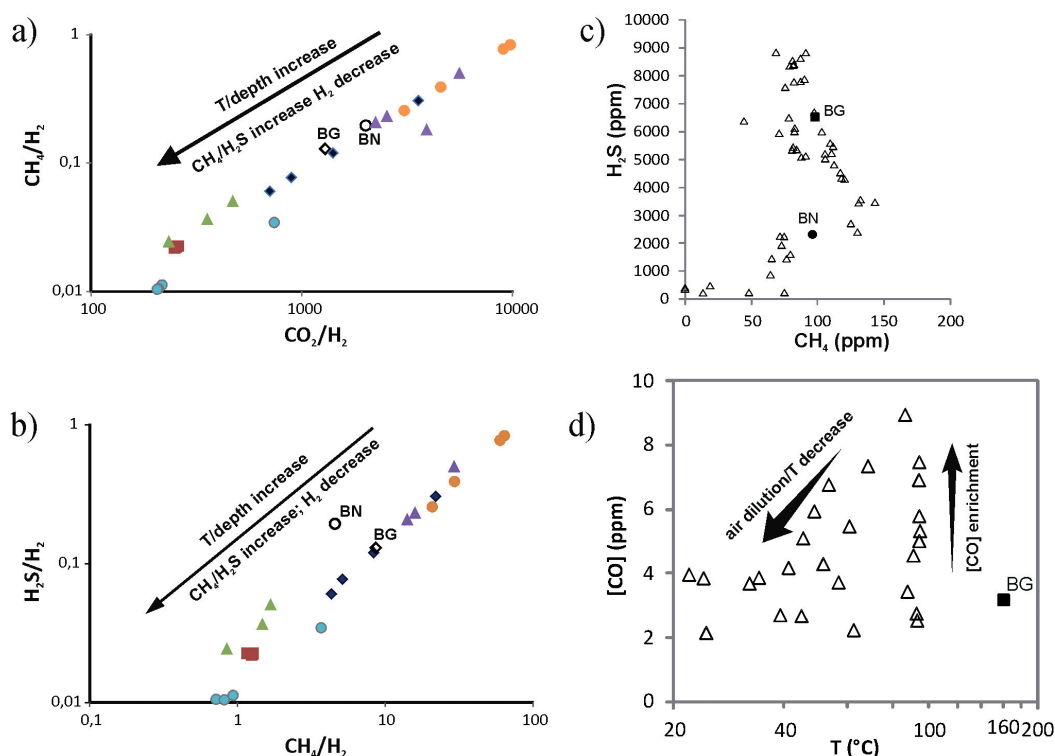


Fig. 3 – Binary plot of: a)  $\text{CH}_4/\text{H}_2$  vs  $\text{CO}_2/\text{H}_2$ ; b)  $\text{H}_2\text{S}/\text{H}_2$  vs  $\text{CH}_4/\text{H}_2$ ; both plots are relative to the 7 points transect at different depths (0.3, 0.5, 0.8, 1 m) compared with fumaroles values (BG; BN) c) Scatter plot of  $\text{CH}_4$  vs  $\text{H}_2\text{S}$  at 0.5 m depth of the 50 points grid inside Solfatara crater. d) Variation of soil (CO) as a function of soil temperature.

Our data is in agreement with this model and we can conclude that, as an enhanced magmatic input causes higher fluid emissions and consequently chemical and physical changes, a chemical variation occurs also in the soil gases (in particular  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , CO and  $\text{CH}_4$ ) and a temperature rise in the whole area. The observed  $\text{H}_2/\text{T}$  positive correlation in our work shows us a very shallow system (actually very first meters below ground surface) of multi-equilibrium reactions described by Eqs. 1, 2 and 4, in which near-surface  $f\text{H}_2$  variations justify enrichment in CO,  $\text{CH}_4$  and  $\text{H}_2\text{S}$ .

Results of our study shows up the feasibility of a new approach in monitoring Solfatara gas emissions: the high frequency micro-gaschromatography (Sortino *et al.*, Interpretations on rise up of volcanic fluids through high-frequency gas analysis by micro gas-cromatograph, oral presentation at GNGTS Meeting, Trieste 2015), a newly experimented setup of classical gaschromatography, which could be installed at Solfatara in more easily accessible sites and under less aggressive environmental conditions than the fumarolic sites.

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