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The effects of environmental parameters on diffuse degassing at Stromboli volcano: insights from joint monitoring of soil CO_2 flux and radon activity

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ABSTRACT

Soil CO_2 flux and ^{222}Rn activity measurements may positively contribute to the geochemical monitoring of active volcanoes. The influence of several environmental parameters on the gas signals has been substantially demonstrated. Therefore, the implementation of tools capable of removing (or minimizing) the contribution of the atmospheric effects from the acquired timeseries is a challenge in volcano surveillance. Here, we present four years-long continuous monitoring (from April 2007 to September 2011) of radon activity and soil CO_2 flux collected on the NE flank of Stromboli volcano. Both gases record higher emissions during fall-winter (up to 2700 Bq*m^{-3} for radon and 750 g m^{-2} day^{-1} for CO_2) than during spring-summer seasons. Short-time variations on ^{222}Rn activity are modulated by changes in soil humidity (rainfall), and changes in soil CO_2 flux that may be ascribed to variations in wind speed and direction. The spectral analyses reveal diurnal and semi-diurnal cycles on both gases, outlining that atmospheric variations are capable to modify the gas release rate from the soil. The long-term soil CO_2 flux

shows a slow decreasing trend, not visible in ^{222}Rn activity, suggesting a possible difference in the source depth of the of the gases, CO_2 being deeper and likely related to degassing at depth of the magma batch involved in the February-April 2007 effusive eruption. To minimize the effect of the environmental parameters on the ^{222}Rn concentrations and soil CO_2 fluxes, two different statistical treatments were applied: the Multiple Linear Regression (MLR) and the Principal Component Regression (PCR). These approaches allow to quantify the weight of each environmental factor on the two gas species and show a strong influence of some parameters on the gas transfer processes through soils. The residual values of radon and CO_2 flux, i.e. the values obtained after correction for the environmental influence, were then compared with the eruptive episodes that occurred at Stromboli during the analysed time span (2007-2011) but no clear correlations emerge between soil gas release and volcanic activity. This is probably due to *i)* the distal location of the monitoring stations with respect to the active craters and to *ii)* the fact that during the investigated period no major eruptive phenomena (paroxysmal explosion, flank eruption) occurred. Comparison of MLR and PCR methods in time-series analysis indicates that MLR can be more easily applied to real time data processing in monitoring of open conduit active volcanoes (like Stromboli) where the transition to an eruptive phase may occur in relatively short times.

1 – Introduction

Real-time monitoring of gas release (output and composition) at active volcanoes is useful to forecast changes in volcanic activity. Active volcanoes are characterized by persistent huge gas emissions from craters, fumaroles and also diffusively from soils (Allard et al., 1991; Burton et al., 2013; Inguaggiato et al., 2013) and systematic gas monitoring may help to detect precursory signals of incoming eruptions (e.g., Aiuppa et al., 2009; Padrón et al., 2013). In recent years, this approach was applied at several volcanoes to record geochemical changes during volcanic activity and to investigate their role before, during and after major eruptive episodes (including flank instabilities; e.g., Carapezza et al., 2004 and 2009; Alparone et al. 2005; Cigolini et al., 2005). Another open and debated issue is the role of degassing prior the onset of earthquakes (Toutain and Baubron, 1999; Salazar et al., 2001) and during earthquake-volcano interactions including seismic-volcanic unrest (Cigolini et al., 2007; Padilla et al., 2014).

Carbon dioxide, after water, is the most abundant volatile dissolved in magmas and, because of its relatively low solubility in magmatic liquids, it is essentially released at higher depths and before other gas species (Pan et al., 1991, Papale et al., 2006). Notably, measurements of soil CO_2 fluxes or CO_2 concentrations in volcanic plumes, are critical for detecting degassing processes related to changes in the plumbing system of the volcano.

Radon is a noble gas, a daughter decay product of ^{226}Ra and belongs to the ^{238}U decay chain. Due to its short half-life ($t_{1/2}$= 3.82 days), ^{222}Rn can be used as a tracer of both diffuse and localized degassing since it can substantially be measured everywhere. Radon concentrations may be moderate during diffuse degassing, but during fracture opening they may reach extremely high values (higher than 10^6 Bq/m^3, as measured in Stromboli crater area; Cigolini et al., 2013). Its ascent towards the surface is strictly ruled by the mobility of other gas phases, such as CO_2 and H_2O defined as "carrier gases" (Gauthier and Condomines, 1999). The joint measurements of soil CO_2 flux and ^{222}Rn activity have been used to search possible volcanic and seismic precursors (Makario Londoño, 2009), as well as to track fluid migration and outgassing along active faults, fractures or fumaroles (Baubron et al., 2002; Faber et al., 2003; Zimmer and Erzinger, 2003). Moreover, combined surveys of ^{222}Rn, ^{220}Rn and CO_2 give us a clue to discriminate distinct gas sources (i.e. rock fracturing, hydrothermal, magmatic) (Giammanco et al., 2007; Siniscalchi et al., 2010) and, to track the evolution of a volcanic unrest phase (Padilla et al., 2013).

Continuous and automatic measurements substantially increase the possibility to identify precursory signals, since the data are easily collected, transferred and processed in near real-time (Brusca et al., 2004; Viveiros et al., 2008; Cigolini et al., 2009; Carapezza et al., 2009). Environmental parameters are critical in modulating gas release from soils, including radon and CO_2 (Pinault and Baubron, 1996; Carapezza and Granieri, 2004; Pérez et al., 2007; Cigolini et al., 2009) and their effects must be considered during continuous geochemical monitoring.

In this respect, a promising challenge is to establish a fully-automated data processing able to minimize the effects of environmental factors on the acquired data. In this way, data obtained by the geochemical monitoring networks can be easily transferred to the authority responsible of volcano surveillance. The statistical treatment or the spectral analysis of the data are the mostly used methods to recognize and remove the contribution of the atmospheric factors (e.g. Carapezza et al., 2009; Laiolo et al., 2012; Rinaldi et al., 2012; Silva et al., 2015; Viveiros et al., 2008; 2014). Particularly, the spectral analysis may be positively applied to recognize diurnal to seasonal cycles and to investigate the processes ruling the release of gases from soils (Rinaldi et al., 2012; Martin-Luis et al., 2015).

Radon concentrations can be diluted by major fluxes of CO_2 and water vapor (e.g., Giammanco et al., 2007; Siniscalchi et al., 2010). Recently, Girault et al. (2014) and Girault and Perrier (2014) have shown, at the Syabru-Bensi hydrothermal system (Central Nepal), that radon is generated from a shallow source (a rock thickness of 100 m is sufficient to account for the observed radon discharge) and incorporated into upraising CO_2. In active volcanoes radon can be carried to the surface from great depths along major faults. Cigolini et al. (2013) have shown that high radon emissions can be related to the ascent of CO_2-bearing hot fluids along the fractures (200-300 m deep) surrounding the crater rim of Stromboli volcano (at about 700-720 m a.s.l.) and well correlate with the estimated depth of the source region of VLP events (e.g., (Chouet et al., 1997; Marchetti and Ripepe, 2005). Previous investigations have shown that CO_2 fluxes and ^{222}Rn concentrations at Stromboli are within the range of those measured in other open-conduit active volcanoes (Cigolini et al., 2013; Inguaggiato et al., 2013).

In this paper, we present four years of continuous monitoring of ^{222}Rn activity and soil CO_2 flux collected by two automatic stations located on the north-eastern upper flank of Stromboli Island (Fig. 1). The measurement sites have been chosen in the light of previous surveys: anomalous radon values were recorded in this site during periods of sustained volcanic activity and before, during and after the paroxysmal explosion of March 15, 2007 (Cigolini et al., 2013). Similarly, systematic measurements of soil CO_2 flux revealed anomalous degassing areas on the volcano slopes and this site has been identified as a potential target for continuous monitoring (Carapezza et al., 2009).

2 – Stromboli volcano

Stromboli is the north-easternmost island of the Aeolian archipelago and reaches an elevation of 924 m a.s.l. (Fig. 1). It is a composite stratovolcano consisting of lava flows alternated with abundant tephra deposits. The emerged part of the volcanic edifice was built in the last 100 ky (Francalanci et al., 1989; Hornig-Kjiarsgaard et al., 1993). The morphology of the island results from periods of extrusive growth alternated to lateral collapses, in turn related to dyke intrusions, magma upwelling and regional tectonics (Tibaldi, 2003 and 2004; Corazzato et al., 2008). The volcano is well known for its typical persistent explosive activity called Strombolian, that started approximately 2 ky ago (Rosi et al., 2000; Arrighi et al., 2004). Strombolian activity is characterised by continuous degassing with the emission, on average every 15-20 minutes, of juvenile material (glowing scoriae, lapilli and ash) ejected from the active vents located within the crater terrace at ~700 m. a.s.l. This mild explosive activity is episodically interrupted by lava flows, major and paroxysmal explosions (Barberi et al., 1993 and 2009) that can be accompanied by flank failure and collapses, which may also generate tsunamis, like in 1930 and recently in December 2002 (Tinti et al., 2006). Paroxysmal events, such as the ones occurred on April 5, 2003 and March 15, 2007, are the most violent volcanic explosions of Stromboli and are characterized by the ejection of the so-called "golden pumices" (nearly aphyric, phenocrysts < 10 vol%, highly vesicular > 50 vol%, low viscosity K-basaltic pumiceous materials; Métrich et al., 2005 and 2010). These ejecta are generally mixed with degassed scorias (the latter also ejected during the typically mild Strombolian activity) and with ballistic solid blocks. The CO_2 and H_2O contents measured in primitive melt inclusions, found within forsteritic olivines of the golden pumices, indicate that these materials represent the undegassed magma residing in the deeper part of the Stromboli plumbing system (Bertagnini et al., 2003; Francalanci et al., 2004; Métrich et al., 2005; Cigolini et al., 2008; 2014).

Soon after the 2002-2003 effusive event, a great improvement of the monitoring system was undertaken under the coordination of the Italian Civil Protection Department. This advance on ground-based monitoring allowed the scientific community to acquire a great amount of geophysical, geochemical and geodetic data during the most recent effusive episodes, as well as during the span of time characterized by low to high explosive activity (cf. Barberi et al., 2009; Ripepe et al., 2009; Calvari et al., 2014; Rizzo et al., 2014). Recent investigations have also shown that within the latter years there was an increase in the radiative heat power associated to several minor lava overflows within the summit area (Coppola et al., 2012; Calvari et al., 2014). Geochemical monitoring at Stromboli has involved the following activities: soil radon concentration (Cigolini et al., 2009 and 2013), soil CO_2 flux (Carapezza et al., 2004 and 2009; Federico et al., 2008; Rizzo et al., 2009 and 2014), SO_2 plume measurements by COSPEC (Burton et al., 2009), continuous measurements of CO_2/SO_2 ratios within the volcanic plume (Aiuppa et al., 2009 and 2011). These methods were tested to eventually forecast paroxysms and major explosions; in addition, the continuous monitoring of low-temperature fumaroles was useful to detect short-time changes in volcanic activity (Madonia and Fiordilino, 2013). The extension and structure of the complex hydrothermal system of the volcano has been investigated by multidisciplinary studies (involving electrical resistivity, soil CO_2 concentration, temperature and self-potential measurements; Finizola et al., 2006 and 2009; Revil et al., 2011). Geochemical studies on the geothermal aquifer at the periphery of the volcano is an additional tool to detect precursory signals of an impending eruption (Carapezza et al., 2004; Capasso et al., 2005).

3 – Methods and Techniques

Preliminary radon and carbon dioxide surveys were conducted to find the most appropriate sites for continuous monitoring. A network of 21 radon stations has been operative at Stromboli since 2002 (Cigolini et al., 2005; 2009; 2013). Systematic measurements were undertaken by using LR115 track-etches alpha-detectors exposed from two to six weeks (Bonetti et al., 1991), in order to obtain continuous time series on ^{222}Rn emissions. Additionally, periodic short-term measurements has been performed by means of EPERM® electretes (Kotrappa et al., 1993) that allowed to better correlate radon emissions with the variations of volcanic activity (Cigolini et al., 2005 and 2007). These periodic measurements demonstrated that diffuse degassing occurs at Stromboli mainly along the main structural discontinuities. After the February-April 2007 effusive-explosive event, a real-time station for radon measurements was first installed at 520 m a.s.l. at Liscione, on the northeastern side of the cone (see Fig. 1 and Fig. 2a). Similarly, a soil CO_2 flux survey first outlined the main sectors of gas emanation (Carapezza and Federico, 2000) and two automatic soil CO_2 flux stations (and environmental parameters) were installed at Stromboli: one at the summit (Pizzo sopra La Fossa) in 1999, and the second one near the sea-shore in 2001 (Pizzillo). In the following years, CO_2 soil concentration surveys, within the crater terrace and surrounding areas, were performed to identify the sectors of major degassing and higher hydrothermal activity (Finizola et al., 2002 and 2003). Furthermore, Carapezza et al. (2009) performed a wide detailed survey of soil CO_2 flux on the island and sectors of anomalous degassing were detected. Therefore, two soil CO_2 flux and multiparametric fully-automated stations were installed along the ENE flank of the volcano (respectively at Rina Grande and Nel Cannestrà) where anomalous gas emissions were found (Carapezza et al., 2009) (Fig. 2b).

Dataset analysed in this paper refer to the ^{222}Rn and CO_2 measurements acquired by fully automated stations located in the Nel Cannestrà sector (see Fig. 1 and 2). The area is confined between two major structural discontinuities (the N40°E fault, and the N60°E fault) that cross-cut the north-eastern sector of Stromboli. These automated stations consist of two units, one for measuring the isotope of the radon progeny (together with soil temperature and atmospheric pressure) and the other for measuring soil CO_2 flux (by accumulation chamber) together with environmental parameters (atmospheric temperature, humidity and pressure; soil humidity and temperature; wind direction and horizontal speed). The radon unit provides near real-time measurements of ^{222}Rn concentrations (by using a DOSEMan, Sarad Gmbh, Germany) connected to an electronic board able to acquire and transfer the collected data to a radio-modem that sends, by means of a directional antenna, the signal to the COA volcano observatory. The station acquires data every 30 minutes and the radon concentration and soil temperature are measured at 1 m depth. The DOSEMan radonmeter measures α-particles within a 4.5-10 MeV energy window, including both ^{218}Po and ^{214}Po peaks (Gründel and Postendörfer, 2003). An exhaustive description of the radon dosimeter and of the real-time ^{222}Rn station can be found in Cigolini et al. (2009) and Laiolo et al. (2012). Soil CO_2 flux and environmental parameters are measured hourly with a fully equipped automated station produced by West Systems (see Carapezza et al., 2009 for method description). Soil temperature and humidity are measured at 50 cm depth; air CO_2 concentration is measured 30 cm above the soil/air interface (Carapezza et al., 2009). Data are stored on a non-volatile memory and can be retrieved by means of a telemetry system at the volcano observatory (COA, see Fig. 1). The main technical characteristics of the sensors used in both stations are reported in the supplementary materials (Table S1).

The timespan investigated in this work (April 2007 - September 2011) matches the period in which both instrumentations were mostly operative. In fact, the ^{222}Rn station was installed in early April 2007 and is still operative whereas the automated CO_2 flux station, installed in mid March 2007, was dismissed in late September 2011.

4 – Results

4.1 – Time series of soil CO_2 flux and ^{222}Rn activity

The overall behaviour of the CO_2 and ^{222}Rn signals is somehow similar in the first two years: they both show bell-shaped profiles, strongly ruled by seasonal trend, that reach their lower and stable values during summer and the higher values, with a wider variation range, in winter. A similar behaviour is observed also in multi-modal distributions (see histograms in Fig. 3). Both trends display several marked spikes within each time series (Fig. 3a and 3b) and numerous peaks of the two gases are essentially concordant. In the last two years, soil CO_2 flux shows a decreasing trend, whereas radon activity maintains nearly the same annual average, or simply increase (see Table 1).

Compared with other active volcanic areas, radon shows relatively low concentration (cf. Cigolini et al., 2013 and references therein). Values are essentially below 2000 Bq/m^3 for a large part of the year and may exhibit a short-term variability; the average activity in the four years is around 2000 Bq/m^3 with a standard deviation of 1200 Bq/m^3 (Table 1). During winter (November-February), radon typically exhibits higher average values (Fig. 3a) with peaks up to 7900 Bq/m^3. We remind that the ^{222}Rn activity in the summit area, close to the active vents, shows significantly higher average values reaching 12,500 Bq/m^3 (± 4,200; Laiolo et al., 2012; Cigolini et al., 2013).

Radon seasonal minima refer to late spring-summer periods (March-October) with average values of ~1200 Bq/m^3 and hourly minima close to 200 Bq/m^3. The ^{222}Rn long-term stability on low values seems closely related to the absence of marked weather changes during this season.

The time-series of environmental parameters are shown in Fig. 4; a preliminary analysis of their effects, supported by the correlation coefficients (Table 2), shows that both the ^{222}Rn and CO_2 signals are inversely correlated to soil and air temperature, and positively correlated (especially radon) to soil humidity, in turn depending on rainfall. It is interesting to point out that sudden variations in radon concentrations normally occur within few hours of continuous raining and/or temperature drops. A similar phenomenon has been observed at Furnas volcano (Azores archipelago) during continuous monitoring of CO_2 flux (Viveiros et al., 2008) and radon activity (Silva et al., 2015).

The relation between temperature and ^{222}Rn activity is ascribed to the local thermal gradient (between soil and air temperatures) that affects the efficiency of the in-soil convective cells and, consequently, the migration of gas toward the surface (Mogro-Campero and Fleisher, 1977; Cigolini et al., 2001). Therefore, a marked difference between soil and air temperatures, typical of the fall-winter season, causes an increase in the measured radon activities. The entire dataset shows a clear positive correlation (R= 0.74; Table 2) between soil moisture and radon emissions; indeed, an increase in soil moisture may increase the ^{222}Rn emanation coefficient (i.e. exhalation rate) by one order of magnitude (Nazaroff, 1992; Sakoda et al., 2010; Girault and Perrier, 2012). However, to evaluate the relation between ^{222}Rn activity and soil humidity, we have also to consider the confinement of the box containing the radon detector. The device is placed in an impermeable polycarbonate case (permeable to ^{222}Rn but not to water) at a depth of about 1 m. Thus, if the soil matrix surrounding the case is affected by water saturation, the preferential pathway for radon migration will follow the interface soil-bottom of the case, leading to an increase in α decay counts. Another possibility is that, during a rainfall episode, only the higher portions of soil (down to about 10-30 cm) undergo water saturation that, in turn, temporarily inhibits the free motion of the radon particles toward the surface. Consequently, radon will preferentially be confined at lower levels (i.e., where water content is low or absent) so that decay counts will be drastically higher in the portion of soil where the case (containing the detector) is inserted. As the relation between soil humidity and radon activity essentially depends from soil permeability, the observed behaviour can be inhomogeneous over a given sector of the volcano (Perrier et al., 2009).

Soil CO_2 flux measurements acquired by the automatic station started on mid-March 2007. The four years average value for CO_2 flux is ~600 (±643) g m^{-2} day^{-}1 with a rather high standard deviation (as for radon) (Table 1). The maximum values were reached in January 2008 with fluxes slightly exceeding 7000 g m^{-2} day^{-1}. As already observed for ^{222}Rn activity, minima in soil CO_2 fluxes occur during summer-early fall when values well below 100 g m^{-2} day^{-1} were recorded. A similar trend outlines that the variation of the local thermal gradient is capable to affect also the CO_2 flux from the soil (Viveiros et al., 2014).

Surprisingly, there is a noticeable correlation between soil CO_2 flux and wind, both speed (positive) and direction (negative) (Table 2). In Fig. 5 it is clear how winds blowing toward SE at speed > 8 m/s are able to produce an efficient gas escape from the soil, causing an increase of the CO_2 flux. Such a behaviour is mainly related to a Venturi effect due to a local condition of the Nel Cannestrà station site, that cannot be extrapolated to other sectors of the volcano, considering that it was not observed in the Rina Grande station (see Fig. 2b for location) (Carapezza et al., 2009).

It is interesting to note that the four years-long dataset exhibits a declining long-term trend (Fig. 3b and annual average in Table 1) which can be likely viewed as a decreasing supply of CO_2-rich magma from the deeper to the upper plumbing system. This hypothesis is supported by the long-term trend observed in the CO_2 emissions from the plume, retrieved by combining CO_2/SO_2 ratios and SO_2 flux measurements (Aiuppa et al., 2011). The decreasing trend of the soil CO_2 flux, marked by the annual average shifting from 920 (in 2007-2008) to 330 g m^{-2} day^{-1} (in 2010-

2011), is not evident in the radon long-term signals that instead show a slight increase from 1777 to 2264 Bq/m^3 in annual averages (see straight lines in Fig. 3a and 3b, respectively and Table 1).

4.2 – Short-term periodicity and long-term trends

In order to identify diurnal and semidiurnal cycles affecting the gas signals, we performed a spectral analysis (Power Spectral Density) over a one year subset of data (sample time = 1 hour), using the method suggested by Viveiros et al. (2014). The analysis identified the 12h and the 24h frequency peaks in both CO_2 flux and ^{222}Rn activity (Fig. 6), confirming previous findings (Perrier et al., 2009 and 2012; Rinaldi et al., 2012). In our case, the ^{222}Rn signal seems to be modulated by temperature and barometric changes, although we do not exclude that this periodicity could be related with solar tides (e.g., Steinitz et al. 2011). On the other hand, the soil CO_2 flux reveals a main 12h period. It is worth noting that such a behaviour slightly differs from previous results suggesting a major influence of temperature rather than pressure (Rinaldi et al., 2012).

By analysing the long-time series of soil CO_2 flux and ^{222}Rn activity, we performed a calculation of the mean value of the whole data for each specific day of the year and the same computation was carried out also on soil and air temperature data. The emerging annual trend (see Fig. 7a, b) highlights the inverse relation between temperature and soil gas release, as well as an apparent correlation between the two gas species. Overall, we observe a 100% increment of the mean values comparing the spring-summer with the fall-winter period. It is also evident that the most significant day-by-day variations occur during the fall and spring season, when the likelihood of drastic atmospheric changes (i.e. heavy rainfall or windstorm) is higher than during summer.

The long-period behaviour is ruled by soil and air temperature (i.e. thermal gradient), whereas short-time oscillations are modulated by soil humidity (e.g., rainy events) and wind conditions (speed and direction), respectively. The correlation coefficients (R) shown in Table 2, allow to better assess the effect of the environmental parameters that actively modulate the trends of ^{222}Rn activity and soil CO_2 flux.

4.3 – Variation of the correlation coefficients

The seasonal variations of average correlation coefficients of the main environmental parameters with ^{222}Rn activity and soil CO_2 flux are reported in Fig. 8, where seasons are gathered and simply subdivided in spring-summer and fall-winter subsets. It can be seen that the correlation coefficients are not so stable throughout the investigated time span, but appear slightly modulated by seasonal effects. For example, both soil CO_2 flux and radon activity display a more distinctive negative correlation with air and soil temperatures during the spring-summer subsets. This behaviour is likely due to the lack of drastic variations in weather conditions during the "dry" season at Stromboli Island. Hence, the correlation between temperature and gas flux and concentration is not perturbed by other atmospheric factors (e.g. soil humidity). Correlation coefficients seem somewhat different in the first subset (spring-summer 2007) compared to all the others; this subset (grey field in Fig. 8) was obtained just after the March 15, 2007 explosive paroxysm when the effects of environmental conditions on degassing dynamics, even in relatively distal areas, seem somehow weaker. In April-June 2007 the lava effusion ceased and the Strombolian activity was not resumed, or more precisely, the source of explosions was too deep to allow glowing scoriae to reach the crater surface. In this time span, there was still a remarkable degassing rate at the craters from a relatively deep-seated magma level (Aiuppa et al., 2009; Barberi et al., 2009).

4.4 – Statistical treatment

Two different statistical methods have been applied on the raw dataset (sample time = 1 hour) of soil CO_2 flux and ^{222}Rn concentration in order to identify and remove the effects due to environmental parameters.

4.4.1 - Multiple Linear Regression Statistics (MLR)

The datasets of radon concentration, soil CO_2 flux and environmental parameters have been analysed by the Multiple Linear Regression (MLR) which is a simple and largely applied method used to identify the contributions of several independent variables and model the fluctuations observed in the investigated signal. The analysis has been performed to predict the values of a dependent variable (Y) given a set of predictor variables (X_1, X_2, …., X_n). The relationship between the dependent variable (Y_{calc}) and the predicted variables is expressed as

$$Y_{calc} = Y_0 + b_1X_1 + b_2X_2 + \ldots + b_nX_n \quad (1)$$

Y_0 is the intercept, X_n are the acquired variables and b_n the calculated regression coefficients (Granieri et al., 2003; Hernandez et al., 2004; and references therein). In order to simplify and reduce the number of predictor variables, MLR takes into account only the factors that are more correlated (positively or negatively) with CO_2 flux and ^{222}Rn activity (Table 3). By considering previous research, we selected only the environmental factors (i.e. independent variables) causing an increment of the R^2 greater or equal to 1% (Viveiros et al., 2008; Silva et al., 2015). Particularly, soil and air temperature were indicated by the regression for both gas species, together with wind speed and direction for CO_2 and soil humidity for ^{222}Rn. In Table 3 we report the main parameters for both gases by the MLR analysis.

Results show that the atmospheric variables taken into account for this analysis are able to predict 45% and 51% (R= 0.67 and R= 0.71) of the variations observed in soil CO_2 flux and ^{222}Rn concentration, respectively. Moreover, soil CO_2 flux and ^{222}Rn values show low dispersions, as respectively the 4.8% and 4.0% of the computed residuals exceed the average ±2 standard deviation range. Predicted values by MLR both for radon concentration and soil CO_2 flux, together with the observed values and the calculated residuals, are plotted in Fig. 9a onto the recorded time series. By looking at the residuals, it can be seen that *i)* the bell shape of the CO_2 flux is smoothed due to the removal of the seasonal trend but it still persists for radon, and *ii)* the residuals of both gases show peaks and major fluctuations that obviously cannot be related to environmental variations. Moreover, in both cases the signals are still characterised by noisy components (as reported by Laiolo et al., 2012 and Viveiros et al., 2014).

This statistical approach has been used at different volcanoes in the attempt to detect short-term variations in volcanic activity (e.g. major explosions at Stromboli; Laiolo et al., 2012), as well as the effects of seismic sequences (due to stress/strain structural changes) on the shallow part of a volcanic edifice (e.g., Masaya as analysed by Padilla et al., 2014).

4.4.2 - Principal Component Regression (PCR)

The second statistical treatment applied to ^{222}Rn activity, soil CO_2 flux and environmental parameters is the Principal Component Regression (PCR). This method differs from the previous one in how predictors are treated: first, a factor analysis is performed on the environmental dataset (X); then a forward step-wise linear regression of measured soil CO_2 flux and radon activity (Y) is performed on the estimated factors. The goal of this approach is firstly to obtain a reduction in the *X* data set in a way that maintains the maximum amount of information (i.e. largest possible variance), and secondly to perform regression of *Y* on orthogonal (uncorrelated) components. The aim is to ensure that highly correlated principal components are not overlooked (Vandeginste et al., 1998).

We performed factor analysis on two separate datasets because the radon station measures soil temperature and air pressure, whereas soil CO_2 flux station also measures air and soil humidity, wind speed and direction. Therefore, we created one dataset for radon with soil temperature and atmospheric pressure measured at the radon station and added the other variables measured at the CO_2 station. The factor analysis of the two datasets shows that three eigenvalues are higher than 1.0 and these three factors can explain the 73% of the total variance (Table 4). In the second step, we performed forward step-wise regressions of ^{222}Rn concentration and soil CO_2 flux on the first three factors. We obtained two theoretical models which explain the 25% and the 47% (R= 0.50 and R= 0.68) respectively of the soil CO_2 flux and ^{222}Rn concentration measurements variance (Table 4b). As in the MLR model, residual values show low dispersion, being less than 5% the portion of the data that exceeds the mean $\pm 2\sigma$ range (4.11% and 4.89% for CO_2 and ^{222}Rn, respectively). The time series of observed, predicted and residual values of radon concentration and soil CO_2 flux are reported in Fig. 9b. An overall comparison of the latter with Fig. 9a shows that the two statistical treatments provide basically the same results.

5 – DISCUSSION

For ^{222}Rn, the applied statistical methods indicate nearly the same percentage of data attributed to environmental variations, whereas the predicted soil CO_2 flux values vary from 45% in MLR to 25% in PCR. The residual computed values are related to processes that are likely related to the volcanic system and occur either within the shallow hydrothermal aquifer or in the deep magmatic plumbing system. It can be noted that the radon treatments provide many significant negative residual values ≤ -2σ, whereas only one negative residual is recorded for soil CO_2 flux (see Fig. 10). This indicates that, according to the statistical treatments, the measured radon concentrations are frequently lower than those calculated by filtering the effects of the environmental factors. We explain the high fluctuations showed by the residuals of radon signal with the relative low sensitivity of the radon dosimeter (Table S1) when settled with a high sampling rate (1 hour) in areas characterised by general low emissions (< 2000 Bq/m^3). In fact, such a noisy signal was not observed in the datasets acquired where the radon emissions are higher (Laiolo et al., 2012). Moreover, a trend characterised by positive and negative fluctuations in the calculated ^{222}Rn residual values, has been already observed in a non-volcanic area (Hayashi et al., 2015).

The residual time series (Fig. 9) retrieved for soil CO_2 flux shows in both treatments a decreasing trend for the first two years (visible also in the raw data) followed by a nearly steady-state signal close or below the zero value. This behaviour supports the hypothesis that the supply of CO_2-rich magma from the deep plumbing system (that started before the 2007 eruption, Aiuppa et al., 2011), besides increasing CO_2 emission in the gas plume itself, induced also a higher CO_2 flux in more distal zones, which lasted for nearly two years.

Comparison of the standard residuals (both by PCR and MLR) for CO_2 soil flux and ^{222}Rn activity versus time (Fig. 10) shows that in the initial two years of monitoring (up to May 2009) the two gases display a similar behaviour with nearly synchronous alternation of periods with anomalous emissions and periods with few or no anomalies (such as the summer of 2007 and

2008). In the last two years considered, only radon shows frequent positive anomalies whereas anomalous CO_2 flux values are only rarely recorded.

The comparison between the two statistical treatments suggests that MLR is more adequate for getting the quick results needed in near-real time volcano monitoring, whereas PCR ensures a more accurate estimate of data, which might be eventually useful for a more accurate post-process analysis and for a more reliable monitoring.

In order to assess the reliability of radon activity and soil CO_2 flux, measured in the distal site of Liscione/Nel Cannestrà, as possible precursors of major changes in the volcanic activity, the residuals time-series obtained by PCR and MLR and exceeding 2σ, have been compared with the main volcanic and seismic events occurred at Stromboli in the same time span (Fig. 10).

The 4.5 years of gas monitoring (April 2007 - September 2011) represent a phase of ordinary volcanic activity of Stromboli. In this period, twelve major explosions, four minor lava overflows and a local earthquake (with M_L= 2.2) were recorded at Stromboli by the INGV monitoring system (Calvari et al., 2014). No explosive paroxysm or effusive eruption occurred. There is no clear correlation between our data and the recorded volcanic events, but some useful considerations can be done.

From Fig. 10, it can be seen that in the first two years (following the 2007 explosive and effusive eruptive phase), frequent and high CO_2 flux and ^{222}Rn anomalies were recorded in coincidence with some anomalous volcanic episodes. Actually, the high number of positive residuals, from October 2007 to June 2008 and from November 2008 to May 2009, coincide with five major explosions and one lava overflow. During the 2007, 2008 and 2009 summers, neither major explosion/lava overflow nor residual CO_2 flux peaks were recorded (very few for radon, apart from 2009 summer when data were not available). In summer 2010, two major explosions occurred in a period of no anomalous gas release. During December 2010 – February 2011 a major explosion and two lava overflows occurred in concurrence with isolated peaks of CO_2 flux and during a phase of anomalous ^{222}Rn emission. Also the most-recent lava overflow in September 2011 coincided with an anomalous radon activity value.

Conversely, we have to consider that the eruptive events that occurred in the above time span seem to be connected to minor changes associated to the dynamics of the upper part of the conduit (e.g., Barberi et al., 1993 and 2009) without any involvement of the deep seated gas-rich magma pockets (typically occurring during major effusive-explosive cycles of Stromboli volcano, such as those of 2002-2003 and 2007).

6 - CONCLUSIONS

The presented data refer to more than four years of soil gas measurements (^{222}Rn concentration and soil CO_2 flux) at relatively distal sites from the active vents (Liscione and Nel Cannestrà sites on the NE flank of Stromboli, Fig. 1) during a the time-span (April 2007–September 2011) without major lava effusions and paroxysmal explosions.

The long-time averages for CO_2 flux and radon concentration exhibit relatively low values (585 g m^{-2} day^{-1} and 2050 Bq/m^3, respectively) when compared to those measured at the summit crater area (Carapezza et al., 2009; Cigolini et al., 2009 and 2013). This means that the advective processes, able to enhance the gas release from soil, are considerably reduced moving away from the crater area. The long term declining trend observed for the soil CO_2 flux (Fig. 9 and Table 1) suggests that the large supply of CO_2-rich magma associated with the 2007 eruption (and invoked to explain the exceptional CO_2 emissions from the plume; Aiuppa et al., 2009 and 2011) affected also the soil gas release in relatively distal areas. So, as already stressed by De Gregorio et al. (2014) for Etna volcano, the soil CO_2 flux measurements represent a key tool to infer the magma supply dynamics and to evaluate the local degassing regime. Furthermore, the combination of soil CO_2 flux and ^{222}Rn concentration measurements can better constrain the gas source in relation to changes in volcanic activity (Faber et al., 2003; Perez et al., 2007; Padilla et al., 2013). In the last two years (2010 - 2011) of our monitoring, anomalous radon concentrations have been frequently recorded in periods with rare or absent soil CO_2 flux anomalies; this likely indicates a different source for the two gases, deeper for CO_2 and somehow shallower for radon.

The four years monitoring of both gas species at Stromboli provided the opportunity of better decoding how gaseous transfer toward the surface is ruled by environmental changes. Our data show that both gases are affected by seasonal temperature variations giving to the time series a bell shaped profile. In particular, higher emissions occur during fall-winter, because fluid convection is promoted by the higher soil-air temperature gradient. Conversely, during summer, this gradient is reversed and near-surface convection is inhibited. Moreover, soil CO_2 flux is locally influenced by wind (>8 m/s in the SE sector), while radon activity by soil humidity.

In summary, the decreasing surface temperature, eventually coupled with increases in soil moisture seems the main factor that controls the variations of radon emissions. The effect of soil humidity on radon activity probably reflects the adopted measurement techniques. In fact the radon measurements at 1 m depth are likely affected by soil humidity (particularly during the raining falls) which affects the radon diffusion and exhalation rates (i.e., Papachristodoulou et al., 2007).

We have shown that the influence of environmental parameters on gaseous time series can be minimised by means of linear statistics to better evaluate possible variations related to changes in volcanic activity. The statistical methods presented in this paper can be adopted for different purposes; the Principal Component Regression (i.e. Factor Analysis) appears the more suitable for an accurate analysis of large datasets following major changes in volcanic activity (post-event data processing): in fact, the application of this method carefully evaluates the contribution of each independent factor by means of precise cross correlations. Conversely, Multiple Linear Regression analysis can be more quickly and easily applied to a nearly real-time soil gas monitoring useful in volcano surveillance since it gives us the opportunity to efficiently track anomalous gas concentrations, or fluxes, that are not related to environmental factors. We thus emphasize that the reported datasets represent a rather unique case, at the global scale as well, of geochemical and environmental data acquired in a very active volcanic area for such a long time. The monitored area represents an anomalous degassing zone (Carapezza et al., 2009; Cigolini et al., 2013) and our results show that a multiparametric geochemical monitoring may play a key role in decoding precursory signals related to major changes of Stromboli volcanic activity.

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Figure Captions

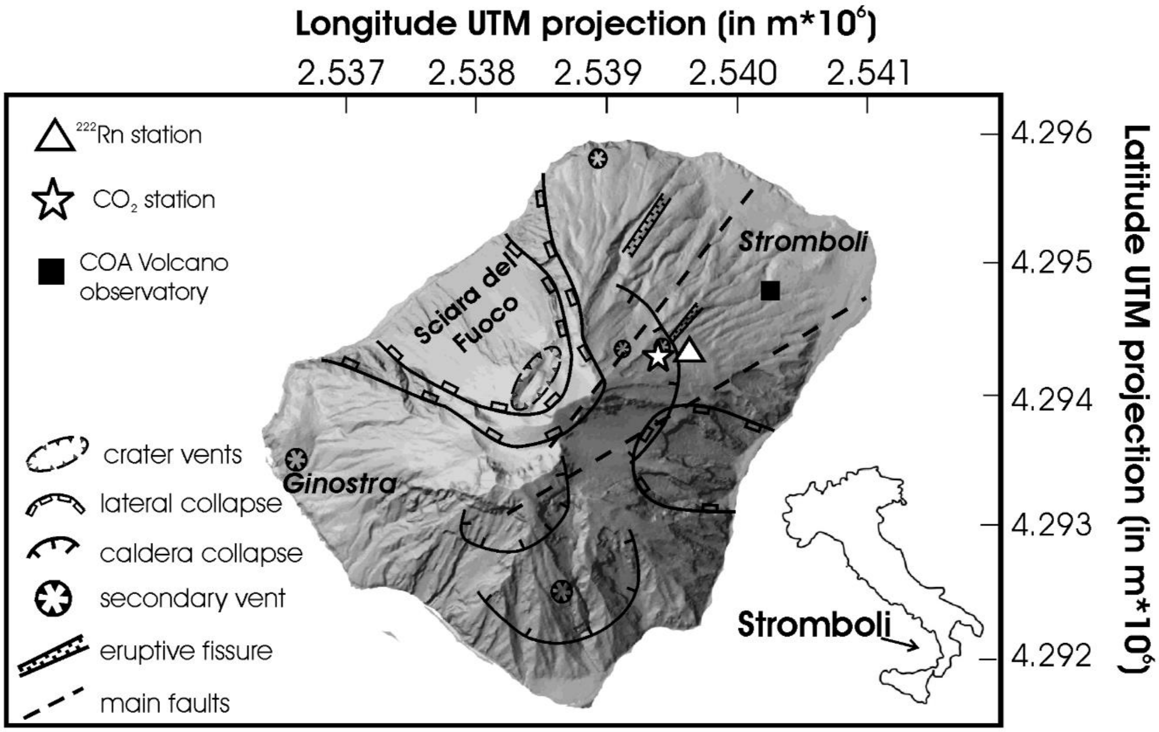

Fig. 1. Digital Elevation Model of Stromboli Island (from Baldi et al., 2005) with major faults and collapsed sectors (simplified from Finizola et al., 2002 and Tibaldi et al., 2009). Locations of the Volcano Observatory (COA) and of the radon and CO_2 flux stations are reported.

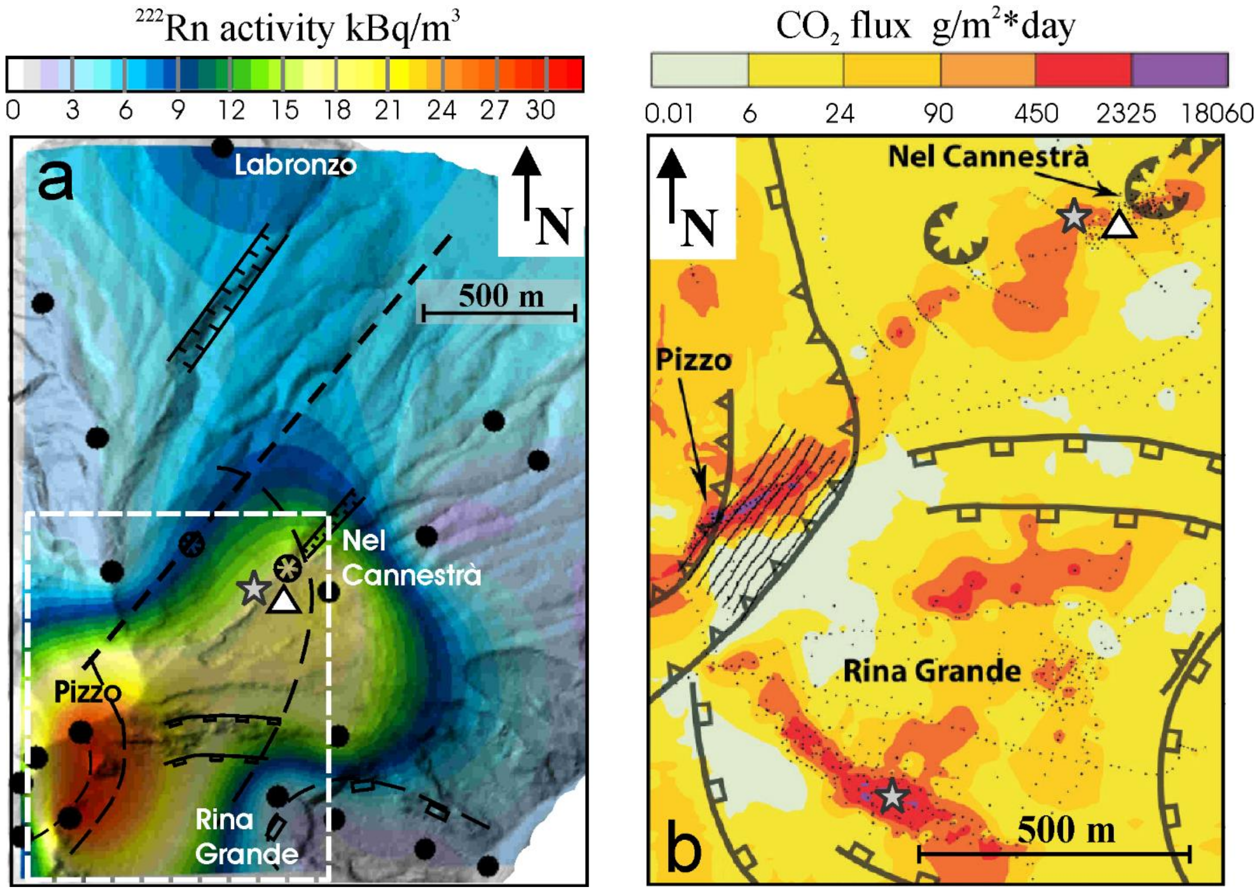

Fig. 2 (a) Map of radon activity measured in March 10-18, 2007 on the NE flank of Stromboli. Full circles indicate measurement sites; the contour lines of radon emissions have been obtained by kriging (Cigolini et al., 2013). The triangle indicates the location of the ^{222}Rn automatic station. Dotted white rectangle marks the area of the soil CO_2 flux map of March 2007 reported in b). Stars are the sites of the automatic CO_2 stations (Carapezza et al., 2009).

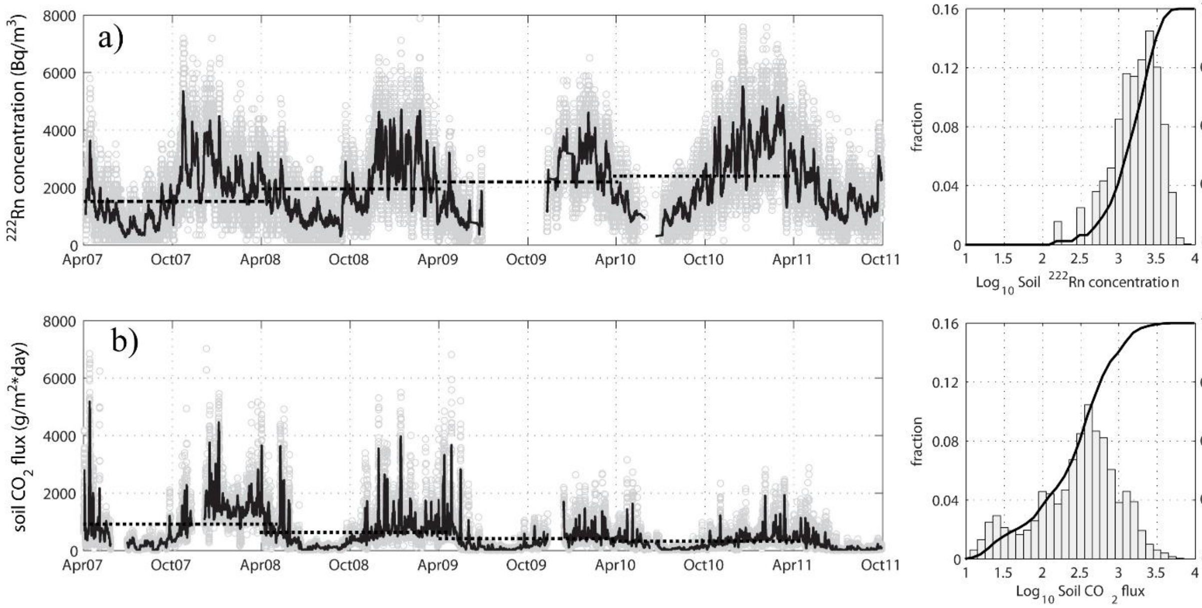

Fig. 3. Time-series of ^{222}Rn activity (a) and soil CO_2 flux (b) recorded hourly from April 2007 to September 2011 (grey dots). Black curves and the straight dotted lines represents the daily and the annual average, respectively. Histograms show the multi-modal distributions.

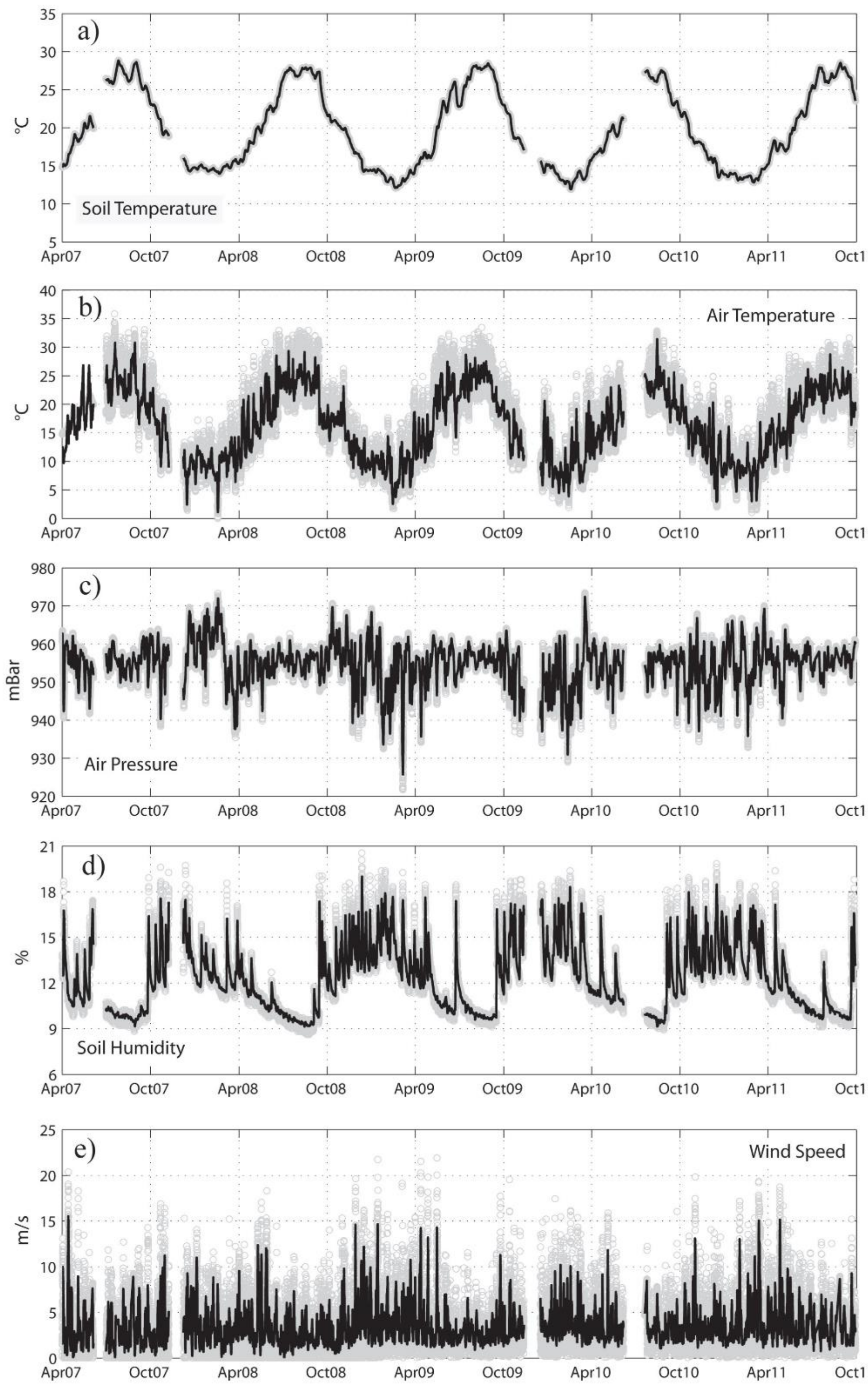

Fig. 4. Time-series of the main environmental parameters measured hourly from April 2007 to September 2011 at NC station (grey dots). Black curves are the daily average.

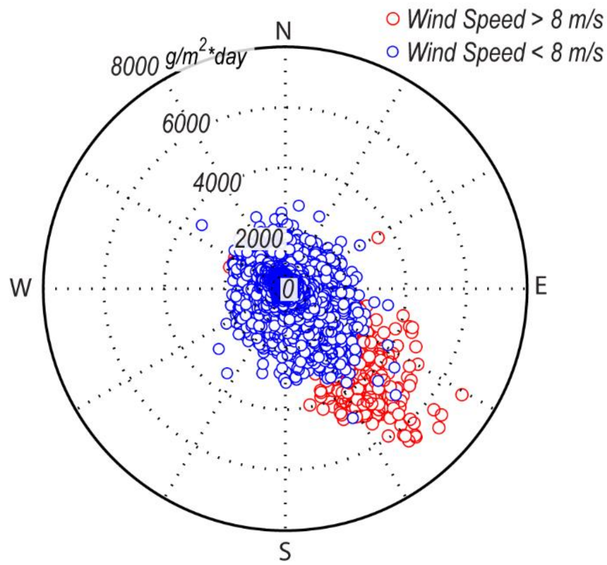

Fig. 5. Soil CO_2 flux vs. wind direction. Red and blue circles refer to data acquired with wind speed above or below 8 m/s respectively. Note that most of the high soil CO_2 fluxes are recorded for wind speed >8m/s in the SE sector.

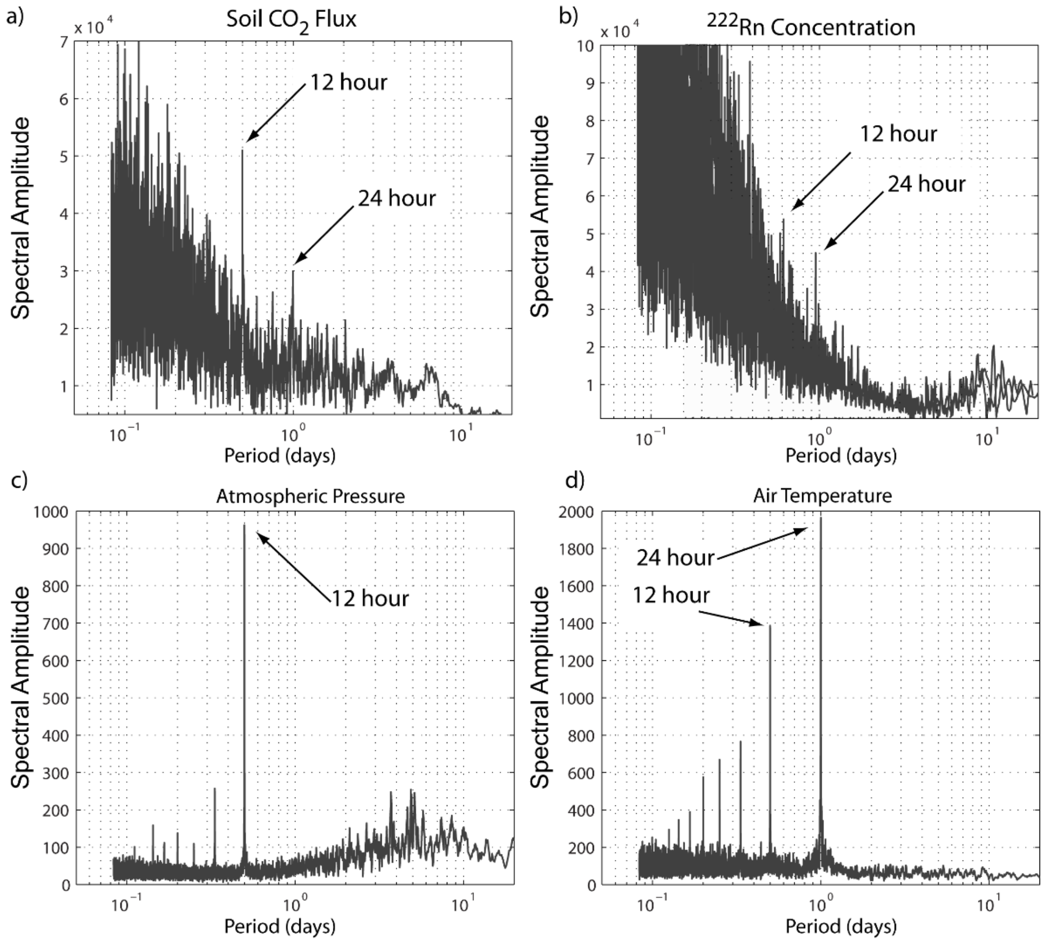

Fig. 6. Spectral amplitude for soil CO_2 flux (a), ^{222}Rn concentration (b), atmospheric pressure (c) and air temperature (d). The analyses were made over one year of hourly data (see text for details).

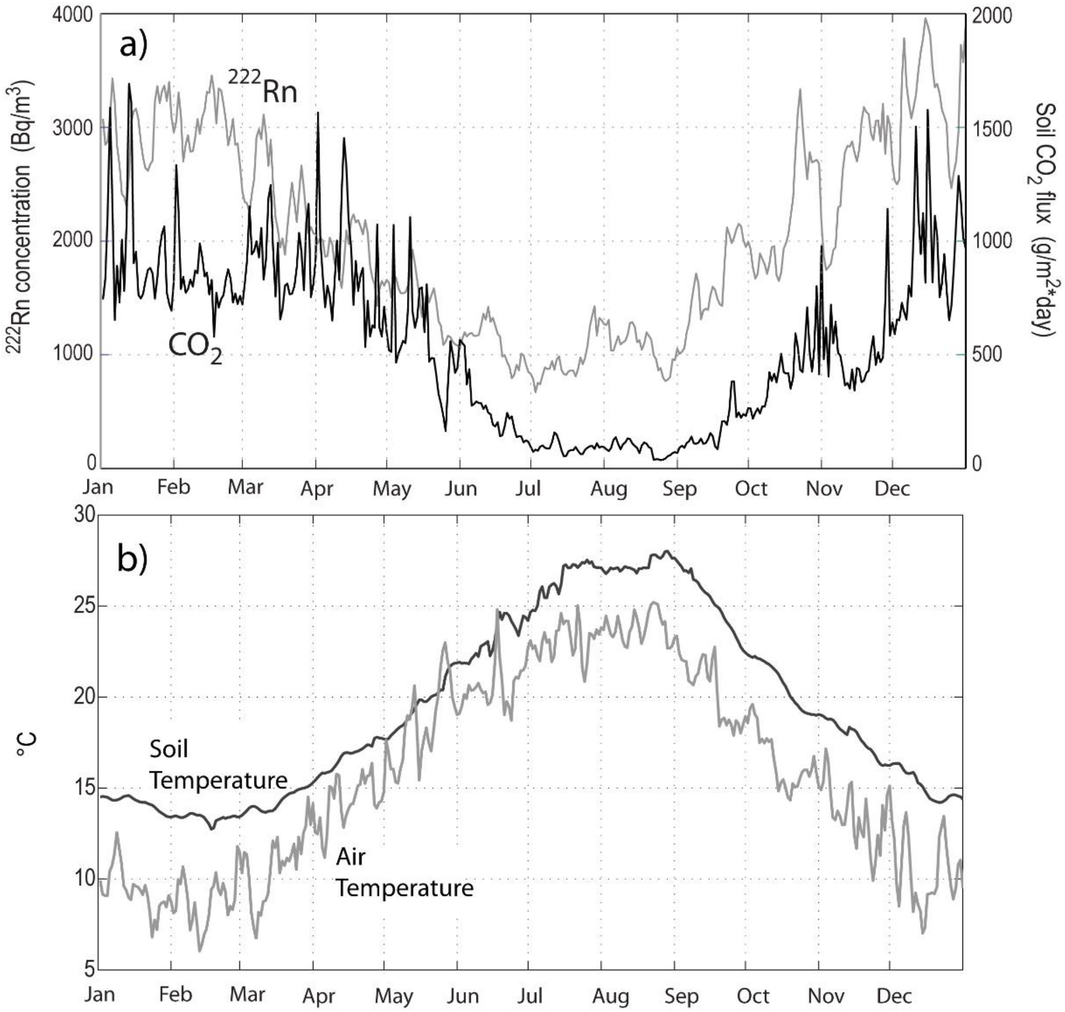

Fig. 7. Bulk annual trend of radon concentration and soil CO_2 flux (a) retrieved from the mean values measured each day in the 4 years monitoring. Results are compared with the annual trend of soil and air temperatures (b).

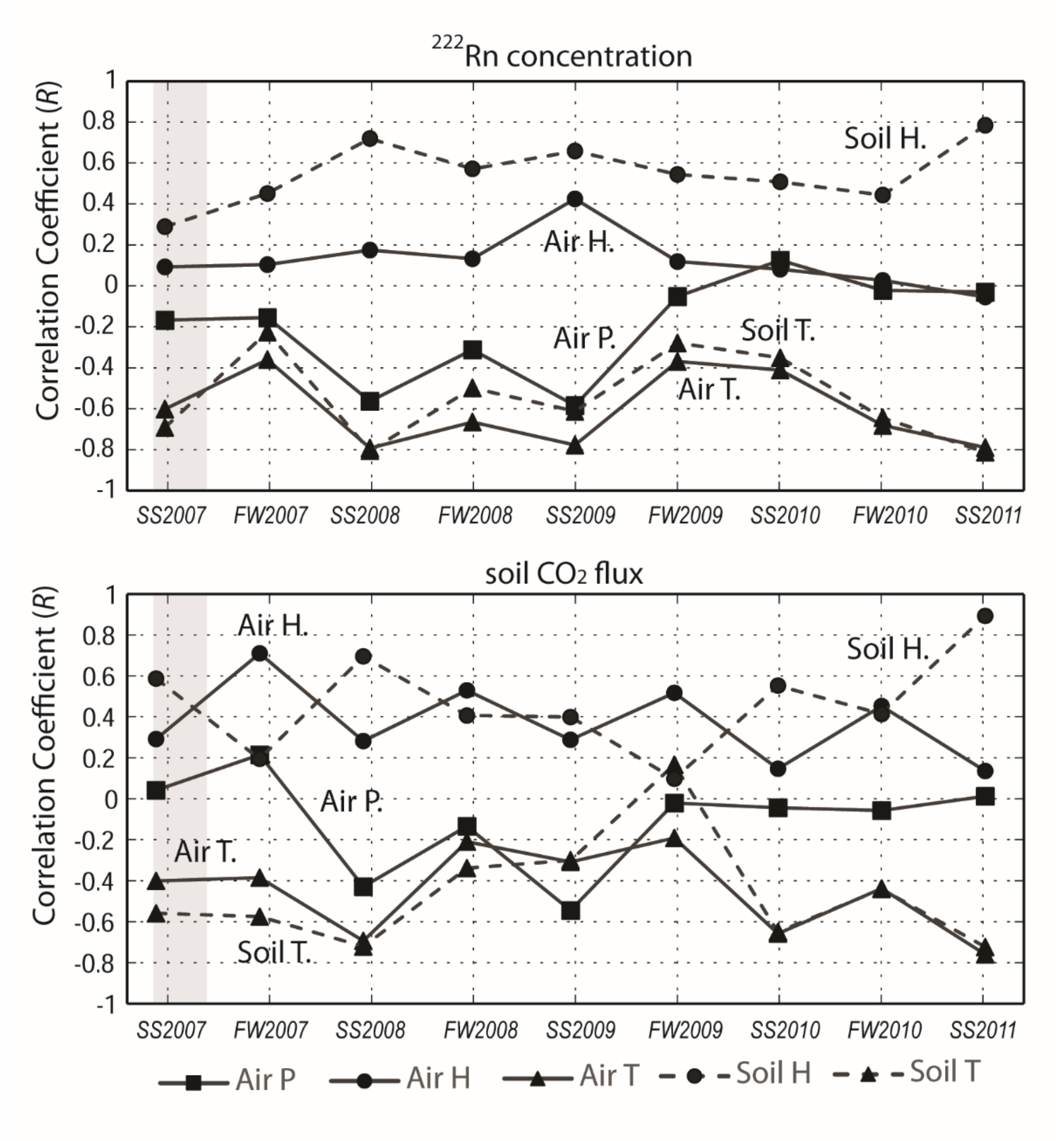

Fig. 8. Seasonal variations of the average correlation coefficients (R) between main atmospheric factors and ^{222}Rn concentration (above) and soil CO_2 flux (below). Air T: air temperature; Soil T: soil temperature; Air P: barometric pressure; Soil H: soil humidity; Air H: air humidity. SS and FW refer to Spring-Summer and Fall-Winter period, respectively.

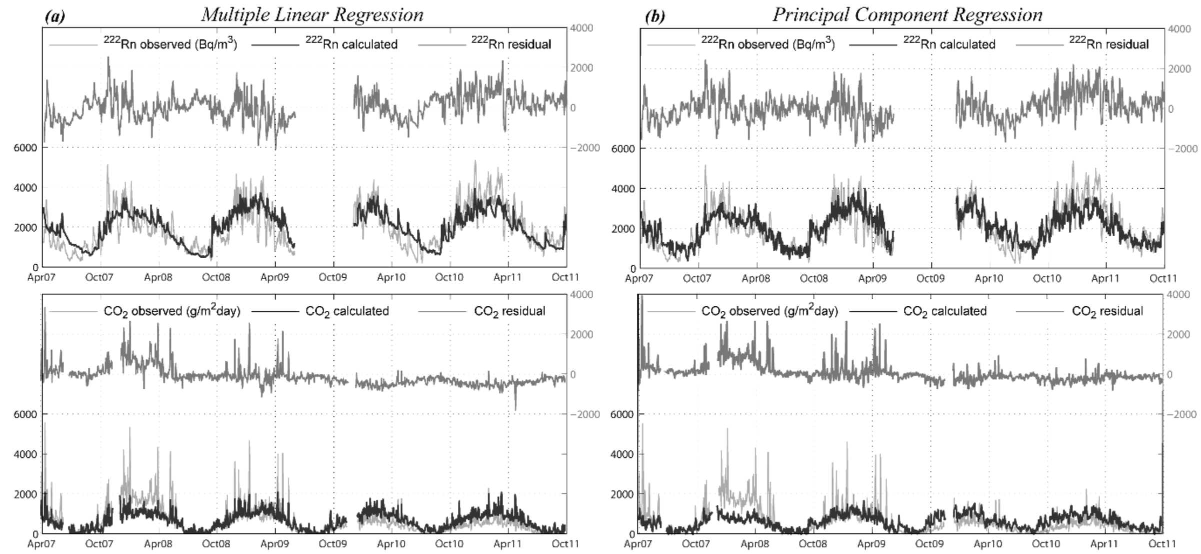

Fig. 9. Results from Multiple Linear Regression (a) and Principal Component Regression (b) for radon activity (above) and soil CO_2 flux (below) during the 4 ½ years of monitoring. Data are reported as daily averages. The observed, calculated and residual values are indicated.

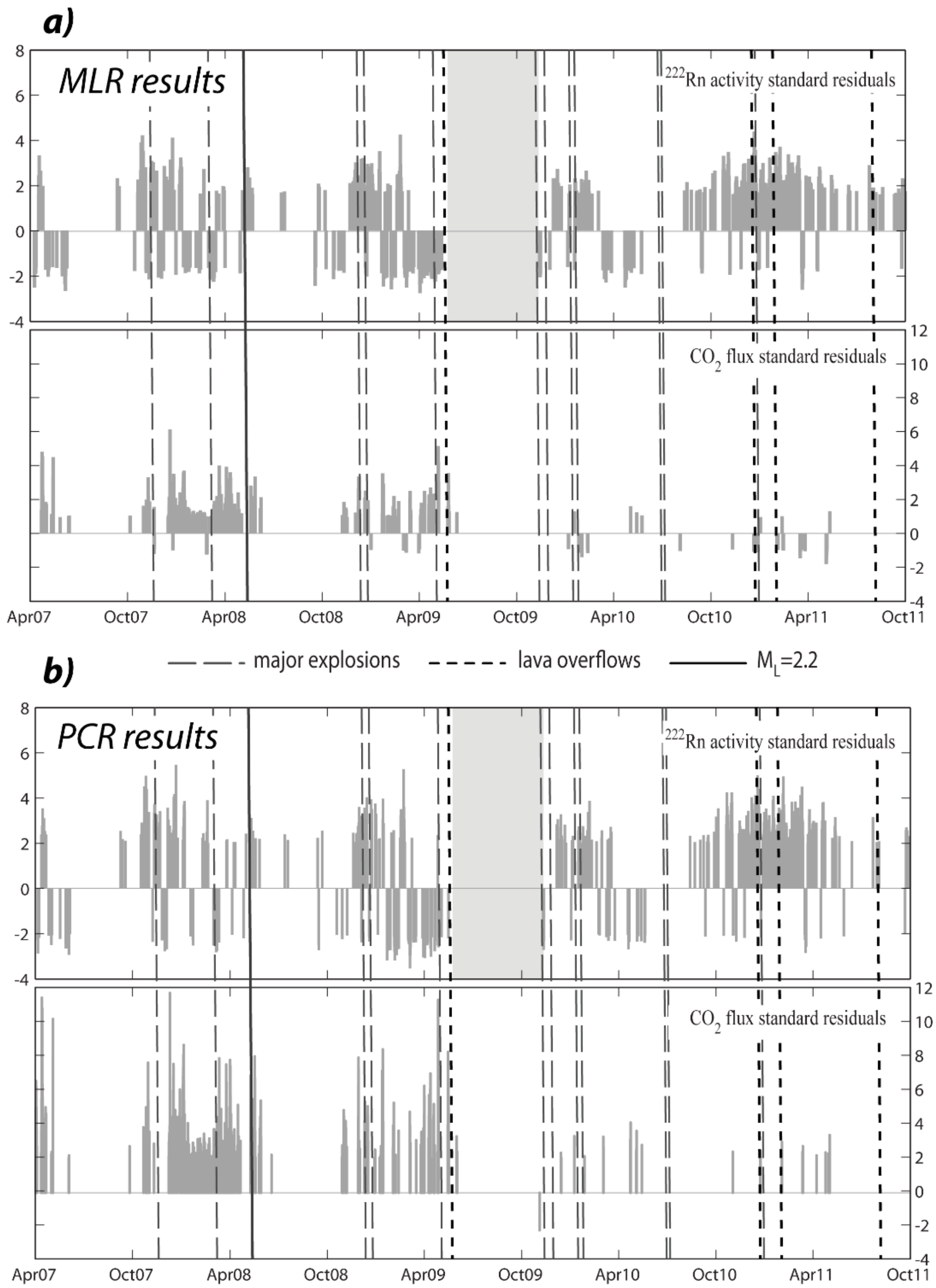

Fig. 10. Time series of the residuals of ^{222}Rn concentration and soil CO_2 flux obtained by MLR (a) and PCR (b) methods with indication of the main volcanic and seismic events occurred at Stromboli from April 2007 to September 2011. Vertical axes express the standard deviation from the mean; only values ≥ 2 σ are plotted. Grey field marks the time span when no radon data were recorded.