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USE OF THE RADIOCARBON ACTIVITY DEFICIT IN VEGETATION AS A SENSOR OF CO_2 SOIL DEGASSING: EXAMPLE FROM LA SOLFATARA (NAPLES, SOUTHERN ITALY)

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ABSTRACT. Soil CO_2 flux measurement is a key method that can be used to monitor the hazards in an active volcanic area. In order to determine accurately the variations of the CO_2 soil emission we propose an approach based on the radiocarbon (^{14}C) deficiency recorded in the plants grown in and around the Solfatara (Naples, Italy). We twice sampled selected poaceae plants in 17 defined sites around the Solfatara volcano. ^{14}C measurements by liquid scintillation counting (LSC) were achieved on the grass samples. The ^{14}C deficiency determined in the sampled plants, compared to the atmosphere ^{14}C activity, ranged from 6.6 to 51.6%. We then compared the proportion of magmatic CO_2 inferred to the instantaneous measurements of CO_2 fluxes from soil performed by the accumulation chamber CO_2 degassing measurement at the moment of the sampling at each site. The results show a clear correlation ($r = 0.88$) between soil CO_2 fluxes and ^{14}C activity. The determination of the plants ^{14}C deficiency provides an estimate of the CO_2 rate within a few square meters, integrating CO_2 soil degassing variations and meteorological incidences over a few months. It can therefore become an efficient bio-sensor and can be used as a proxy to cartography of the soil CO_2 and to determine its variations through time.

KEYWORDS: bio-sensor, CO_2 soil degassing, fumarolic activity, Phlegrean Fields, volcanism.

INTRODUCTION

One of the best approaches for monitoring active volcanoes entails measuring the variations of volcanic gas emissions. Gas release is indeed a typical manifestation of the underground activity of volcanic systems and often the sole one during non-eruptive periods (Chiodini et al. 1998). Degassing on active volcanoes occurs in the form of volcanic plumes, fumaroles, bubbles in thermal waters, and diffuse emanations from the soils (Allard et al. 1991b; Baubron et al. 1991; Farrar et al. 1995; Hernandez et al. 1998; Delmelle and Stix 1999; McGee et al. 2000; Bergfeld et al. 2001; Werner and Cardellini 2006). Diffuse soil degassing, in particular, occurs inside volcanic craters and on the external slopes of volcanic piles, during both quiescent periods and eruptions, and varies significantly in relation to the level of volcanic activity. Being also more accessible than hot crater emissions, it thus provides useful opportunities to survey the evolution of a volcanic system (Badalementi et al. 1991; Baubron et al. 1991; Toutain et al. 1992). Diffuse soil emanations on volcanoes are usually composed of almost pure carbon dioxide, plus trace amounts of H_2, CH_4, and rare gases (Allard et al. 1991b; Baubron et al. 1991; Chiodini et al. 2012). Carbon dioxide (CO_2) is the second-most abundant component of magmatic gases after water and also the first volatile species to form gas bubbles in magmas at depth owing to its low solubility. In low-temperature soil gas emanations, water vapor is previously depleted by condensation, leaving CO_2 as the predominant compound. In such emissions CO_2 concentrations approach 100%, in contrast to only 0.04% in standard atmosphere. Therefore, diffuse CO_2 emanations are able to generate strong local CO_2 anomalies in soils and in air, which can even become lethal when CO_2 concentrations reach 12–15%.

Two different techniques, based on infrared gas sensing, are commonly used to measure CO_2 emissions from volcanic soils: the accumulation chamber method (ACM) (Parkinson 1981;

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Norman et al. 1992; Chiodini et al. 1998; Allard et al. 2014) and the dynamic concentration method (DCM) (Gurrieri and Valenza 1988; Camarda et al. 2006). These two techniques can be operated for either discrete measurements or permanent gas survey. However, both imply punctual measurement at a given site and require measuring, numerous sites in order to access the overall CO_2 degassing pattern and flux. Alternative approaches to determine CO_2 fluxes from soil degassing and fumaroles on volcanoes include the use of a CO_2 Lidar (Pedone et al. 2015) or local eddy covariance, a key atmospheric measurement technique to calculate vertical turbulent fluxes within atmospheric boundary layers (Werner et al. 2003; Lewicki et al. 2009, 2012).

Previous studies have demonstrated that volcanic CO_2 emissions can also be indirectly assessed from their record in either living plants or the rings of trees growing on active volcanoes (Bruns et al. 1980; Allard et al. 1997; McGee et al. 1998; Pasquier-Cardin et al. 1999; Cook et al. 2001; Mostacci et al. 2009; Evans et al. 2010; Lewicki et al. 2014). Magma-derived CO_2 emitted by volcanoes is devoid of ^{14}C and thus dilutes the ^{14}C fixed from normal atmosphere during photosynthesis.

We propose an alternative approach of the CO_2 flux measurement based on the depletion of ^{14}C concentration in the plants growing in active volcanic zones, due to their assimilation of a part of mineral CO_2, ^{14}C free, from the soil emanation (Allard et al. 1997; Pasquier-Cardin et al. 1999). Our study will check the possible estimate of the intensity of local volcanic CO_2 emission by measuring the degree of ^{14}C depletion in living plants with respect to the contemporaneous standard atmospheric value: ^{14}C analysis of selected plants in active volcanic areas could provide an indirect opportunity to quantify local CO_2 fluxes averaged over periods of some weeks.

We present the results of a series of radiocarbon measurements on plants growing within and nearby the Solfatara crater (Figure 1), the most active vent of the Campi Flegrei caldera in southern Italy, which is the site of intense fumarolic and diffuse soil degassing.

Volcanological Setting

Located north of the Gulf of Naples and extending partly into the town of Naples (Figure 1), Campi Flegrei is a large volcanic complex that developed over the last 50 ka (Cassignol and Gillot 1982; Scandone et al. 1991). Its evolution was marked by two huge ignimbritic eruptions, which generated two successive caldera collapses: the Campanian Ignimbrite and Neapolitan Yellow Tuff, dated to around 39 ka and 14 ka, respectively (Gillot and Cornette 1986; De Vivo et al. 2001; Blockley et al. 2008).

Subsequent activity has been concentrated within and along the rim of the second caldera. The most important eruptive phase occured during the Bronze Age, between 4400 and 3600 BP (D'Antonio et al. 1999). Most of the events were explosive (Agnano-Monte Spina, Solfatara, Astroni, Senga) and their pyroclastic products covered the Neapolitan area. The most recent eruption in Campi Flegrei happened, in 1538 AD and built Monte Nuovo, a volcanic cone located NW of the central town of Pozzuoli. The volcanic complex remains very active. Throughout historic times it has been affected by a "bradyseismic" activity including important ground deformations, up to several meters, and seismic crises. The phenomenon is well known since the Roman epoch. A strong bradyseismic crisis preceded the 1538 AD eruption of Monte Nuovo, followed by subsidence (Dvorak and Gasparini 1991). Then, two new crises affected the central part of the caldera (Pozzuoli area), one between 1968 and 1972 (0.7 m of ground uplift) and a second one between 1982 and 1985 (1.8 m of uplift on average).

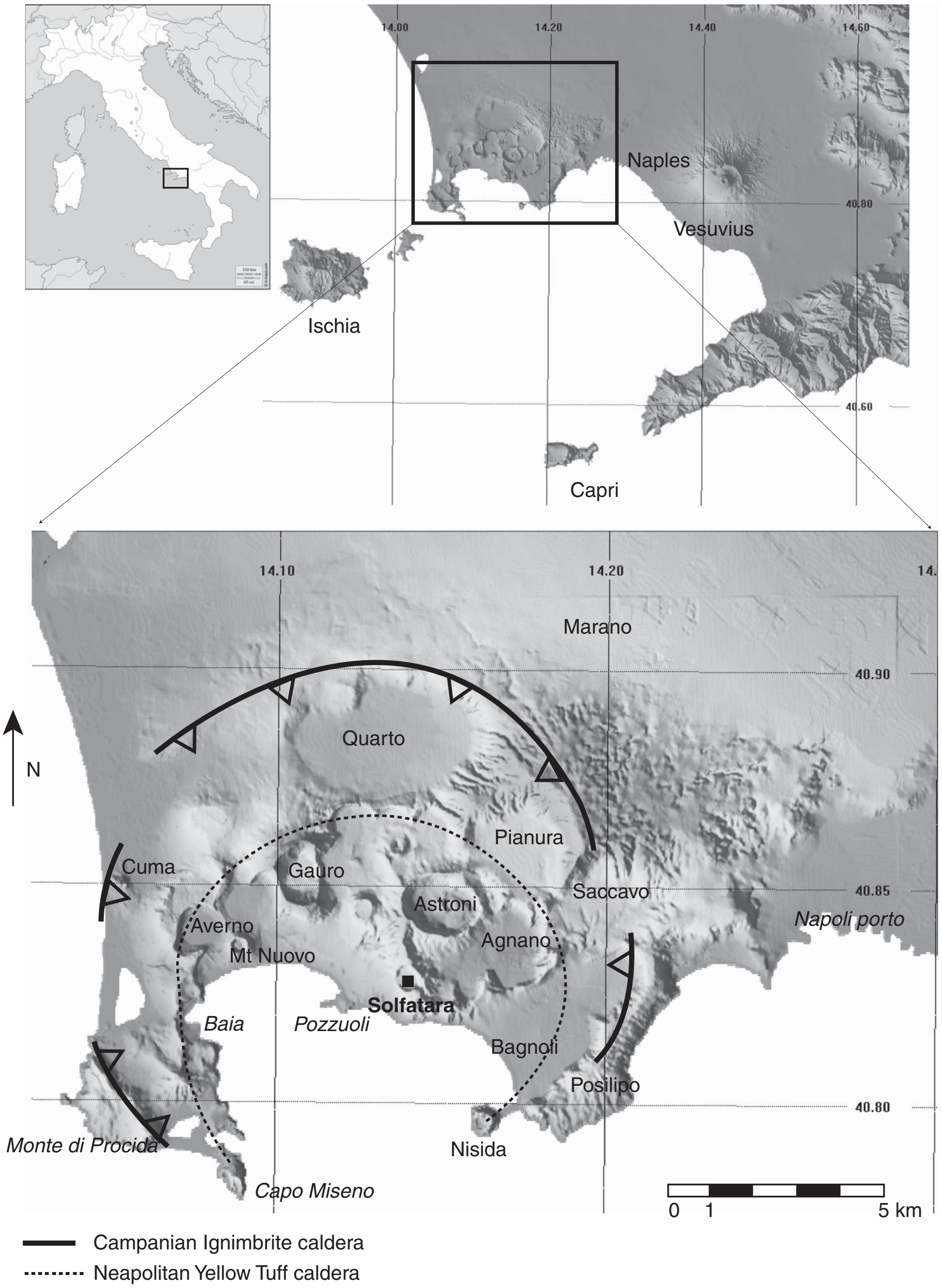

Figure 1 Location map of Campi Flegrei in the Neapolitan area and map of Campi Flegrei showing the limit of the two calderas. The most recent volcanoes, post Neapolitan Yellow Tuff, are all situated along the rim of the youngest one, around the Gulf of Pozzuoli.

These uplifts were attributed to either a pressure increase in the magma chamber (Bonafede et al. 1986), an increasing input of magmatic gas into the shallower hydrothermal system (De Natale et al. 1991; Chiodini et al. 2003; Bonafede and Ferrari 2009) or a magma intrusion (D'Auria et al.2015). Campi Flegrei was affected by extensive CO_2 degassing, thoughout its history, as revealed by a recent isotopic study of the calcite present in the volcanic products of different age (Chiodini et al. 2015a). The recent bradyseismic crises were actually accompanied or even preceded by an increased degassing activity and by a greater efflux of magma-derived CO_2 in the fumarolic emissions (Chiodini et al. 2012). CO_2 degassing to the open air mainly occurs inside and around the central Solfatara volcano. After Mount Etna (Allard et al. 1991a), Solfatara volcano supports the second largest emission of volcanic CO_2 in Europe: 1500 t/day of CO_2 (Chiodini et al. 2001; Granieri et al. 2010), together with 3300 t/day for H_2O. The ^{13}C content of the CO_2 demonstrates its magmatic derivation (Caliro et al. 2007). The rising magmatic gas encounters hydrothermal meteoric aquifers at about 2 km depth, producing hydrothermal steam at 360ºC under 200–250 bar pressure (Gottsmann et al. 2006).

Geochemical studies indicate that the CO_2 content and the temperature of Solfatara fumaroles have gradually increased since 2006, in coincidence with increasing ground deformation and seismicity, probably as a consequence of a greater influx magmatic gas at depth (Chiodini et al. 2011, 2012).

The fumarolic activity at Solfatara volcano also extends outside the crater, especially in the eastern external zone of Pisciarelli (points 12 and 13 in Figure 2), where new and strongly degassing vents recently formed (December 2009). The increased fumarolic activity, together with important compositional variations of the discharged fluids, were recently interpreted as evidence of ongoing volcanic unrest (Chiodini et al. 2015b).

This intense activity raises an important challenge for civil defence because the Campi Flegrei area hosts close to a half million people in addition to the 2 million people living in the nearby Naples urban district up to Mount Vesuvius to the east. This makes the Naples agglomeration one of the most dangerous volcanic zones in the world (Barberi et al. 1984). Continuous volcano monitoring and assessing CO_2 emissions, both in space and time, are therefore essential.

METHODS

The approach developed here, based on the ^{14}C deficit in grass, presents a double interest: first, it allows us to estimate the volcanic CO_2 emission over a period of 2 to 6 months, depending on the growth rate of the plants; and secondly it makes it possible to determine the effect of very low volcanic CO_2 concentrations added to the local atmosphere on apparent ^{14}C plant age. Grass growing at low soil level is indeed more sensitive to CO_2 soil degassing than higher trees and their leaves. Most of the grass sample selected for this study are *poaceae*, also commonly called graminae. It is a typical grass with leaves growing from the base, has a quite rapid growth, and does not exceed 50 cm in height. In order to get fresh samples, the grass was first mowed short (in autumn 2012). Two successive samplings were conducted, in March 2013 (plant growth between October and March), and in May 2013 (plant growth between March and May). We collected grass samples both inside and outside Solfatara crater, at 17 sites, distributed over a 1.5 km^2 area (Figure 2). Sampling sites were chosen as a function of the variability of the soil CO_2 flux already recognized by ACM measurements (Chiodini et al. 2001), taking account of their location with respect to the main fulmarolic vents and the topography of the area. Some sites were located close to the most active fumaroles inside the crater, where the vegetation is reduced due to the temperature and acidity of the soil (points 3 and 4), while others are near the very active new fumaroles of Pisciarelli (base of the

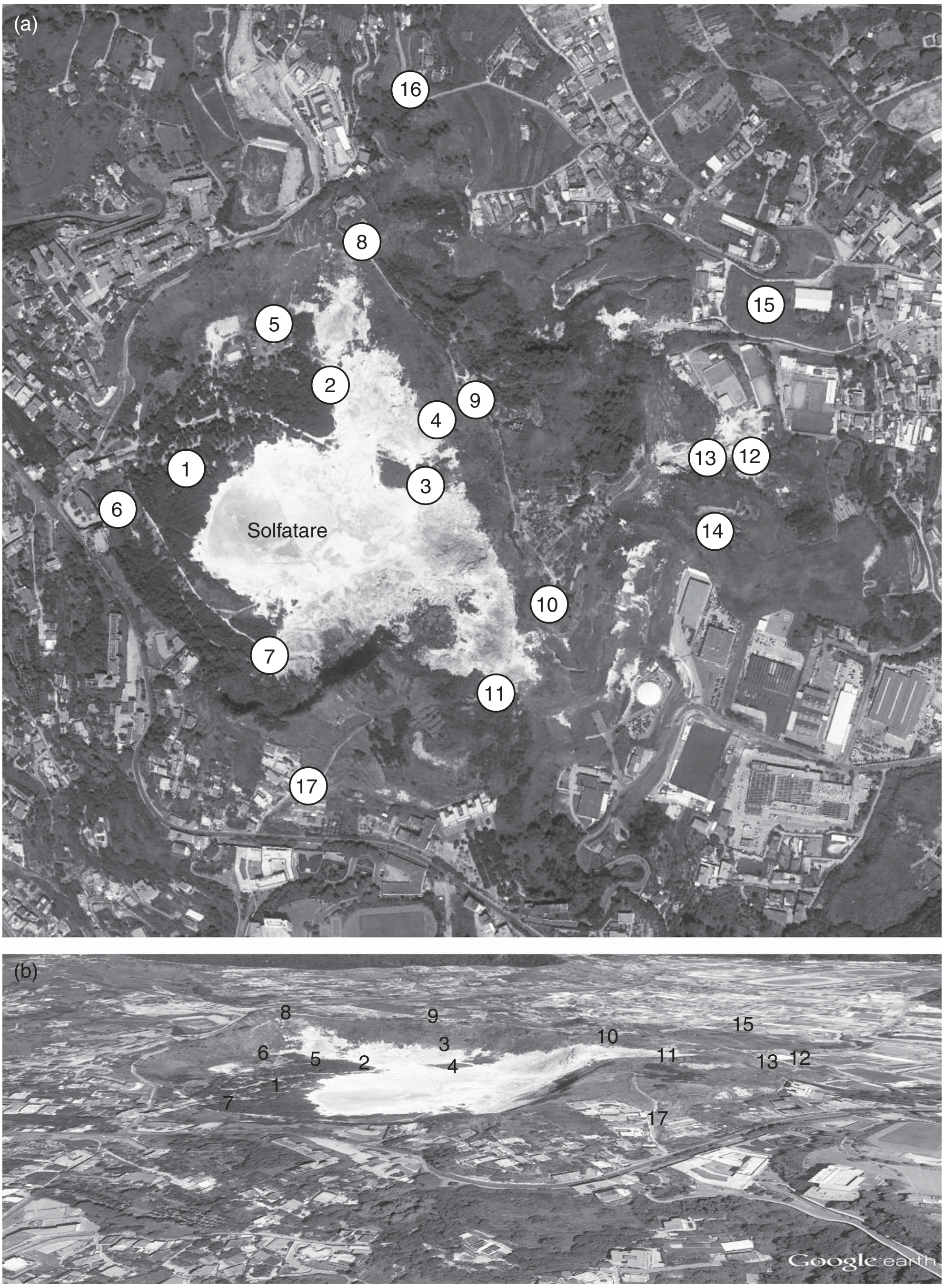

Figure 2 (a) The location of the sampling site; (b) the oblique view reveals the relief.

eastern external slope), and on the rim of the Agnano-Monte Spina plain (12 and 13). Most of the other sites are remote from fumarolic zones and are located, either in suburban area (camping sites, gardens, or fields), or on the crater rim and out of the volcano.

Together with plant sampling, the soil CO_2 flux was measured in situ with the ACM methodology at each site (Chiodini et al. 1998). The ACM comprises an accumulation chamber covering 0.0314 m^2 of the ground, and traps the soil gas emanation. It is connected to an infrared spectro-photometer which measures CO_2 concentrations, in the range 0–20,000 ppm. The gas accumulating in the chamber is pumped through the spectrometer and is re-injected into the chamber to avoid chamber depressurisation. The slope of the temporal increase function provides the CO_2 flux in $g.m^{-2}.day^{-1}$ (Chiodini et al. 1998).

Our plant samples were analyzed in the Centre de Datation par le Radio-Carbone in Lyon (France). Before being processed for radiocarbon analysis, the samples were dried out for about one month. The ^{14}C analysis was made on 30 g of dried plant material, using the classical chemical pretreatment (acid-base-acid); the CO_2 was extracted from about 12 g of the sample, giving about 4 g of synthesized benzene. The radiocarbon activity is then measured by liquid scintillation counting (TRICARB – Packard, Perkin-Elmer), calibrated against international sample references (oxalic acid II and sucrose) (Mann 1983; Stuiver and Polach 1977; Mook and van der Plicht 1999). The ^{14}C age is corrected by taking into account the $^{13}C/^{12}C$ ratio, referenced to PDB standard that was measured at ISA Villeurbanne (France).

RESULTS AND DISCUSSION

The soil CO_2 flux, the $\delta^{13}C$ of the plants and their ^{14}C activity, are reported in Table 1. The standard ^{14}C activity for plants grown in pure atmosphere was measured at 104.0 ± 0.3% or 14.1 dpm for 2013 samples and 103.0 ± 0.3% or 14.0 dpm for 2014 samples (internal laboratory reference). In 2014, we obtained an equivalent reference value of 102.5 ± 0.3% for a same plant growing on the top of Camaldoli Hills, on the external border of Campi Flegrei caldera. This value is slightly lower than the internal laboratory reference, but within the range of the analytical uncertainty.

The locally measured soil CO_2 fluxes range from 15 to 1412 $g.m^{-2}.day^{-1}$. The ^{14}C activity in our plant samples varies between 97.4% and 52.4%, implying an assimilation of between 6.6% and 51.6% of volcanic carbon devoid of ^{14}C. The highest proportion of volcanic CO_2 results in an apparent age of 5194 BP for the corresponding plant samples.

We present in Figure 3 the overall variations of ^{14}C activity in our samples against the in situ measured CO_2 flux (ACM). The data points show some scattering, which can easily be explained by the differences in temporal recording of the two approaches and by the sensitivity of the both CO_2 flux and the amount of air dilution to changing meteorological conditions. The gas flux has been shown to depend on the meteorological conditions (wind, rainfall and barometric pressure) (Carapezza et al. 2009, 2011). However, nearly all the points plot in two envelopes near a regression line showing a relative correlation ($r = 0.88$) between the ^{14}C deficit in plants and the measured CO_2 flux. We consider the lower envelope as best would representing the relationship between the CO_2 emanation rate and the proportion of volcanic carbon integrated in the plants, which is inversely proportional to the measured ^{14}C activity. The data points plotting well above that envelop in Figure 3 likely result from enhanced air dilution of the volcanic CO_2 and its lower integration in the plants, due to a stronger site exposure to wind and meteorological dispersion. This defines an upper envelope in which, however, the proportionality between ^{14}C activity and CO_2 flux still persists.

We thus find that the ^{14}C activity of plants growing at Solfatara volcano clearly records the volcanic emanations of CO_2, with a large range of sensitivity. ^{14}C depletion in each plant

Table 1 Flux measured, $\delta^{13}C$ and ^{14}C activities measured in the 17 selected sampling sites.

			CO$_2$ flux (g/m^2.d)			Plants cut in March 2013			Plants cut in May 2013		
Sample number	East (m) UTM_ED50	North (m) UTM_ED50	October 2012	March 2013	May 2013	$\delta^{13}C$ (‰)	^{14}C Activity (%)	Age ^{14}C (BP)	$\delta^{13}C$ (‰)	^{14}C Activity (%)	Age ^{14}C (BP)
S0	431886	4523429	—	—	—	—	—	—	−30.94	102.5 ± 0.3	—
S1	427340	4520160	232	208	193	−32.56	79.4 ± 0.3	1852 ± 30	−32.91	84.0 ± 0.3	1400 ± 30
S2	427531	4520332	612	597	594	—	—	—	−13.56	65.6 ± 0.3	3387 ± 35
S2 box	427531	4520332	612	597	594	—	—	—	−10.79	38.0 ± 0.2	7800 ± 30
S3	427700	4520198	379	114	213	−14.32	75.2 ± 0.3	2290 ± 30	−13.87	77.2 ± 0.3	2080 ± 30
S4	427691	4520288	447	738	974	−12.72	52.4 ± 0.2	5194 ± 35	−12.1	52.7 ± 0.4	5145 ± 30
S5	427400	4520443	224	364	364	−31.44	82.1 ± 0.3	1589 ± 30	−13.5	86.7 ± 0.3	1147 ± 30
S6	427224	4520135	244	135	—	−30.29	81.0 ± 0.3	1690 ± 30	—	—	—
S7	427418	4519989	192	—	222	—	—	—	−12.4	84.7 ± 0.3	1330 ± 35
S8	427548	4520543	21	21	35	−28.61	85.4 ± 0.3	1265 ± 30	−27.25	87.4 ± 0.3	1080 ± 30
S9	427761	4520323	18	—	20	—	—	—	−17.68	92.4 ± 0.3	630 ± 30
S10	427903	4519999	177	—	137	—	—	—	−20.41	82.1 ± 0.2	1580 ± 25
S11	427810	4519913	723	209	495	−22.12	59.4 ± 0.3	4185 ± 35	−12.43	66.6 ± 0.2	3260 ± 30
S12	428188	4520361	15	98	103	−14.29	82.1 ± 0.3	1581 ± 30	−12.91	81.1 ± 0.3	1685 ± 25
S13	428107	4520300	335	112	159	−31.46	70.1 ± 0.3	2850 ± 30	−27.76	69.1 ± 0.3	2970 ± 30
S14	428211	4520150	113	234	243	—	—	—	−9.65	87.3 ± 0.3	1090 ± 30
S15	428198	4520526	69	60	54	—	—	—	−29.14	96.3 ± 0.3	300 ± 25
S16	427621	4507772	911	1412	854	−33.13	68.7 ± 0.3	3010 ± 35	−13.53	93.9 ± 0.3	505 ± 25
S17	427493	4519564	61	64	64	—	—	—	−14.4	97.4 ± 0.3	210 ± 25

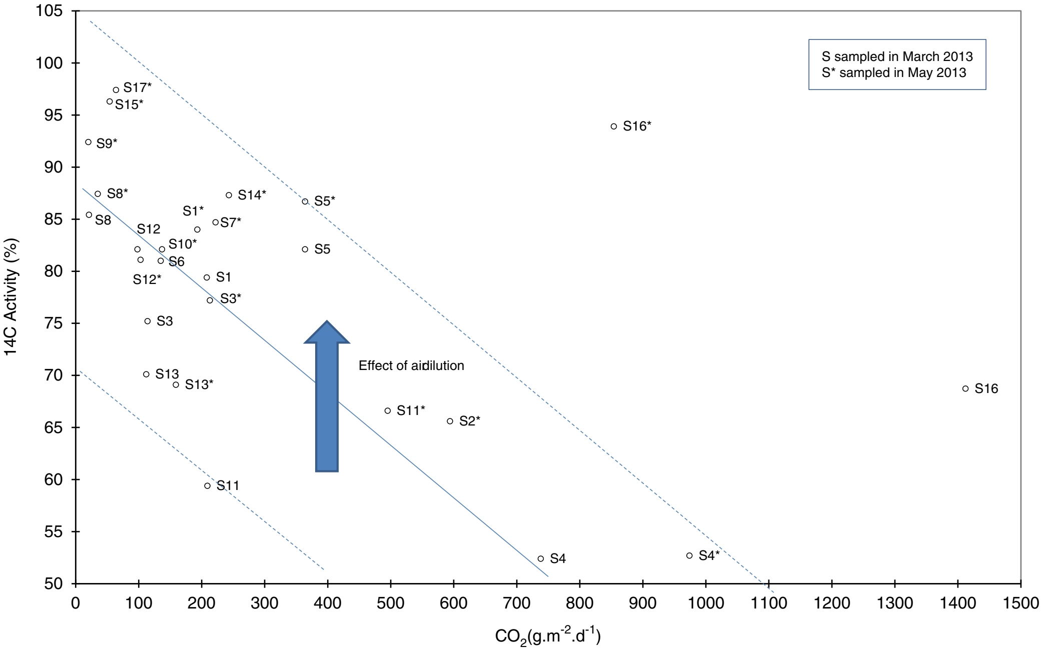

Figure 3 Graph of the ^{14}C activities measured in the plants against the Mean CO$_2$ fluxes measured in each site. The central curve corresponds to the regression line (R = 0.88); the inferior line corresponds to the less contribution of the meteorological conditions; the upper one the larger contribution. Si: sampled in March 2013; Si*: sampled in May 2013.

sample provides an average estimate of the local CO$_2$ emission both in spaces (over a few m^2) and, in time (between two successive sampling) and thus integrates the temporal variability of the gas flux. In order to check the sensitivity of our plant "sensor," we collected and analyzed two plant samples distant by one meter at point S9 (in May 2014). The two results 90.03 ± 0.3% and 91.52 ± 0.32% (ACM: 29.6 g.m^{-2}.day^{-1}), rather comparable, appear nevertheless significantly different beyond the range of the analytical accuracy. The values are near to that measured (92.4 ± 0.2%) on the May 2013 sample and show that the signal can be consistently recognized even at the site with the lowest flux of any measured in our study (18–20 g.m^{-2}.day^{-1}). Most of the results, for a given site, stay within a ± 5% range of variation, except for point 16 where an anomalous variation is observed for both the direct CO$_2$ flux measurement and the radiocarbon activity in the plants. This point is located close to an active fracture system, linked to the Pisciarelli fumaroles. Such a particular location may be responsible important short-term and longer-term variations in the degassing rate, which could thus explain the variability in ^{14}C depletion at that site.

Allard et al. (1997) and Pasquier et al. (1999) demonstrated that ^{14}C depletion in plants growing on volcanoes can also be associated with significant anomalies in δ^{13}C. Here we observe the same effect at Solfatara crater: the bulk δ^{13}C of the plants broadly increases with the local intensity of CO$_2$ degassing, in agreement with the mixing between standard atmospheric CO$_2$ (–8‰) and the volcanic CO$_2$ feeding Campi Flegrei (–0.73 to 1.87‰) (Allard et al. 1991b; Caliro et al. 2007). Figure 4 shows δ^{13}C values against the ^{14}C activity of our samples. We observe a difference between the two groups of C3 and C4 plants (as determined by δ^{13}C measurements) except for three points corresponding likely to mixed sample. The mixing between atmospheric

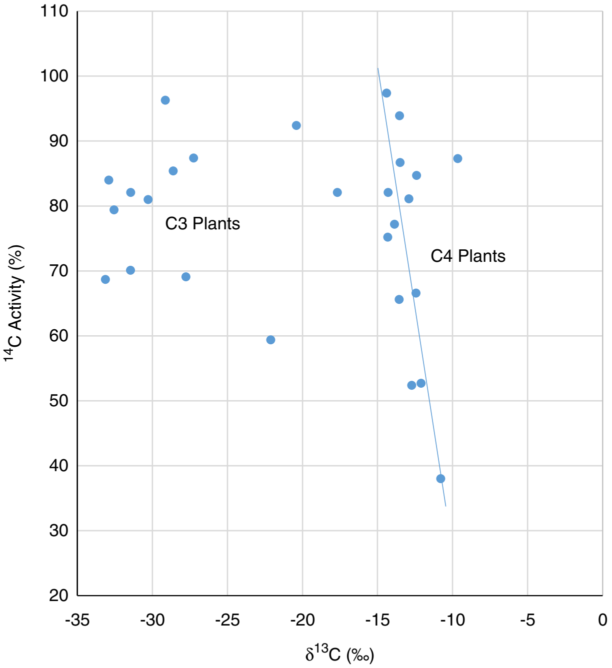

Figure 4 Graph of the ^{14}C activities against δ^{13}C measured in the plants for the C3 and C4 groups.

and volcanic CO_2 is clear for the C4 group of plants but not apparent for the C3 group; indeed, as evidenced by Farquhar et al. (1989), the carbon isotope discrimination evolution versus the ratio of intercellular and ambient partial pressures of CO_2 in the C3 and C4 group is different. Note that the δ^{13}C was determined in order to correct the ^{14}C activity measurements of the isotope fractionation not only due to plant photosynthesis but also to take account of chemical pretreatment and sample burning.

Finally, in 2014 we also sampled plants on the slope of Monte Nuovo, the most recent volcanic vent in Campi Flegrei, but far from any visible fumarolic emission. ^{14}C activity in these plants is measured at 100.9 ± 0.3%, indicating a small ^{14}C deficit of 1.5% compared to atmosphere, which is above our analytical uncertainty. Such a value, which corresponds to an apparent age of around 150 yr BP, indicates some contamination of the plants by a diffuse degassing of CO_2 through the volcanic soil. We thus find that plants living within the central part of Campi Flegrei caldera display apparent radiocarbon ages ranging from 5194 yr BP to 156 yr BP. These new data raise again the possibility of biased ^{14}C dating of volcanic deposits due to active ^{14}C devoid emanations of magma-derived CO_2 in volcanic areas (Saupé et al. 1980; Rolandi et al. 1998; Passariello et al. 2009).

To improve the detectability of ^{14}C depletion in the plants as a sensor of the local CO_2 soil degassing and to limit as far as possible the air dilution effect due to the wind, we positioned a greenhouse-like plastic box over an area about 1 m^2 of grass within the point 2 zone. By doing this, we measured that the ^{14}C activity in the plants decreased from 76.3% (sampled in October 2012) down to 38.0% while the δ^{13}C was lowered from –12.62 to –10.79‰. Therefore, the use of such a plastic box can significantly increase the actual volcanic CO_2 signal at a given site of emission. The sensitivity of such a "bio-sensor" can be extended to other applications (e.g. very low soil degassing or to detect possible leak in CO_2 storage sites).

CONCLUSIONS

Our results are compared with the data obtained from contemporaneous ACM CO_2 flux measurements at the same sites and thus allow investigating the impact of CO_2 emissions in Solfatara crater. We have correlated the ^{14}C deficit in plants with the mean CO_2 flux measured. It demonstrates that grass and plants growing in degassing areas of the Campi Flegrei volcanic complex (Solfatara crater, Pisciarelli zone, Monte Nuovo) typically record the imprint of CO_2 emanations in terms of both ^{14}C depletion and $\delta^{13}C$ mixing anomalies. Campi Flegrei is thus another volcanic area where such an effect of volcanic degassing is estimated using the ^{14}C deficit in plants.

Grass sampling at the sites used for our study could be renewed with a few weeks' periodicity between March and November; as such, they would provide the average degassing behavior making it possible to analyze more in detail the spatial and temporal variations of volcanic degassing. Moreover, the grass growing at low soil level is indeed more sensitive to CO_2 soil degassing. Therefore, future studies on plants growing in active volcanic zones should be systematically focused on grass within a few centimeters above soil surface. Complementary to ACM repeated measurements, our approach gives a weighted mean integrating the daily variations; it allows the mapping of protracted degassing on active volcanoes and may thus usefully contribute to the surveillance of quiescent volcanoes during long and dangerous phases of unrest.

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