

# Origin of the gases released from the Acqua Passante and Ermeta wells (Mt. Amiata, central Italy) and possible environmental implications for their closure

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## ABSTRACT

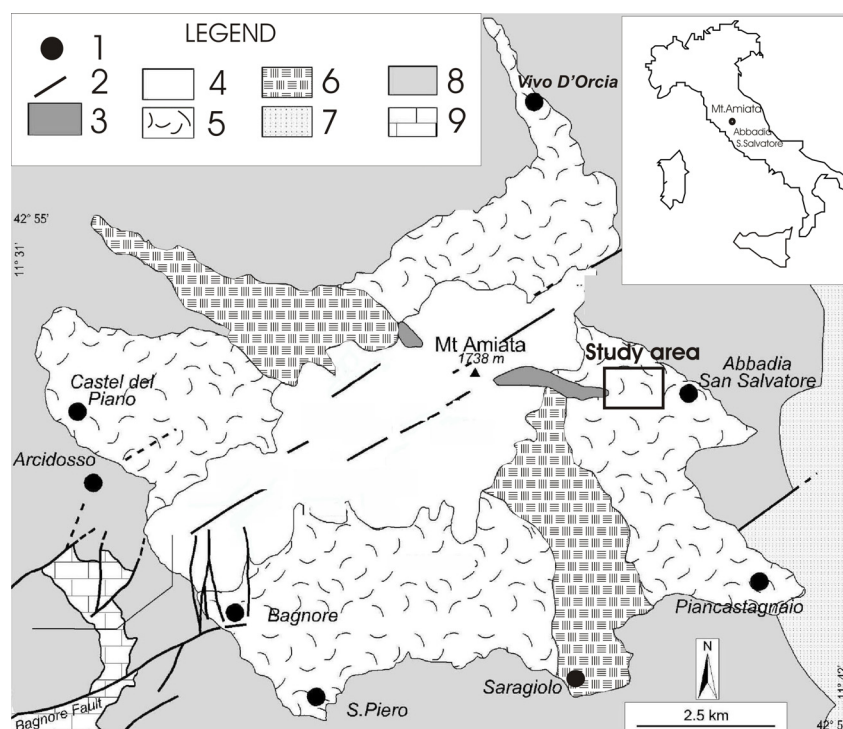
The Mt. Amiata volcano (Tuscany, central Italy) hosts the second largest geothermal field of Italy. Its SW and NE sectors are characterized by the presence of several CO<sub>2</sub>-rich (>95% by vol.) gas discharges. An intense Hg mining activity had taken place from the 19th century up to the end of the '70s, particularly close to Abbadia San Salvatore, during which two drillings (Acqua Passante and Ermeta) intercepted a CO<sub>2</sub>-rich gas fertile horizon. The related gases are emitted in the atmosphere since 1938 and 1959, respectively, causing severe concerns for the local air quality. In this work the results of a geochemical and isotopic survey carried out on these gas emissions from March 2009 to January 2014 are presented. CO<sub>2</sub> fluxes from both the two wells and soil from an area of about 653,500 m<sup>2</sup> located between them were measured. The two wells are emitting up to 15,000, 92 and 8 tons y<sup>-1</sup> of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S, respectively, while the computed soil CO<sub>2</sub> output was estimated at 4,311 ton y<sup>-1</sup>. The spatial distribution of the CO<sub>2</sub> soil flux suggests the presence of preferential patterns, indicating sites of higher permeability. Since the local municipality is evaluating the possibility to plug the Ermeta vent, a temporarily closure should first be carried out to test the possible influence of this operation on the diffuse soil degassing of deep-originated CO<sub>2</sub> in the surrounding area. This implies that diffuse soil gases should carefully be monitored before proceeding with its definitive closure.

## 1. Introduction

The occurrence of CO<sub>2</sub>-rich gas discharges is typical of active, quiescent and recent volcanic activity [e.g. Allard et al. 1991, Burton et al. 2013 and references therein]. Natural subsurface fluid reservoirs accumulating CO<sub>2</sub> produced by magma degassing and/or

thermo-metamorphic reactions of carbonates are indeed a relatively common geological feature, particularly in areas affected by subduction processes or lithospheric thinning where volcanic [e.g. Gerlach 1991] and/or geothermal [e.g. Brombach et al. 2001, Chiodini et al. 2004a, 2005] systems occur. Carbon dioxide released from these reservoirs is discharged into the atmosphere through soil diffuse degassing and/or punctual gas manifestations [e.g. Chiodini et al. 1999, 2010, Rogie et al. 2001, Minissale 2004].

In the peri-Tyrrhenian Italy, a region characterized by geothermal systems (e.g. Larderello, Mt. Amiata) and Quaternary (Roman Co-magmatic Province) and present (e.g. Vesuvius, Phlegrean Fields, Aeolian Islands) volcanic activity related to crustal thinning generated by the opening of the Tyrrhenian Sea [e.g. Zitellini et al. 1986, Bartole 1995, Mauffret et al. 1999, Peccerillo 2003, 2005, Peccerillo and Lustrino 2005], a large amount of deep-originated CO<sub>2</sub> is discharged from gas vents and diffuse soil emissions, and is present as dissolved inorganic carbon in ground waters [e.g. Minissale et al. 1997a, Chiodini et al. 1998, 2004b, Gambardella et al. 2004, Minissale 2004]. It has been estimated that >25.000 ton CO<sub>2</sub> day<sup>-1</sup> are naturally discharged by the Tuscan-Roman and Campanian Degassing Systems (TRDS and CDS, respectively) [Chiodini et al. 2004a]. In these areas, CO<sub>2</sub>-rich (>90 % by volume) gases discharged from gas vents located in sub-circular-shaped craters and associated to fissures, frac-



**Figure 1.** Geological sketch map of Mt. Amiata and location of the study area. Legend: (1) town; (2) fault; (3) third volcanic complex: the Ermeta olivine-latite lava flow:  $209 \pm 0.29$  ka; (4) second volcanic complex: porphyritic rhyodacite dome and lava flow, from  $300 \pm 0.04$  ka to  $190 \pm 0.23$  ka; (5) first volcanic complex, upper unit: trachydacite: from  $318 \pm 0.08$  ka to  $217 \pm 0.01$  ka; (6) first volcanic complex, lower unit: trachydacite: from  $305 \pm 0.005$  ka to  $241 \pm 0.07$  ka; (7) clay and sand: Early Pliocene; (8) Ligurian Units: Jurassic-Middle Eocene; (9) Tuscan Nappe: late Triassic-Oligocene (modified after Brogi et al. [2010]).

tures and structural lows (e.g. sinkholes), have caused fatal accidents, which have involved animals and human beings [e.g. Carapezza et al. 2003, Vaselli et al. 2006a, Tassi et al. 2009]. Locally,  $\text{CO}_2$  accumulation in air may be favored since this gas is relatively heavy (gas density of  $\text{CO}_2$  and air being of  $0.001977$  and  $0.001280 \text{ g mL}^{-1}$ , respectively). As a consequence, when the climatic conditions are characterized by low wind, cloudy weather and cold air temperature, the morphologically depressed areas hosting these gas vents may become deadly traps. Such  $\text{CO}_2$ -rich gas discharges are commonly accompanied by the presence of other toxic, dangerous and inflammable gases such as  $\text{H}_2\text{S}$  and/or  $\text{CH}_4$ , whose contents can be up to a few percentages [e.g. Minissale et al. 1997a, Minissale 2004].

The Mt. Amiata volcanic edifice is located in southern Tuscany (Figure 1). It represents the biggest and youngest volcano ( $\sim 200,000$  years old) of this region and hosts the second largest geothermal field of Italy after Larderello. Its south-westernmost (e.g. Selvena, Banditella and Zancona; Minissale et al. [1997b], Frondini et al. [2009]) and east-northernmost (e.g. Bagni San Filippo and Pietrineri; Minissale et al. [1997b], Frondini et al. [2009], Tassi et al. [2009]) flanks are characterized by the presence of several  $\text{CO}_2$ -rich ( $>95\%$  by volume) gas discharges, mostly recognized during mercury (cinnabar) exploitation in the eastern part of this volcanic complex. In 1938 and 1959 two wells, named

Acqua Passante (1,048 a.s.l.) and Ermeta (1,079 m a.s.l.), were drilled close to the town of Abbadia San Salvatore (Figure 2) in the volcanic cover at the depth of 116 and 298 m, respectively. It is worth to point out that, despite the large number of mining galleries, none of them was intercepted during the drilling activity. Currently, gases from these wells are discharged at the height of about 6 m above the ground, as two chimneys were built to minimize the disagreeable effects for the people approaching these areas due to the presence of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , the latter having the typical smell of rotten eggs.

Once the Hg mining activity was terminated, the owner of the mining concession (E.N.I.: National Agency for Hydrocarbons, AGIP Division) produced a series of documentation for the reclamation of the Hg extraction and processing areas. Finally, in 2008, an agreement between E.N.I. and the municipality of Abbadia San Salvatore was signed and, consequently, the ownership of the reclamation passed to the public agency [e.g. Vaselli et al. 2013]. In the agreement the Ermeta and Acqua Passante wells were also mentioned, since the local municipality was in charge to: i) periodically monitor the discharged gases; ii) efficiently maintain the chimneys and iii) propose alternative strategies to reduce the impact of the discharged gases released to the atmosphere.

The Acqua Passante well is located close to a picnic area along the main road that leads to the top of Mt.



**Figure 2.** Location of the i) Ermeta and Acqua Passante wells and ii) soil diffuse  $\varphi\text{CO}_2$  measurement sites.

Amiata, where skiing and trekking facilities are present. That of Ermeta is close the homonymous church (built in 1296) that is an important tourist and religious site.

In this paper we present the results of a geochemical and isotopic survey (from March 2009 to January 2014) carried out on the gases discharged from these two chimneys. The CO<sub>2</sub> flux from both the two vents and those from the soil carried out in July 2011 in an area of 653,550 m<sup>2</sup> located SE of the Ermeta chimney (Figure 2), was measured by using the hot-wire anemometer and accumulation chamber method [Baubron et al. 1990, 1991], respectively. The chemical composition of the gas discharges located close to the study area [Tassi et al. 2009] was reported for comparison.

The main goals of this study were those to: i) investigate the genetic relationships between the well gases and those naturally discharging nearby and ii) verify the possible implications related to the closure of the Ermeta and Acqua Passante wells by the local municipality to reduce the impact of the discharged gases on the local population and tourists.

## 2. Geological setting and mining activity

The Mt. Amiata area (southern Tuscany, central Italy; Figure 1) is characterized by a volcanic activity that lasted ca. 100,000 years, the related deposits, dominated by a trachydacitic composition, being emplaced between 300 and 190 ka [Ferrari et al. 1996, Cadoux and Pinti 2009]. The “residual” volcanic activity of this edifice related to the emplacement, at 6-7 km below the sea level, of a magmatic body in the Pliocene, produced

two geothermal reservoirs, which are feeding a number of CO<sub>2</sub>-rich gas manifestations and Ca-SO<sub>4</sub>-rich thermo-mineral waters, mainly located in NE and SW sector of the volcanic edifice [Minissale et al. 1997b, Frondini et al. 2009, Tassi et al. 2009]. Presently, two geothermal plants are operating at Bagnore and Piancastagnaio (Figure 1).

The geodynamic setting of the Mt. Amiata geothermal area is dominated by extensional structures developed from the Middle Miocene to the Quaternary, whilst collisional structures occurred from the Cretaceous to the Early Miocene [e.g. Brogi et al. 2010 and references therein]. The anomalous heat flux related to the Pliocene magmatic body, likely caused the emplacement of Hg ore deposits [Tanelli 1983, Klemm and Neumann 1984]. In the recent past, Mt. Amiata was one of the biggest Hg producers in the world [e.g. Rimondi et al. 2011, Vaselli et al. 2013 and references therein]. The Mt. Amiata Hg district is mainly distributed in the central-eastern and south-western sectors of this volcanic complex, although the principal mining activity was located in the municipality of Abbadia San Salvatore (Figure 1). The extraction and metallurgy of cinnabar (HgS) was aimed to produce metallic mercury from historic times until the middle seventies, when most of the Hg mines in the world were shut down due to environmental concerns. In the second half of the last century several wells, including those of Ermeta and Acqua Passante, were drilled for mining exploration close to Abbadia San Salvatore (Figure 2). It is worthwhile to mention that some of the mining gal-

leries were affected by dangerous CO<sub>2</sub> emissions, occasionally causing fatalities, and CO<sub>2</sub> is still abundantly present in some of them [Vaselli et al. 2006a, 2011]. Both the Ermeta and Acqua Passante wells are located in the volcanic cover and that of Ermeta is situated few hundreds meters from the Ermeta olivine-latitude lava flow that marked the latest event of the volcanic history of Mt. Amiata [e.g. Ferrari et al. 1996].

### 3. Material and methods

#### 3.1. Sampling and analysis of gases

The Ermeta well is located to the east of Abbazia San Salvatore whilst that of Acqua Passante is about 1 km NE on a fly of bird from Ermeta (Figure 2). From the two wells, 18 gas samples were collected from March 2009 to January 2014.

The well gases were collected using a 40 cm long Tygon® tube inserted into an artificial opening (25 mm in diameter) located at the base of the two ~6 m high chimneys (whose diameters are 300 mm) and connected to a pre-evacuated 60 mL glass thorian-tapped flask filled with 20 mL of a 4N NaOH and 0.15 M Cd(OH)<sub>2</sub> suspension [Vaselli et al. 2006b and references therein]. The analysis of the inorganic gases stored in the headspace of the sampling flasks (N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, He, CH<sub>4</sub>, Ar and Ne) was carried out with a Shimadzu 15A gas-chromatograph equipped with a 10 m long 5A molecular sieve column and a Thermal Conductivity Detector (TCD). The alkaline solution, separated from the solid precipitate by centrifugation, was used for the determination of CO<sub>2</sub>, as CO<sub>3</sub><sup>2-</sup>, by titration (Metrohm Basic Titrino) with a 0.5N HCl solution. The solid CdS was oxidized to SO<sub>4</sub><sup>2-</sup> with H<sub>2</sub>O<sub>2</sub> and analyzed for the determination of H<sub>2</sub>S by ion-chromatography [Montegrossi et al. 2001]. Analytical error was <5%. The <sup>13</sup>C/<sup>12</sup>C isotopic ratio of CO<sub>2</sub> (expressed as δ<sup>13</sup>C-CO<sub>2</sub> ‰ V-PDB) was measured after the purification and extraction of CO<sub>2</sub> by using the two cryogenic traps method [Vaselli et al. 2006b]. The analytical error and the reproducibility were ±0.05‰ and ±0.1‰, respectively. The determination of the <sup>3</sup>He/<sup>4</sup>He ratios (expressed as R/R<sub>a</sub>, where R is the <sup>3</sup>He/<sup>4</sup>He measured ratio and R<sub>a</sub> is the <sup>3</sup>He/<sup>4</sup>He ratio in the air: 1.39\*10<sup>-6</sup>; Mamyryn and Tolstikhin [1984]) was carried out at the University of Rochester Rare Gas Facility using a VG 5400 Rare Gas Mass Spectrometer by using the method described in Poreda and Farley [1992]. The measured <sup>3</sup>He/<sup>4</sup>He ratios were corrected for the addition of air on the basis of the <sup>4</sup>He/<sup>20</sup>Ne ratios measured by mass spectrometry, assuming that <sup>20</sup>Ne had an atmospheric origin [Craig and Lupton 1976, Sano and Wakita 1988]. Analytical error for R/R<sub>a</sub> determination was ≤0.3 %.

#### 3.2. Measurements of the CO<sub>2</sub> flux from the chimneys and diffuse soil

The CO<sub>2</sub> flux of the two chimneys was determined by inserting into the chimneys (whose section had an area of 0.07 m<sup>2</sup>) a Delta Ohm model HD2103.2 hot-wire anemometer probe. CO<sub>2</sub> flux records were set to acquire the data from August 5 to September 5, 2011, during which the CO<sub>2</sub> flux was measured every 5 minutes and was calculated on the basis of the discharged gas velocity and temperature inside the pipelines. The CO<sub>2</sub> flux values were normalized at 20°C. The temperature of the Ermeta chimney was ranging between 26.8 and 29°C, while that of Acqua Passante was between 16.9 and 22.5°C.

The survey of diffuse soil CO<sub>2</sub> flux (July 2011) covered an area of 653,550 m<sup>2</sup> with 301 evenly distributed measuring sites and was carried out in the SE sector of the Ermeta chimney (Figure 2). All the measurements were carried out where soils developed on the Mt. Amiata volcanic products, avoiding those areas where the volcanic rocks were cropping out.

To measure the CO<sub>2</sub> flux from the soil, a direct and dynamic method that follows the principle of the so-called accumulation chamber [Baubron et al. 1990, 1991] was used. This method, initially used to determine soil respiration [i.e. Kanemasu et al. 1974, Parkinson 1981], has been widely applied for measuring diffuse soil CO<sub>2</sub> flux in volcanic and geothermal [e.g. Tonani and Miele 1991, Chiodini et al. 1996, 1998, 2000, 2003, 2004a, Pancioli et al. 2009, Tassi et al. 2009] and solid waste disposal landfills [e.g. Raco et al. 2006, 2008, Moretti et al. 2007]. The instrument consisted of: i) an inverted chamber equipped with a system to mix the air in the chamber headspace (volume = 3.06 × 10<sup>-3</sup> m<sup>3</sup> and area height = 100 mm), ii) an Infra-Red (IR) spectrophotometer with LICOR Li-820 sensor (measuring range of 0-20,000 ppm, accuracy of 4% of reading), iii) an analogue-digital (AD) converter and iv) a palmtop computer (PC). In order to prevent damages to both the pump and the CO<sub>2</sub> detector, a magnesium perchlorate desiccant trap was placed between the outlet fitting of the accumulation chamber and the inlet of the PTFE Filter to adsorb soil humidity.

Once the accumulation chamber was positioned on the ground a low-flux pump (20 mL s<sup>-1</sup>) continuously conveyed the soil gas from the chamber to the IR sensor. To minimize the disturbance effects due to changes of barometric conditions, the soil gas was re-injected into the chamber.

The  $dC_{CO_2}/dt$  values were computed in the field with the PC connected with the IR through the AD. The soil φCO<sub>2</sub> was calculated on the basis of the measured CO<sub>2</sub> concentration increment inside the chamber over time ( $dC_{CO_2}/dt$ ), according to the following equation:

THE CO<sub>2</sub>-RICH GASES FROM THE ACQUA PASSANTE AND ERMETA WELLS (MT. AMIATA, ITALY)

Name	Date	CO <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub>	CH <sub>4</sub>	Ar	O <sub>2</sub>	H <sub>2</sub>	He	δ <sup>13</sup> C-CO <sub>2</sub>	R/Ra
Ermeta	Mar-09	986	0.30	2.8	10	0.014	0.16	0.074	0.00064	n.d.	0.33
Ermeta	Jul-09	982	0.77	14	2.8	0.048	0.057	0.078	0.00097	-3.39	
Ermeta	Oct-09	978	0.62	15	5.7	0.025	0.004	0.68	0.0013	-3.39	
Ermeta	Dec-09	986	0.56	4.2	8.9	0.038	0.23	0.12	0.0012	-3.33	
Ermeta	Apr-09	986	0.36	5.1	7.7	0.056	0.16	0.21	0.0014	-3.35	
Ermeta	Jul-10	987	0.33	5.5	6.9	0.053	0.19	0.12	0.00089	-3.48	0.32
Ermeta	Oct-10	987	0.40	6.2	5.8	0.045	0.16	0.24	0.00055	-3.13	
Ermeta	Nov-10	987	0.33	6.3	5.6	0.049	0.16	0.21	0.00069	-3.27	
Ermeta	Apr-11	989	0.58	4.6	5.5	0.032	0.14	0.54	0.00091	-3.27	
Ermeta	Jun-11	987	0.42	5.6	6.7	0.037	0.15	0.55	0.00075	-3.41	
Ermeta	Oct-11	983	0.77	6.1	9.5	0.045	0.14	0.44	0.00074	-3.45	
Ermeta	Dec-11	987	0.34	5.6	6.6	0.056	0.19	0.25	0.00066	-3.09	
Ermeta	Mar-12	988	0.55	5.3	5.1	0.052	0.21	0.34	0.00039	-3.33	
Ermeta	Apr-12	989	0.45	5.2	5.0	0.046	0.21	0.28	0.00031	n.d.	
Ermeta	Jul-12	988	0.52	5.6	5.0	0.056	0.15	0.30	0.00028	-3.36	
Ermeta	Jan-13	989	0.72	5.1	4.9	0.052	0.19	0.26	0.00018	-3.27	
Ermeta	Jul-13	989	0.81	5.0	4.6	0.061	0.22	0.27	0.00011	-3.32	
Ermeta	Jan-14	989	0.66	5.5	4.8	0.036	0.16	0.22	0.00016		
Acqua Passante	Mar-09	987	0.34	6.4	5.9	0.029	0.11	0.080	0.00069	-3.31	0.29
Acqua Passante	Jul-09	977	0.33	12	11	0.043	0.73	0.069	0.0022	-2.92	
Acqua Passante	Oct-09	988	0.30	7.5	4.0	0.020	0.01	0.12	0.00063	-3.38	
Acqua Passante	Dec-09	988	0.39	6.1	5.0	0.032	0.16	0.085	0.00087	-3.33	
Acqua Passante	Apr-09	988	0.22	6.7	4.5	0.063	0.22	0.076	0.00061	-3.31	
Acqua Passante	Jul-10	988	0.22	6.4	5.2	0.060	0.20	0.087	0.00055	-3.47	0.40
Acqua Passante	Oct-10	989	0.32	5.9	4.4	0.053	0.13	0.18	0.00087	-3.26	
Acqua Passante	Nov-10	988	0.36	6.1	4.9	0.056	0.11	0.22	0.00065	-3.13	
Acqua Passante	Apr-11	989	0.59	5.2	5.0	0.036	0.14	0.39	0.00086	-3.13	
Acqua Passante	Jun-11	987	0.37	5.7	6.0	0.041	0.16	0.34	0.00061	-3.11	
Acqua Passante	Oct-11	985	0.66	6.4	7.8	0.030	0.12	0.33	0.00066	-3.39	
Acqua Passante	Dec-11	986	0.30	6.3	6.6	0.061	0.27	0.14	0.00044	-3.25	
Acqua Passante	Mar-12	989	0.40	5.5	5.0	0.061	0.24	0.26	0.00035	-2.84	
Acqua Passante	Apr-12	989	0.41	5.4	5.1	0.053	0.19	0.23	0.00025	n.d.	
Acqua Passante	Jul-12	989	0.45	5.3	4.9	0.055	0.18	0.25	0.00024	-3.33	
Acqua Passante	Jan-13	989	0.56	5.1	4.6	0.056	0.22	0.25	0.00015	-3.21	
Acqua Passante	Jul-13	989	0.63	5.1	4.8	0.050	0.19	0.31	0.00013	-3.35	
Acqua Passante	Jan-14	989	0.58	5.3	4.9	0.054	0.18	0.26	0.00019		
Name	ID	CO <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub>	CH <sub>4</sub>	Ar	O <sub>2</sub>	H <sub>2</sub>	He	δ <sup>13</sup> C-CO <sub>2</sub>	R/Ra
Polla nera*	PN	980	0.54	11	8.7	0.025	0.0047	0.0020	0.0031		
Spuntone*	SP	972	0.55	16	11	0.032	0.0027	0.00003	0.0045	-2.87	
Hole*	HO	982	0.61	11	6.0	0.021	0.0020	0.0014	0.0033	-2.61	
Poggio all'Olivio*	PO	983	0.95	8.6	7.2	0.018	0.0038	0.00043	0.0026	-3.24	
Polla Grigia*	PG	976	0.79	13	11	0.029	0.0028	0.0034	0.0039		
Mammellone*	MA	978	0.81	14	7.5	0.022	0.0021	0.00057	0.00086	-2.63	0.13

**Table 1.** Chemical (in mmol/mol) and isotopic (carbon: as δ<sup>13</sup>C-CO<sub>2</sub> vs. V-PDB ‰; and helium as R/Ra) composition of the Ermeta and Acqua Passante gases and of the bubbling pools and dry vents (PN, SP, HO, PO, PG and MA). (\*): data from Tassi et al. [2009].

$$\phi\text{CO}_2 = cf \times (dC_{\text{CO}_2}/dt) \quad (1)$$

where the proportionality factor ( $cf$ ) between  $dC_{\text{CO}_2}/dt$  and  $\phi\text{CO}_2$  was determined by laboratory tests through an artificial soil, during which an interval of controlled  $\phi\text{CO}_2$  values (from 10 to 10,000  $\text{g m}^{-2} \text{day}^{-1}$ ) was measured (at least 6 measurements were repeated for each  $\phi\text{CO}_2$  value). The  $cf$  factor was then computed as the slope of the linear best-fit line of  $\phi\text{CO}_2$  vs.  $dC_{\text{CO}_2}/dt$ .

## 4. Results

### 4.1. Chemical and isotopic ( $\delta^{13}\text{C-CO}_2$ and $R/R_a$ ) compositions of gases from wells, bubbling pools and dry vents

The chemical and isotopic ( $\delta^{13}\text{C-CO}_2$  and  $R/R_a$  values) compositions of the Ermeta and Acqua Passante gases and, for comparison, those of six bubbling pools and dry gas vents (namely PN, SP HO, PO, PG and MA; see Tassi et al. [2009] for their location), located at about 5 km NE of Abbadia San Salvatore, are reported in Table 1.

The Ermeta and Acqua Passante wells discharged gases having a similar composition, being both dominated by  $\text{CO}_2$  (up to 989  $\text{mmol mol}^{-1}$ ), with significant concentrations of  $\text{N}_2$  (up to 14 and 12  $\text{mmol mol}^{-1}$ , respectively),  $\text{CH}_4$  (up to 10 and 11  $\text{mmol mol}^{-1}$ , respectively) and  $\text{H}_2\text{S}$  (up to 0.81 and 0.66  $\text{mmol mol}^{-1}$ , respectively). Hydrogen concentrations ranged from 0.069 (Acqua Passante, July 2009) to 0.55  $\text{mmol mol}^{-1}$  (Ermeta, June 2011), while those of noble gases, i.e. Ar, He and Ne, were up to 0.061, 0.00022, and 0.00003,  $\text{mmol mol}^{-1}$ , respectively. The chemical composition of the bubbling pools was basically identical to that of the two wells, with the only exception of  $\text{H}_2$ , whose concentration in the well gases was up to 3 orders of magnitude lower than in the wells. Helium ( $R/R_a$ ) and carbon ( $\delta^{13}\text{C-CO}_2$ ) isotopic compositions in the wells were in a narrow range, from 0.32 to 0.40 and from  $-3.48$  to  $-2.84\text{‰}$  vs. V-PDB, respectively. The helium isotopic ratio for the natural gas discharges was only available for MA, whose value was moderately lower ( $R/R_a=0.13$ ) than those of the Ermeta and Acqua Passante gases, while those of carbon in  $\text{CO}_2$  were, on average, slightly more positive (between  $-3.24$  and  $-2.61\text{‰}$  vs. V-PDB).

### 4.2. $\text{CO}_2$ flux from the chimneys and diffuse soil

The database of the  $\text{CO}_2$  flux measurements from the Ermeta and Acqua Passante chimneys consisted of more than 9,000 measurements (not reported) and ranged from 8.86 to 11.06 (mean value:  $10.05 \pm 0.45$ )  $\text{mol sec}^{-1}$  and from 0.89 to 2.51 (mean value:  $1.32 \pm 0.17$ )  $\text{mol sec}^{-1}$ , respectively. The calculated  $\text{CO}_2$  output from Ermeta was  $\approx 13,000 \text{ ton y}^{-1}$ , whereas that of Acqua Passante clustered around  $1,800 \text{ ton y}^{-1}$ .

The spatial distribution of the soil diffuse  $\text{CO}_2$  flux measurements was partly dictated by the rough and intensely vegetated territory. The measured  $\phi\text{CO}_2$  values (301 data), ranging from 0.07 to  $3.42 \text{ mol m}^{-2} \text{day}^{-1}$  with an average value of  $0.38 \text{ mol m}^{-2} \text{day}^{-1}$  (Table 2), showed a normal logarithmic behavior with a 0.05 significance level (Figure 3), indicating that the  $\ln(\phi\text{CO}_2)$  values had a modal density distribution. Mean, median, minimum, maximum  $\phi\text{CO}_2$  values and standard deviation are reported as  $\ln$ -values in Table 3.

## 5. Discussion

### 5.1. Origin of gases

The chemical composition of the Ermeta and Acqua Passante gases is basically consistent with that shown by the gas discharges located NE of Mt. Amiata, which are likely fed by a hydrothermal system consisting of two aquifers at distinct depth (500-1,000 m and  $>3,000$  m, respectively) and temperature (up to 230 and  $350^\circ\text{C}$ , respectively) [Calamai et al. 1970, Gianelli et al. 1988]. The  $\delta^{13}\text{C-CO}_2$  values (Table 1) are slightly heavier than the typical range of mantle  $\text{CO}_2$  [Rollinson 1993, Hoefs 1997, Ohmoto and Goldhaber 1997], suggesting that  $\text{CO}_2$  has a twofold origin, i.e. mantle degassing and thermometamorphic reactions acting on limestone [Minissale et al. 1997a, Frondini et al. 2009]. This feature is common to the great majority of the gas emissions from the peri-Tyrrhenian central Italy (Tuscan-Roman Degassing System, TRDS; Chiodini et al. [2004a]). In this region, a significant mantle contamination by crustal fluids released from the subducted Adriatic plate occurs [Martelli et al. 2004, Frondini et al. 2009], as testified by the relatively low  $R/R_a$  values ( $<0.4$ ; Table 1). Thermogenic processes involving organic material buried in sedimentary formation are the most likely source for the high  $\text{N}_2/\text{Ar}$  ratios and  $\text{CH}_4$  and  $\text{H}_2\text{S}$  concentrations measured in gases from both the two wells and the nearby gas discharges. The relatively high  $\text{H}_2$  concentrations characterizing the Ermeta and Acqua Passante gases, significantly higher than those of the Mt. Amiata gas discharges (Figure 4), are likely resulting by the corrosion of the internal iron tubing of the wells, which is favored by the presence of  $\text{CO}_2$ - and  $\text{H}_2\text{S}$ -rich gases. It is likely that this alteration process allows air to enter the chimneys. This would also explain the Ar enrichment shown by the wells gases with respect to the naturally discharges ones (Figure 5).

### 5.2. Spatial variation and output of soil diffuse $\phi\text{CO}_2$

In order to better constrain the total  $\phi\text{CO}_2$  and visualize its spatial distribution, the  $\text{CO}_2$  iso-flux map is reported in Figure 6, which was drawn by means of the

THE CO<sub>2</sub>-RICH GASES FROM THE ACQUA PASSANTE AND ERMETA WELLS (MT. AMIATA, ITALY)

Date	UTM-WEST		UTM-NORTH		Date	φCO <sub>2</sub>	UTM-WEST		UTM-NORTH		Date	φCO <sub>2</sub>	UTM-WEST		UTM-NORTH		φCO <sub>2</sub>
	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32			(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32			(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	
Jul-11	715923	4751610	717023	4751410	Jul-11	0.38	717023	4751410	716523	4751210	Jul-11	0.64	717023	4750860	717023	4750860	0.15
Jul-11	715973	4751610	717073	4751410	Jul-11	0.21	717073	4751410	716573	4751210	Jul-11	0.45	716223	4751010	716223	4751010	0.49
Jul-11	716023	4751610	717123	4751410	Jul-11	0.22	717123	4751410	716623	4751210	Jul-11	0.27	716273	4751010	716273	4751010	0.41
Jul-11	716073	4751610	715973	4751360	Jul-11	0.59	715973	4751360	716673	4751210	Jul-11	0.35	716323	4751010	716323	4751010	0.46
Jul-11	716123	4751610	716023	4751360	Jul-11	0.23	716023	4751360	716723	4751210	Jul-11	0.40	716373	4751010	716373	4751010	0.33
Jul-11	716173	4751610	716073	4751360	Jul-11	0.28	716073	4751360	716773	4751210	Jul-11	0.17	716423	4751010	716423	4751010	0.47
Jul-11	716223	4751610	716123	4751360	Jul-11	0.39	716123	4751360	716823	4751210	Jul-11	0.29	716473	4751010	716473	4751010	0.28
Jul-11	715923	4751560	716173	4751360	Jul-11	0.26	716173	4751360	716873	4751210	Jul-11	0.71	716523	4751010	716523	4751010	0.57
Jul-11	715973	4751560	716223	4751360	Jul-11	0.32	716223	4751360	716923	4751210	Jul-11	0.91	716573	4751010	716573	4751010	0.65
Jul-11	716023	4751560	716273	4751360	Jul-11	0.25	716273	4751360	716973	4751210	Jul-11	0.40	716623	4751010	716623	4751010	0.77
Jul-11	716073	4751560	716323	4751360	Jul-11	0.46	716323	4751360	717023	4751210	Jul-11	0.45	716673	4751010	716673	4751010	0.14
Jul-11	716123	4751560	716373	4751360	Jul-11	0.55	716373	4751360	717073	4751210	Jul-11	0.75	716723	4751010	716723	4751010	0.71
Jul-11	716173	4751560	716423	4751360	Jul-11	0.42	716423	4751360	717123	4751210	Jul-11	1.65	716773	4751010	716773	4751010	0.35
Jul-11	716223	4751560	716473	4751360	Jul-11	0.84	716473	4751360	716173	4751160	Jul-11	0.18	717073	4750910	717073	4750910	0.45
Jul-11	715973	4751510	716523	4751360	Jul-11	0.44	716523	4751360	716223	4751160	Jul-11	0.12	717123	4750910	717123	4750910	0.35
Jul-11	716023	4751510	716573	4751360	Jul-11	0.54	716573	4751360	716273	4751160	Jul-11	0.32	716173	4750860	716173	4750860	0.60
Jul-11	716073	4751510	716623	4751360	Jul-11	0.24	716623	4751360	716323	4751160	Jul-11	0.22	716223	4750860	716223	4750860	0.49
Jul-11	716123	4751510	716673	4751360	Jul-11	0.46	716673	4751360	716373	4751160	Jul-11	0.23	716273	4750860	716273	4750860	0.86
Jul-11	716173	4751510	716723	4751360	Jul-11	0.38	716723	4751360	716423	4751160	Jul-11	0.53	716323	4750860	716323	4750860	0.21
Jul-11	716223	4751510	716773	4751360	Jul-11	0.64	716773	4751360	716473	4751160	Jul-11	0.29	716373	4750860	716373	4750860	0.57
Jul-11	716273	4751510	716823	4751360	Jul-11	0.23	716823	4751360	716523	4751160	Jul-11	0.66	716423	4750860	716423	4750860	0.22
Jul-11	716323	4751510	716873	4751360	Jul-11	0.22	716873	4751360	716573	4751160	Jul-11	0.39	716473	4750860	716473	4750860	0.27
Jul-11	716373	4751510	716923	4751360	Jul-11	0.65	716923	4751360	716623	4751160	Jul-11	0.30	716523	4750860	716523	4750860	0.45
Jul-11	716423	4751510	716973	4751360	Jul-11	0.31	716973	4751360	716673	4751160	Jul-11	0.47	716573	4750860	716573	4750860	0.36
Jul-11	716473	4751510	717023	4751360	Jul-11	0.26	717023	4751360	716723	4751160	Jul-11	0.41	716623	4750860	716623	4750860	0.43

Table 2 (continues on pages 8 and 9). Sampling date, geographical coordinates (in UTM) and φCO<sub>2</sub> values (in mol m<sup>-2</sup> day<sup>-1</sup>).

Date	UTM-WEST		UTM-NORTH		$\varphi\text{CO}_2$	Date	UTM-WEST		UTM-NORTH		$\varphi\text{CO}_2$	Date	UTM-WEST		UTM-NORTH		$\varphi\text{CO}_2$
	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32			(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32			(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	
Jul-11	716523	4751510	717073	4751360	0.43	Jul-11	717073	4751360	0.29	Jul-11	716773	4751160	0.38	Jul-11	716673	4750860	0.57
Jul-11	716573	4751510	717123	4751360	0.35	Jul-11	717123	4751360	0.39	Jul-11	716823	4751160	0.53	Jul-11	717123	4750860	0.57
Jul-11	716623	4751510	716173	4751310	0.38	Jul-11	716173	4751310	0.31	Jul-11	716873	4751160	1.93	Jul-11	716973	4750860	0.32
Jul-11	716673	4751510	716223	4751310	0.26	Jul-11	716223	4751310	0.47	Jul-11	716923	4751160	1.01	Jul-11	716823	4751010	0.45
Jul-11	716723	4751510	716273	4751310	0.24	Jul-11	716273	4751310	0.36	Jul-11	716973	4751160	0.45	Jul-11	716873	4751010	1.25
Jul-11	716773	4751510	716323	4751310	1.12	Jul-11	716323	4751310	1.23	Jul-11	717023	4751160	0.46	Jul-11	716923	4751010	0.27
Jul-11	716823	4751510	716373	4751310	0.11	Jul-11	716373	4751310	0.92	Jul-11	717073	4751160	0.88	Jul-11	716973	4751010	0.23
Jul-11	716873	4751510	716423	4751310	0.40	Jul-11	716423	4751310	0.33	Jul-11	717123	4751160	1.76	Jul-11	717023	4751010	0.36
Jul-11	716923	4751510	716473	4751310	0.63	Jul-11	716473	4751310	0.71	Jul-11	716173	4751110	0.27	Jul-11	717073	4751010	0.64
Jul-11	715973	4751460	716523	4751310	0.34	Jul-11	716523	4751310	0.59	Jul-11	716223	4751110	0.26	Jul-11	717123	4751010	0.24
Jul-11	716023	4751460	716573	4751310	0.26	Jul-11	716573	4751310	0.11	Jul-11	716273	4751110	0.27	Jul-11	716173	4750960	0.24
Jul-11	716073	4751460	716623	4751310	0.32	Jul-11	716623	4751310	0.56	Jul-11	716323	4751110	0.18	Jul-11	716223	4750960	0.13
Jul-11	716123	4751460	716673	4751310	0.26	Jul-11	716673	4751310	0.53	Jul-11	716373	4751110	0.61	Jul-11	716273	4750960	0.41
Jul-11	716173	4751460	716723	4751310	0.44	Jul-11	716723	4751310	0.46	Jul-11	716423	4751110	0.17	Jul-11	716323	4750960	0.37
Jul-11	716223	4751460	716773	4751310	0.58	Jul-11	716773	4751310	1.12	Jul-11	716473	4751110	0.38	Jul-11	716373	4750960	0.42
Jul-11	716323	4751460	716823	4751310	0.46	Jul-11	716823	4751310	0.59	Jul-11	716523	4751110	0.17	Jul-11	716423	4750910	1.21
Jul-11	716373	4751460	716873	4751310	0.24	Jul-11	716873	4751310	0.51	Jul-11	716573	4751110	0.07	Jul-11	716473	4750910	0.58
Jul-11	716423	4751460	716923	4751310	0.29	Jul-11	716923	4751310	0.27	Jul-11	716623	4751110	0.18	Jul-11	716523	4750910	0.49
Jul-11	716473	4751460	716973	4751310	0.20	Jul-11	716973	4751310	1.07	Jul-11	716673	4751110	0.47	Jul-11	716573	4750910	0.45
Jul-11	716523	4751460	717023	4751310	0.52	Jul-11	717023	4751310	0.30	Jul-11	716723	4751110	0.83	Jul-11	716623	4750910	0.27
Jul-11	716573	4751460	717073	4751310	0.34	Jul-11	717073	4751310	0.39	Jul-11	716773	4751110	0.79	Jul-11	716673	4750910	0.40
Jul-11	716623	4751460	717123	4751310	0.24	Jul-11	717123	4751310	0.13	Jul-11	716823	4751110	0.32	Jul-11	716723	4750910	0.39
Jul-11	716673	4751460	716173	4751260	0.47	Jul-11	716173	4751260	0.35	Jul-11	716873	4751110	0.52	Jul-11	716773	4750910	0.43
Jul-11	716723	4751460	716223	4751260	0.38	Jul-11	716223	4751260	0.63	Jul-11	716923	4751110	0.20	Jul-11	716823	4750910	0.34
Jul-11	716773	4751460	716273	4751260	0.53	Jul-11	716273	4751260	0.20	Jul-11	716973	4751110	0.27	Jul-11	716873	4750910	0.20

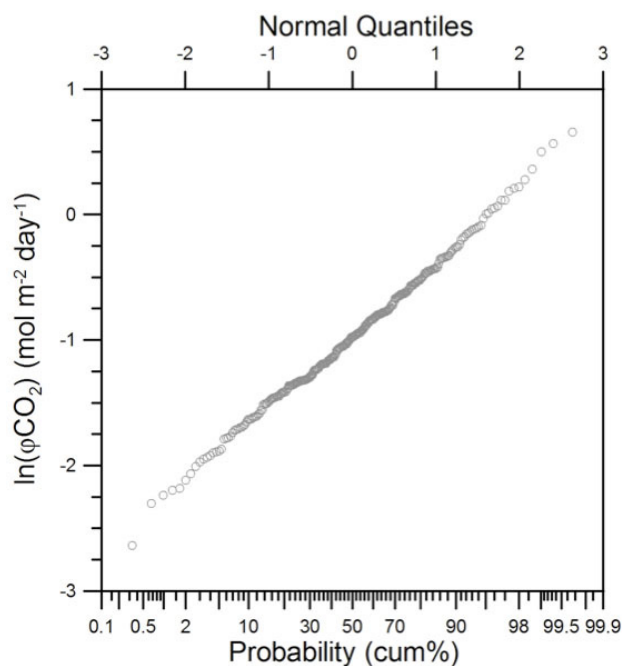
**Table 2** (continued from previous page). Sampling date, geographical coordinates (in UTM) and  $\varphi\text{CO}_2$  values (in  $\text{mol m}^{-2} \text{day}^{-1}$ ).



THE CO<sub>2</sub>-RICH GASES FROM THE ACQUA PASSANTE AND ERMETA WELLS (MT. AMIATA, ITALY)

Date	UTM-WEST		UTM-NORTH		Date	φCO <sub>2</sub>	UTM-WEST		UTM-NORTH		Date	φCO <sub>2</sub>	UTM-WEST		UTM-NORTH		φCO <sub>2</sub>
	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32			(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32			(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	(WGS84) Zone 32	
Jul-11	716823	4751460	716323	4751260	Jul-11	1.44	717023	4751110	716923	4750910	Jul-11	0.23	716923	4750910	0.32		
Jul-11	716873	4751460	716373	4751260	Jul-11	0.41	717073	4751110	716973	4750910	Jul-11	0.20	716973	4750910	0.72		
Jul-11	716923	4751460	716423	4751260	Jul-11	0.63	717123	4751110	717023	4750910	Jul-11	1.05	717023	4750910	0.17		
Jul-11	715973	4751410	716473	4751260	Jul-11	0.27	716173	4751060	716923	4750860	Jul-11	0.71	716923	4750860	0.30		
Jul-11	716023	4751410	716523	4751260	Jul-11	0.26	716223	4751060	716423	4750960	Jul-11	0.26	716423	4750960	0.70		
Jul-11	716073	4751410	716573	4751260	Jul-11	0.42	716273	4751060	716473	4750960	Jul-11	0.64	716473	4750960	0.59		
Jul-11	716123	4751410	716623	4751260	Jul-11	0.66	716323	4751060	716523	4750960	Jul-11	0.86	716523	4750960	0.54		
Jul-11	716173	4751410	716673	4751260	Jul-11	0.51	716373	4751060	716573	4750960	Jul-11	0.44	716573	4750960	0.23		
Jul-11	716223	4751410	716723	4751260	Jul-11	0.35	716423	4751060	716623	4750960	Jul-11	0.45	716623	4750960	0.29		
Jul-11	716273	4751410	716773	4751260	Jul-11	0.31	716473	4751060	716673	4750960	Jul-11	0.36	716673	4750960	0.19		
Jul-11	716323	4751410	716823	4751260	Jul-11	0.53	716523	4751060	716723	4750960	Jul-11	0.19	716723	4750960	0.21		
Jul-11	716373	4751410	716873	4751260	Jul-11	0.35	716573	4751060	716773	4750960	Jul-11	0.26	716773	4750960	0.11		
Jul-11	716423	4751410	716923	4751260	Jul-11	0.32	716623	4751060	716823	4750960	Jul-11	0.10	716823	4750960	0.24		
Jul-11	716473	4751410	716973	4751260	Jul-11	0.30	716673	4751060	716873	4750960	Jul-11	0.52	716873	4750960	0.37		
Jul-11	716523	4751410	717023	4751260	Jul-11	0.14	716723	4751060	716923	4750960	Jul-11	0.60	716923	4750960	0.55		
Jul-11	716573	4751410	717073	4751260	Jul-11	0.61	716773	4751060	716973	4750960	Jul-11	0.36	716973	4750960	0.20		
Jul-11	716623	4751410	717123	4751260	Jul-11	0.58	716823	4751060	717023	4750960	Jul-11	0.65	717023	4750960	3.42		
Jul-11	716673	4751410	716173	4751210	Jul-11	0.20	716873	4751060	717073	4750960	Jul-11	0.36	717073	4750960	0.38		
Jul-11	716723	4751410	716223	4751210	Jul-11	0.29	716923	4751060	717123	4750960	Jul-11	0.90	717123	4750960	0.50		
Jul-11	716773	4751410	716273	4751210	Jul-11	0.43	716973	4751060	716173	4750910	Jul-11	0.31	716173	4750910	0.71		
Jul-11	716823	4751410	716323	4751210	Jul-11	0.19	717023	4751060	716223	4750910	Jul-11	0.14	716223	4750910	0.39		
Jul-11	716873	4751410	716373	4751210	Jul-11	0.35	717073	4751060	716273	4750910	Jul-11	0.43	716273	4750910	0.32		
Jul-11	716923	4751410	716423	4751210	Jul-11	1.32	717123	4751060	716323	4750910	Jul-11	0.26	716323	4750910	0.30		
Jul-11	716973	4751410	716473	4751210	Jul-11	0.67	716173	4751010	716373	4750910	Jul-11	0.28	716373	4750910	0.43		
Jul-11	717073	4750860	716823	4750860	Jul-11	0.30	716873	4750860	716723	4750860	Jul-11	0.30	716723	4750860	0.37		
					Jul-11				716773	4750860	Jul-11		716773	4750860	0.23		

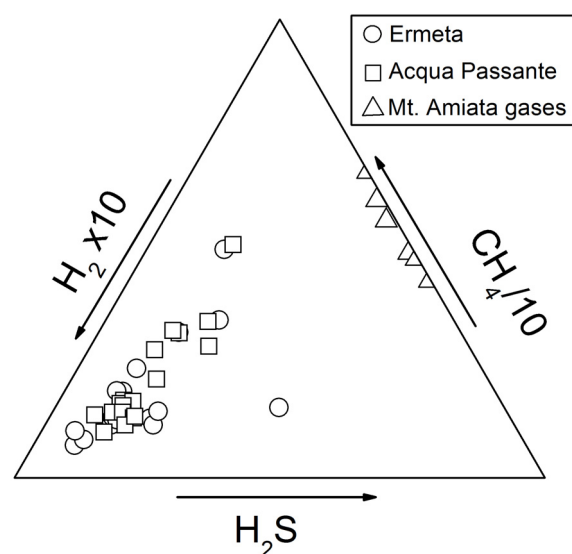
Table 2 (continued from previous page). Sampling date, geographical coordinates (in UTM) and φCO<sub>2</sub> values (in mol m<sup>-2</sup> day<sup>-1</sup>).



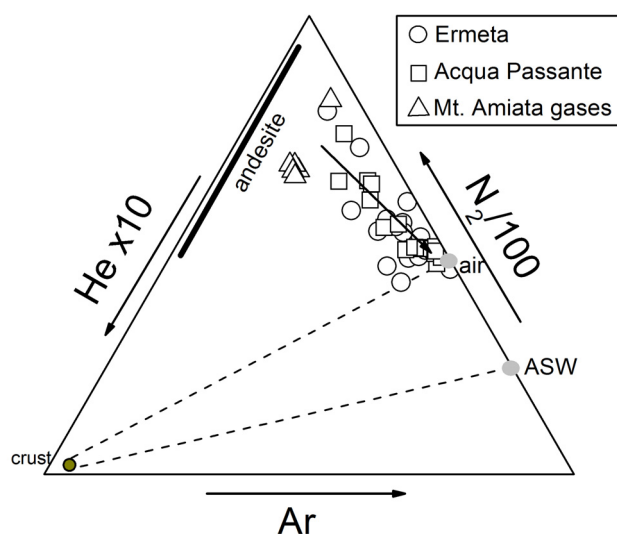
**Figure 3.** Probability plots of  $\phi\text{CO}_2$  values obtained by applying the partitioning method of Sinclair [1974, 1991]. Circles show the measured soil diffuse  $\phi\text{CO}_2$  (in  $\text{mol m}^{-2} \text{day}^{-1}$ ).

log-normal Kriging method [e.g. Krige 1951, Matheron 1970] using the ISATIS© software package of Geovariances. The processing of the geostatistical data indicates that the spherical model with a nugget effect is the best model to describe the spatial variability of  $\phi\text{CO}_2$ . The variogram parameters have a range of 115 m, a sill of 0.12 and a nugget of 0.2  $\phi\text{CO}_2 \text{ mol m}^{-2} \text{day}^{-1}$ . The iso-flux map shows that the diffuse  $\phi\text{CO}_2$  is generally low (average value of 0.38  $\text{mol m}^{-2} \text{day}^{-1}$ ), although values  $>0.6$  and up to 3.42  $\text{mol m}^{-2} \text{day}^{-1}$  were occasionally measured at NW and SW and E, respectively, of the studied area (Figure 6). Since the  $\text{CO}_2$  flux values tended to be log-normally distributed, the whole frequency distribution was analyzed by using a Gaussian (normal) distribution in the complete data set (Figure 3), and the  $\ln(\phi\text{CO}_2)$  data were processed according to the method proposed by Sinclair [1974].

The Sinclair procedure allows to choose threshold values between anomalous and background data using probability graphs. On a log-probability plot, a single log-normal population results as a straight line, whereas a curve with an inflection point describes the theoretical distribution of two overlapping log-normal populations and  $n$  overlapping log-normal populations result



**Figure 4.**  $\text{H}_2\text{S}$ – $\text{CH}_4$ – $\text{H}_2$  ternary diagram for the Ermeta and Acqua Passante gases and the Mt. Amiata gas discharges (by Tassi et. al. [2009]).

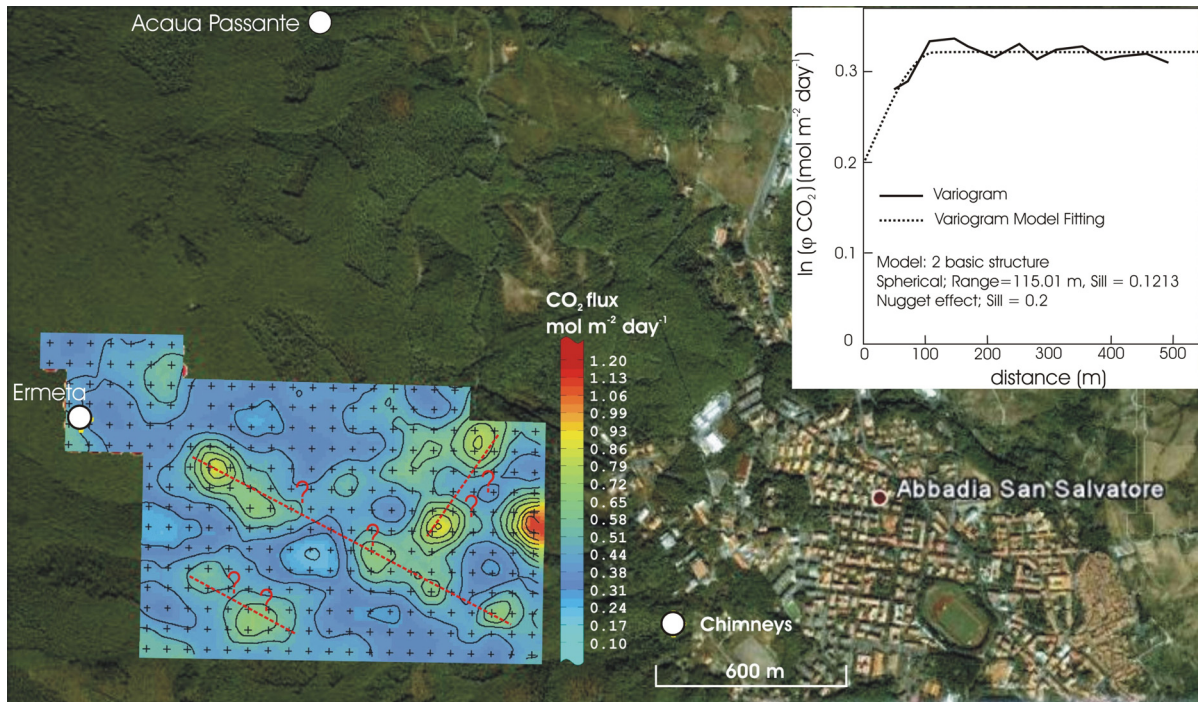


**Figure 5.**  $\text{N}_2$ – $\text{He}$ – $\text{Ar}$  ternary diagram for the Ermeta and Acqua Passante gases and the Mt. Amiata gas discharges (by Tassi et. al. [2009]). ASW: air-saturated-water (ASW).

on a curve characterized by  $n-1$  inflection points. Generally speaking, the log-probability plot shows a straight line for the  $\text{CO}_2$  flux data related to the Ermeta area (Figure 3).

Surveyed surface ( $\text{m}^2$ )	Number of measurements	Mean	Median	Minimum	Maximum	Std. Dev.
653,550	301	-0.95	-0.97	-2.63	1.23	0.56

**Table 3.** Surveyed surface (in  $\text{m}^2$ ), number of measurements and statistical parameters (mean, median, minimum, maximum and standard deviation) of the  $\phi\text{CO}_2$ , expressed as  $\ln(\phi\text{CO}_2)$  ( $\text{mol m}^{-2} \text{day}^{-1}$ ).



**Figure 6.** Map of soil diffuse  $\phi\text{CO}_2$  (in  $\text{mol m}^{-2} \text{day}^{-1}$ ) for the area close to the Ermeta well. Red dashed lines refer to preferential alignments (faults or fractures) where highest  $\text{CO}_2$  flux values were measured.

On the basis of this reasonable consideration, the data set can be modeled with a population that can be considered as the “local  $\text{CO}_2$  flux” (average value of  $0.38 \text{ mol m}^{-2} \text{day}^{-1}$ ) and comparable with the mean biological  $\text{CO}_2$  flux ( $\sim 0.11 \text{ mol m}^{-2} \text{day}^{-1}$ ; e.g. Raich and Schleisinger [1992]). The respective statistical parameters of the considered population are reported in Table 4.

The total  $\text{CO}_2$  output for the Ermeta area was calculated by applying the Sichel’s  $t$ -estimator ( $M_i$ ) [David 1977], whose value was derived by multiplying  $M_i$  times the area covered by the population (Table 4). In the same way, the central 95% confidence intervals of the total  $\text{CO}_2$  output were used to calculate the uncertainty of the population. According to the Sichel’s  $t$ -estimator ( $M_i$ ), the total amount of  $\text{CO}_2$  released through diffuse degassing is estimated to be  $11.81 \text{ ton day}^{-1}$ .

### 5.3. Computation of the amount of dangerous gases released from the Ermeta and Acqua Passante wells since their construction and their relationships with the soil diffuse gases

The impact of the hydrothermal gases released to the atmosphere from the two chimneys is of critical im-

portance for the municipality of Abbadia San Salvatore since disagreeable effects for people approaching these areas, such as odor of rotten eggs, are clearly felt. Furthermore, locally lethal gas accumulation in air may occur as testified by the presence, though rare, of dead animals found in proximity of the wells.

Our data show that the chemical composition of the well gases in the last 5 years had no significant variations and the  $\text{CO}_2$  flow rate from the two chimneys has remained fairly constant during the period of observation. Consequently, we may reasonably assume that the amount of  $\text{CO}_2$  has not significantly changed since the construction of the Ermeta and Acqua Passante wells, i.e. 54 and 75 years ago, respectively. This allows us to compute that since then the two wells have emitted up to 850,000 tons of  $\text{CO}_2$  in the atmosphere. This calculation can be extended to  $\text{H}_2\text{S}$  and  $\text{CH}_4$  on the basis of the measured mean values of the  $\text{H}_2\text{S}/\text{CO}_2$  (Ermeta = 0.0005 and Acquapassante = 0.0004) and  $\text{CH}_4/\text{CO}_2$  (Ermeta = 0.0063 and Acquapassante = 0.0056) ratios, obtained by the 5 years of periodic sampling collection of the well gases. Thus, the total amount of  $\text{H}_2\text{S}$  and  $\text{CH}_4$  emitted from the two chim-

Population	Number of measurements	$\text{CO}_2$ flux population	mean $\ln(\phi\text{CO}_2)$ flux value ( $M_i$ )	total diffuse $\text{CO}_2$ output (ton/day)	95% confidence interval (ton/day)
1	301	local background	-1.076	11.81	13.07-10.84

**Table 4.** Estimated parameters of partitioned populations and derived total  $\text{CO}_2$  output calculated according to Sinclair [1974] and Sichel’s  $t$ -estimator ( $M_i$ ) [David 1977].

neys is of about 430 and 5,150 tons, respectively, the Ermeta well discharging slightly less than one order of magnitude the amount of  $H_2S$  and  $CH_4$  released by that of Acqua Passante.

It is worth noting that the sum of  $CO_2$  released on a year basis from Ermeta and Acqua Passante wells was up to twice the amount of  $CO_2$  emitted from bubbling pools and dry vents computed in the surrounding areas of Mt. Amiata, such as: Acqua Borra at Castelnuovo Berardenga (Siena) ( $5 \text{ ton y}^{-1}$ ; Vaselli et al., unpublished data), Lo Spuntone, Il Palazzo and Buca alle Colline at Campiglia d'Orcia (Siena) ( $\approx 370 \text{ ton y}^{-1}$  at each site; Vaselli et al. [2006a], Tassi et al. [2009]), Bossoleto at Rapolano (Siena) ( $4,380 \text{ ton y}^{-1}$ ; Van Gardingen et al. [1995], Vaselli et al. unpublished data), Pienza ( $5,475 \text{ ton y}^{-1}$ ; Giuli et al. [1997]) and Ambra River ( $7,300 \text{ ton/year}$ ; Cuccoli et al. [2006]). A similar comparison was not computed for  $H_2S$  and  $CH_4$  since in most cases the  $CO_2$  flux was determined by open-path IR laser measurements [Belotti et al. 2003], which were related to the gas discharges from various vents, contributing to the calculated amount of  $CO_2$ . No specific investigations were performed to highlight possible differences in the  $H_2S/CH_4$  ratios from each emission discharging from a certain site. If present, the calculated amount of  $H_2S$  and  $CH_4$  might be affected by a large error.

The generally low  $CO_2$  soil flux values measured in SE the Ermeta well seem to indicate that the diffuse gas emission from the soil is mainly related to soil respiration. Plant roots and soil microbial activities are expected to produce a relatively homogeneous distribution of the diffuse soil  $CO_2$  when a soil cover is present, likely modulated by seasonal patterns of moisture availability, land use and biological cycles [e.g. Almagro et al. 2009, Elío et al. 2013 and references therein]. As previously mentioned, the studied area is generally characterized by a well-developed vegetation and no measurements were performed where the volcanic rocks were outcropping. Nevertheless, the spatial distribution of the  $CO_2$  fluxes (Figure 6) shows the occurrence of preferential NW-SE and NNE-SSW oriented alignments characterized by relatively high  $CO_2$  flux values, which might be related to weakness zones, such as fractures and/or faults. As a first approximation, these sites may suggest the presence of gases fed by the deep-seated reservoir. In this respect, an isotopic survey of the  $CO_2$  soil gases is required to assess whether these zones can be regarded as the preferential pathways for the uprising of deep-originated  $CO_2$ . The carbon isotopic signature of the Ermeta gas ( $-3.5 \text{ V-PDB } \text{‰}$ ), as well as that of Acqua Passante, is indeed significantly different with respect to that associated with a biogenic source ( $\sim -20 \text{ V-PDB } \text{‰}$ ; Schoell [1980]). To further

support this hypothesis a geostructural survey is required to verify the correspondence between the geochemical and geological signals.

#### 5.4. Is the closure of the Ermeta and Acqua Passante wells feasible and safe?

Since 2008, the municipality of Abbadia San Salvatore has become the owner of the mining concession from where cinnabar was extracted and in agreement with the authorities of the Tuscany Region it was appointed to i) monitor the gases discharged from the Ermeta and Acqua Passante wells and ii) actuate prevention measurements to minimize such emissions to the atmosphere. As previously mentioned, the two wells are located in the proximity of tourist areas and the reduction of their gas discharges is expected to provide benefits in terms of safety and healthy conditions.

Presently,  $\sim 15,000$  tons of  $CO_2$ , along with 8 and 92 tons of  $H_2S$  and  $CH_4$ , respectively, are emitted on a yearly basis from the Ermeta and Acqua Passante chimneys and they are related to the discharge of a natural subsurface  $CO_2$  reservoir intercepted during Hg prospection campaigns few kms away from Abbadia San Salvatore. The Ermeta well contributes for  $>85\%$  of the total  $CO_2$  discharge. The amount of  $CO_2$  is more than three times higher than that released by diffuse soil degassing released from an area of  $653,550 \text{ m}^2$  located SE of the Ermeta chimney, this value being of  $4,310 \text{ ton y}^{-1}$ .

According to the aforementioned agreement, the municipality of Abbadia San Salvatore would intend to proceed with the closure of one of the wells and that of Ermeta was thought to be considered as the most suitable since it is i) discharging a larger quantity of gas, ii) located more far away from the main roads and iii) surrounded by a vegetation (and soil) cover (Figure 2), similar to that where  $\phi CO_2$  fluxes were directly measured suggesting that the diffuse soil  $CO_2$  can be assumed to be only affected by soil respiration, e.g. no gas discharges are present at the surface.

Nevertheless, one of the most critical points is to understand and recognize which are those sites that might possibly be affected by potential leakage or micro-seepage of  $CO_2$  [e.g. Klusman 2013, Elío et al. 2013, Nisi et al. 2013 and references therein] as gases in deep reservoirs are buoyant and tend to vertically or laterally migrate following the most permeable pathways in response to pressure. Several authors have proposed buoyancy of gas (micro)bubbles [e.g. MacElvain 1969, Davidson 1982, Klusman 1993, Klusman and Saeed 1996] as a potential process of vertical migrations of gases and gas overpressuring underground, as that expected once the closure of the Ermeta well will occur, plays an important role [Klusman 1997]. In this respect,

faults and fractures, may then vehiculate the CO<sub>2</sub>-rich gases upwards [e.g. Etiope 1999, Brown 2000 and references therein]. As pinpointed by Klusman [2013], the rapidity of transport is another important parameter to be taken into account.

It appears to be realistic the fact that the weakness zones, individuated by the direct measurements of the CO<sub>2</sub> soil fluxes (Figure 6), can likely be affected by an increase in the CO<sub>2</sub> flux, being these areas characterized by a higher permeability. This would theoretically imply the possibility to recognize those areas from where a higher probability of CO<sub>2</sub> leakage is expected in the case of a gas overpressure by applying a relatively simple, though effective, method such as that of the accumulation chamber. Owing to the lack of specific investigations addressed to a detailed geostructural study in the surrounding areas of the Ermeta well, to tentatively reduce the discharge of CO<sub>4</sub>, CH<sub>4</sub> and H<sub>2</sub>S we highly recommend the municipality of Abbadia San Salvatore to solely temporarily close the Ermeta well by using N<sub>2</sub>-filled air-bags before a definitive cementation. Although it is difficult to predict the side effects deriving by such an action, we may speculate that an increasing gas flow rate could be expected. Furthermore, no indications are also presently available about the timing before a modification of the soil diffuse CO<sub>2</sub> is to be recorded. This implies that a geochemical and isotopic monitoring program has to be designed and mainly focused on the diffuse soil CO<sub>2</sub> with particularly reference to the recognized weakness zones. In the case of increasing activity in terms of release of soil CO<sub>2</sub>, the tube closing being temporary, previous conditions could easily be restored by re-opening the Ermeta well. Thus, currently there are no sufficient clues to definitively shut down the Ermeta well. A similar approach should be considered if the closure of the Acqua Passante well is to be considered.

## 6. Conclusions

The municipality of Abbadia San Salvatore is intending to reduce the impact related to the emission in the atmosphere of CO<sub>2</sub>(H<sub>2</sub>S,CH<sub>4</sub>)-rich gases by two wells: Acqua Passante and Ermeta, built in 1938 and 1959, respectively, during Hg prospection campaigns and located in the eastern part of the Mt. Amiata volcanic system. The easiest solution to avoid the gas discharge is to close down the wells, the Ermeta drilling being the one to be tested first.

In this work we have determined that the Ermeta and Acqua Passante drillings are emitting up to 15,000 ton y<sup>-1</sup> of CO<sub>2</sub> and 92 and 8 ton y<sup>-1</sup> of CH<sub>4</sub> and H<sub>2</sub>S, respectively. These gases can be regarded as the discharge of a natural subsurface CO<sub>2</sub>-rich reservoir. The origin

of these gases is similar to those naturally released from dry vents and bubbling pools located few kilometers away from the two wells, with the exception of H<sub>2</sub>, whose higher content is apparently related to corrosion processes of the iron tubing of the chimneys as the deep-seated gases flow through them. We have also estimated the CO<sub>2</sub> output from soil (4,310 ton y<sup>-1</sup> in an area of about 653,500 m<sup>2</sup>) close to the Ermeta well and determined by the accumulation chamber method. Relatively high CO<sub>2</sub> fluxes were recognized along preferential alignments, possibly associated with the presence of faults or fractures (Figure 6).

Standing the absence of detailed geostructural investigations nearby Ermeta, we strongly recommend a temporarily closure of the Ermeta well by means of N<sub>2</sub>-filled air-bags before proceeding with a definitive cementation. Afterwards, an appropriate geochemical and isotopic monitoring activity of the soil gas is required to verify the presence of leakage and micro-seepage of CO<sub>2</sub>.

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