A multi-statistical approach for estimating the total output of CO₂ from diffuse soil degassing by the accumulation chamber method

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ABSTRACT

CO₂ flux measurements at the soil–atmosphere interface are commonly carried out as part of site characterization in areas elected for CO₂ geological storage purposes. This approach represents an important monitoring tool to detect and quantify leakages during operational and post-operational stages related to the injection of anthropogenic CO₂.

A large variety of techniques to measure diffuse CO₂ soil flux is available and one of the most widely used is the accumulation chamber method. With this method, the total output is statistically estimated after measuring the CO₂ flux in selected points of a certain area. Several statistical approaches can be applied and it is important to select the most representative and significant procedure. Consequently, in this paper six different methods were used to calculate the total CO₂ output, as follows: arithmetic mean, minimum variances unbiased estimator, bootstrap resample, partitioning of data into different populations with graphical and maximum likelihood procedures, and sequential Gaussian simulation.

Eight campaigns were carried out in the Hontomín CO₂ Storage Technology Development Plant (Burgos, Spain) and in natural analogs of CO₂ storage (Campo de Calatrava, Spain and Mt. Amiata, Caprese Michelangelo and La Solfatara, Italy). Our results showed that sequential Gaussian simulation is the most precise method for evaluating the total CO₂ output and the respective confidence interval. Nevertheless, the estimation of the total CO₂ output with other statistical methodologies allowed to develop an application procedure for choosing the most reliable and realistic approach.

Keywords:
CO₂ storage
Diffuse CO₂ soil flux
Accumulation chamber
Statistical approaches

1. Introduction

Carbon Capture and Storage (CCS) techniques are expected to reduce the emission of anthropogenic CO₂ into the atmosphere. However, a correct monitoring and verification program to control the potential risks on human health and environment is mandatory. CO₂ storage monitoring programs cover a wide range of geophysical and geochemical techniques, which are aimed to predict the fate of the stored carbon dioxide and detects leakages to the environment (De Lary et al., 2012; IPCC, 2005; Korre et al., 2011).

Measuring diffuse CO₂ flux from the soil to the atmosphere is one of the most commonly used techniques in CCS projects (Förster et al., 2006; Klusman, 2011; Strutt et al., 2003). Usually CO₂ fluxes are measured with the accumulation chamber method, which has

been widely and successfully applied to volcanic and geothermal areas (e.g., Chiodini et al., 1998; Farrar et al., 1999), soil respiration (e.g., Hui Yim et al., 2002), and diffuse emissions in CO₂ storage projects (e.g., Elío et al., 2013; Klusman, 2003a,b,c, 2005; Lewicki et al., 2005a).

Although fast and simple, diffuse CO₂ flux measurements by accumulation chamber can be affected by some drawbacks (Welles et al., 2001; Evans et al., 2001), such as sampling methodology, variability of the sub-surface and surface parameters (porosity, permeability), biological respiration, meteorological parameters (atmospheric pressure and gradients, temperature, wind speed) and depth of the source of the CO₂ detectable at the surface.

Diffuse CO₂ fluxes can actually be affected by a high spatial and temporal variability, even at the scale of few meters or hours and an accurate estimation of the mean flux (and the variance) over an area is not an easy task. Nevertheless, in some cases the quantification of the amount of gas released to the atmosphere is an important parameter to be determined for estimating the leakage of CO₂ in

Fig. 1. Sampling zones: Hontomín (HO-C1, HO-C2; modified from [Elío et al., 2013](#)), Campo de Calatrava (CC-C1, CC-C2; this work), Mt. Amiata (MA-C1, MA-C2; modified from [Nisi et al., 2014](#)), Caprese (CA-C1, this work) and La Solfatara (SO-C1; this work).

CCS and volcanic/geothermal areas (e.g. [Chiodini et al., 2015](#) and references therein) and man-made environments (e.g. municipal landfills; [Raco et al., 2010](#) and references therein).

In CCS monitoring surveys CO₂ fluxes are expected to be low and homogenous, with seasonal variations mainly produced by biological activity ([Etheridge et al., 2005](#)). As a consequence, diffuse leakages are aimed to distinguish between deep and shallow sources since small variations in the CO₂ flux with a high “noise” in the signal are expected. Hence, this implies that it is of utmost importance to assess the optimum methodology for measuring CO₂ fluxes in order to obtain accurate measurements ([Elío et al., 2012](#)) and estimations of the total CO₂ emission rate of a leakage.

There is a wide range of methodologies to estimate the CO₂ emission rate once diffuse CO₂ flux measurements with an accumulation chamber are performed (e.g. [Chiodini et al., 1998](#); [De Bortoli et al., 2011](#); [Lewicki et al., 2005b](#)). Each approach has to be properly investigated to apply the best statistical procedure. A single operating statistical strategy cannot indeed be valid for all sites since it might be affected by each sample dataset. Thus, in this paper we present a comparative study where six different statistical methods to estimate the total CO₂ emission were applied. The final aim is that to develop an application procedure for choosing the more reliable methods, which can also allow to evaluate an acceptable confidence interval of the total CO₂ output.

It is important to mention that the detection of CO₂ seepage in CCS may not require a rigorous determination of the soil flux that can significantly be affected by meteorological parameters as they vary. Thus, the comparison of individual points over time, which show an increase of the CO₂ flux is likely more useful to detect a leakage. However, once a leakage is recognized the statistical methods are to be applied to quantify the CO₂ output.

For the comparative study each method was applied to two different scenarios, where eight diffuse soil CO₂ campaigns were

carried out ([Fig. 1](#)), as follows: (i) the Hontomín CO₂ Storage Technology Development Plant (HO); this CCS site area is characterized by low CO₂ flux mainly related to biological activity (campaigns HO-C1 and HO-C2) and (ii) natural analogs of CO₂ storage. The selected sites covered a large interval of diffuse CO₂ fluxes: hot spot emissions associated with fault zones (the Calatrava Volcanic Province; campaigns CC-C1 and CC-C2), a geothermal area where the presence of deep CO₂ source was well known (Mt. Amiata; campaigns MA-C1 and MA-C2), possible leakages associated with an abandoned deep (ca. 5000 m) well (Caprese Michelangelo, CA-C1) and a high CO₂ flux from a volcanic area (Solfatara of Pozzuoli; SO-C1).

2. Materials and methods

2.1. Study sites

The Hontomín CO₂ Storage Technology Development Plant (Burgos, Spain) is operated by CIUDEN, as a part of the EC-funded OXYCFB300 project (European Energy Program for Recovery – EEPR, <http://www.compostillaproject.eu>), where 20 kTon of CO_{2sc} are planned to be injected into a deep dome saline formation ([Alcalde et al., 2013](#)). Triassic to Quaternary sedimentary rocks dominate the geology of the area of Hontomín ([IGME, 1991](#)). The target aquifer for the CO₂ injection is at the depth of 1450 m and it is made up of Jurassic limestones and dolostones, which contain a highly saline aquifer (up to 30 g/L as NaCl, [Buil et al., 2012](#); [Nisi et al., 2013](#)). At the top of the reservoir, characterized by a dome-like structure ([Alcalde et al., 2013](#)), the sealing formation consists of clays and marls. Since 2009, as part of monitoring program, CO₂ flux measurements were conducted to establish the baseline of CO₂ flux before injection. The measured fluxes were low, the mean values varying from 5 to 13 g m⁻² day⁻¹. A few outliers were identified,

although they were not related to a deep source of CO₂ but rather to increased biological activity (Elío et al., 2013).

The Calatrava Volcanic Province along with that of Selva-Emborda (NE Spain) likely represents the highest output zone of CO₂ in the whole continental Spain (e.g. Vaselli et al., 2013b). It is located in the Hercynian basement, which is covered by late Cenozoic sediments. This basement is unconformably overlain by upper Miocene to Quaternary fluvial and lacustrine sediments deposited within a series of fault-bounded Tertiary-Quaternary sedimentary basins of up to 200 km². The Calatrava Volcanic Province is referred to late Miocene to Quaternary intracontinental plate magmatism, dominated by leucitites, melilitites, nephelinites and olivine basalts (e.g. Cebriá and López-Ruiz, 1995). The area is characterized by several gas and water discharges (Elío et al., 2015 and references therein). It is to be pointed out that the geochemical and isotopic features of the gas seeps indicate a high concentration of CO₂ (up to 98% by vol.) whose origin is likely a deep (mantle)-related source as suggested by the helium isotopic ratios (Pérez et al., 1996; Vaselli et al., 2013a,b).

Mt. Amiata volcano is located in central-southern Tuscany (Italy). The age of volcanic products is from about 300–240 ky (Laurenzi et al., 2015 and references therein). The presence of two geothermal areas exploited for the production of electricity indicates the presence of a fluid reservoir that likely feeds the abundant vents and thermal springs mainly located in the NE and SW sectors of the mountain (e.g. Frondini et al., 2009; Minissale et al., 1997; Tassi et al., 2009). Mt. Amiata also had an important mining activity up to the seventies since Hg was produced by the exploitation of cinnabar (e.g. Vaselli et al., 2013a,b and references therein). During the mining exploration, two wells (Acqua Passante and Ermeta) were drilled north of Abbadia San Salvatore that is located in the eastern flank of the volcano. Presently, they discharge up to 15,000 ton day⁻¹ of CO₂ in the air (Nisi et al., 2014).

San Cassiano is located between Pieve Santo Stefano and Caprese Michelangelo (central-eastern Tuscany, Italy). This area is characterized by an about 5000 m deep well (PSS-1) drilled in 1982–1984 by E.N.I. (Ente Nazionale Idrocarburi) for hydrocarbon exploration (Anelli et al., 1994), with several CO₂-rich fertile horizons clustering around the depth of 3700 m. Pressure and temperature were 700 bar and 120 °C, respectively while the CO₂ density was of 0.86 g cm⁻³ (e.g. Bicocchi et al., 2013; Bonini, 2009). According to Anelli et al. (1994), the PSS-1 stratigraphic sequence is, from the bottom to the top, as follows: (i) Mesozoic formations (limestones and marls) down to 3295 m, followed by the Triassic Burano Fm. (dolostone and gypsum layers), which is interbedded with altered calc-alkaline andesitic volcanics and (ii) sedimentary Neogene and Ligurian Units are overlaying the turbiditic Cervarola-Falterona Unit, with a major tectonic discontinuity at the depth of 1853 m, which separates this unit from the underlying Palaeogene–Mesozoic carbonate sequence.

La Solfatara of Pozzuoli (Naples, Italy) is part of the Phlegraean Fields caldera. The latter was formed about 35,000 years ago with the eruption of the Campanian Ignimbrite while the last eruption occurred in 1538 (e.g. Scandone et al., 2006). La Solfatara crater, formed about 4000 years ago, is a monogenic volcano that hosts hot mud pools and fumaroles up to 160 °C. A high diffuse degassing (e.g. Cardellini et al., 2003; Granieri et al., 2010; Tassi et al., 2013) characterizes this area and a total amount of CO₂ of >1500 ton day⁻¹ (e.g. Aiuppa et al., 2013) is released.

In this work the CO₂ flux data from Hontomín and the Calatrava Volcanic Province are from Elío et al. (2013) and Elío et al. (2015), respectively, while those close to the Acqua Passante and Ermeta wells (Mt. Amiata) are from Nisi et al. (2014). All the remaining CO₂ measurements, i.e. Caprese Michelangelo, Mt. Amiata and La Solfatara, are unpublished.

2.2. Field measurement

Carbon dioxide soil fluxes were measured using the accumulation chamber method (Cardellini et al., 2003; Chiodini et al., 1998; Klusman, 2011), which is based on the measurement of the CO₂ concentrations with time by an inverted chamber placed on the ground. The equipment used in this work is manufactured by the company WEST Systems (WS-LI820) and fitted with a LICOR (LI-820) infrared detector (West Systems, 2009). The accumulation chamber device consists of: (i) a metal cylindrical chamber with an inlet net area and inner volume of 3.14×10^{-2} m² and 3.06×10^{-3} m³, respectively, (ii) an Infra-Red (IR) spectrophotometer (Licor® Li-820, infra-red sensor detector, measuring range of 0–20,000 ppm, accuracy of 4% of reading), (iii) an analog-digital (AD) converter, and (iv) a palmtop computer (PC).

A low-flux pump (20 ml s⁻¹) continuously conveys the soil gas from the chamber to the IR sensor. To minimize the disturbance effects due to changes of barometric conditions, the soil gas is re-injected into the chamber. The soil CO₂ flux is calculated on the basis of the measured CO₂ concentration increment inside the chamber in time (dC_{CO_2}/dt). This increment is computed according to the relation between the rate and the CO₂ flux $= \alpha \times dC_{CO_2}/dt$. The parameter α is a proportionality factor determined experimentally in the laboratory and is computed as the slope of the linear best-fit line of the imposed CO₂ flux versus the measured dC_{CO_2}/dt (Elío et al., 2012).

Measurement protocol was, as follows: (i) cleaning and removal of the vegetal cover and the first compact layer of the soil in the measurement point, (ii) waiting to prevent flux perturbation due to soil removal (about 1 h) and, (iii) measuring the CO₂ flux (Elío et al., 2012). In all campaigns the CO₂ soil flux measurements were repeatedly carried out to test the reproducibility and the repeatability of the data. In addition to the CO₂ flux, in each site meteorological parameters such as pressure, temperature, relative humidity and wind speed were measured.

2.3. Data analysis

The total emission output of CO₂ was estimated by applying six statistical methods: (i) arithmetic mean (AM), (ii) minimum variances unbiased estimator (MVUE), (iii) partitioning of data into different populations with graphic Sinclair method (SM) and (iv) maximum-likelihood method (ML), (v) bootstrap resampling and (vi) sequential Gaussians simulation geostatistic method (SGs).

2.3.1. Arithmetic mean (AM)

The arithmetic mean is adequate for normal distributed data. The average CO₂ flux with the confidence interval is defined by Eq. (1), where n is the number of data, x_i ($i = 1, 2, \dots, n$) is the value in each point and s the standard deviation.

$$\bar{x} = \frac{1}{n} \sum_i x_i \pm t_{(\frac{\alpha}{2}, n-1)} \times \sqrt{\frac{s^2}{n}} \quad (1)$$

To estimate the total emission rate the arithmetic mean (g m⁻² day⁻¹) is multiplied by the grid area (m²). Although fast and easy the arithmetic mean has two main problems. Firstly, the arithmetic mean is strongly influenced by anomalous values, e.g. when the CO₂ flux measurements are log-normally distributed, AM cannot directly be applied because it is an inefficient estimator. Secondly, Eq. (1) supposes data independence, thus, if not corrected, the confidential interval is wrong and this has to be estimated with the extension variance σ_e^2 , calculated with the variogram model (γ) of Eqs. (2) and (3) (Armstrong, 1998).

Fig. 2. Histogram and probability plot of two-component log-normal distributions mixture.

However, it is computationally difficult and slow and thus, it is not worthwhile to be applied.

$$\pm t_{(\frac{\alpha}{2}, n-1)} \times \sqrt{\sigma_E^2(v, V)} \quad (2)$$

$$\sigma_E^2(v, V) = \frac{2}{NV} \sum_i \bar{\gamma}(\bar{x}_i, V) - \frac{1}{N^2} \sum_i \sum_j \gamma(\bar{x}_i, \bar{x}_j) - \bar{\gamma}(V, V) \quad (3)$$

2.3.2. Minimum variances unbiased estimator (MVUE)

The minimum variance unbiased estimator (MVUE) is applied when the data are log-normally distributed and it is based on the Sichel function (ψ) (Koch and Link, 1970). Eqs. (4)–(9) were used to estimate the mean:

$$m = e^{\bar{u}} \cdot \psi_n \left(\frac{1}{2} S_u^2 \right) \\ = e^{\bar{u}} \cdot \left[1 + \frac{n-1}{n} S_u^2 + \sum_{j=2}^{\infty} \frac{(n-1)^{2j-1}}{n^j + (n+1) \cdot (n+3) \cdot \dots \cdot (n+2j-1)} \cdot \frac{S_u^{2j}}{j!} \right] \quad (4)$$

Where:

$$u_i = \ln(x_i) \quad (5)$$

$$\bar{u} = \frac{1}{n} \cdot \sum_i u_i \quad (6)$$

$$S_u^2 = \frac{1}{n-1} \cdot \sum_i (u_i - \bar{u})^2 \quad (7)$$

The 95% confidence intervals were calculated according to:

$$m_L = e^{u_L} \cdot \psi_n \left(\frac{1}{2} S_u^2 \right); \quad u_L = \bar{u} - t_{(\frac{\alpha}{2}, n-1)} \cdot \sqrt{\frac{S_u^2}{n}} \quad (8)$$

$$m_U = e^{u_U} \cdot \psi_n \left(\frac{1}{2} S_u^2 \right); \quad u_U = \bar{u} + t_{(\frac{\alpha}{2}, n-1)} \cdot \sqrt{\frac{S_u^2}{n}} \quad (9)$$

The total emission rate and the confidence intervals are calculated by multiplying these values (m, m_L, m_U [g m⁻² day⁻¹]) by the sampling area (m²). This method also assumes data independence and, as seen before, if there is not independency, the confidence interval is miscalculated.

2.3.3. Partitioning of CO₂ flux data into different log-normal populations

Usually, the distribution of the CO₂ fluxes is characterized by two or more log-normal populations, which are indicative of either

different geochemical processes or mixing between two or more sources. The partitioning in different populations is useful to distinguish the background values of biological activity from those related to geogenic sources. For example, in geothermal areas it is common to recognize two populations, which are referred to background (low) and deep (high) CO₂ fluxes, the latter being commonly connected to the degassing processes from hydrothermal, magmatic or thermometamorphic sources (Cardellini et al., 2003; Chiodini et al., 1998).

In this case, the estimation of emission rate can be carried out by partitioning the data into different log-normal distributions to evaluate the parameters of each population (mean, standard deviation and proportion). The total emission rate is thus the sum of what is emitted from each population, as described in Eq. (10):

$$\text{Emission} = \sum_{i=1}^n [\Phi_{\text{CO}_2 i} \cdot P_i \cdot A] \quad (10)$$

where n is the number of populations, $\Phi_{\text{CO}_2 i}$ is the average CO₂ flux of i -th population, A is the total sample area and P_i is the proportion of i -th population.

The partitioning of the CO₂ values into different log-normal populations to estimate the parameters can be performed by two different approaches. The first one is based on the graphical Sinclair method (Sinclair, 1974), representing the probabilistic graph (Fig. 2), while the second one applies a maximum-likelihood method (Benaglia et al., 2009; Young and Hunter, 2010).

The maximum-likelihood (ML) method is carried out by the package “mixtools” of the “R” statistical program, whose function is to fit finite mixtures of univariate or multivariate normal distributions (Benaglia et al., 2009; Young and Hunter, 2010), better solutions of flux partitioning have less negative log-likelihood (Fig. 3). To confirm the number of populations in the dataset a likelihood ratio test was carried out by iteratively comparing a null model, H_0 with “ n ” population, and an alternative model, H_1 with “ $n+1$ ” population ($D = -2 \{ \log[\text{likelihood}(H_0)] - \log[\text{likelihood}(H_1)] \}$). When the statistic “ D ” is less than the chi-squared distribution (significance level $\alpha = 0.05$), with degree of freedom equal to the different of the degree of freedom of each model ($df_1 - df_0$), the null model (H_0) is confirmed.

With the parameter of the different lognormal population, back transformation is performed according to the Sichel method (Eq. (4)), and the total emission is calculated with Eq. (10). The estimation of the confidence intervals cannot properly be assessed with the Sinclair method since it cannot be calculated by simply

Fig. 3. Partitioning of CO₂ flux data into different log-normal populations with maximum likelihood.

summing up the bottom and top confidence intervals of each population. This problem can be solved with data simulations to be applied after the maximum-likelihood partitioning. Accordingly, the emission rate can be computed by simulating new data with the same number of data sampling and the same population parameters (means, standard deviations and proportions). If this process is reiterated an appropriate number of times (in our case 1000 times) the distribution of total emission rate is obtained. Consequently, the average value and the 95% confidence interval (CI is the 2.5th and 97.5th percentile of the generated estimations) can be calculated. Similarly to AM and MVUE, these methods also have the problem of assuming the data independence.

2.3.4. Bootstrap resampling

Bootstrap methods consider a random resampling with replacement of the observed data, which is carried out a large number of times to infer about the population, estimating the distribution of an unknown parameter (e.g., the sample mean). Thus, the confidence interval can be estimated (US-EPA, 2002, 2007). In this paper the package “boot” of R software was used and the confidence intervals was calculated as the bootstrap percentile interval, where CI is the 2.5th and 97.5th percentile of the generated means (Canty and Ripley, 2012; Davison and Hinkley, 1997). Bootstrap procedures are nonparametric statistical methods and assume that the data are representative of the population. In practice it is sufficient a random sampling, although these methods are inappropriate to be used with data that were idiosyncratically collected or focused especially on hot spots (US-EPA, 2002).

2.3.5. Geostatistical method

The previously described methods are data independence. This implies that when there is an autocorrelation, defined with a variogram, they are not appropriate. In this case is better to apply a geostatistical analysis. The basis of geostatistical methods is the variogram, which is the arithmetic mean of the square difference for all pairs of experimental values separated by a distance h (Bivand et al., 2008), as described in Eq. (17):

$$\hat{\gamma}(h) = \frac{1}{2N_h} \sum_{i=1}^{N_h} \{Z(X_i) - Z(X_i + h)\}^2 \quad (17)$$

A variogram explains the spatial relationship among the measured points. Generally speaking, it decreases with distance until a point where there is no correlation among points. From this point

onward the variogram is a horizontal line (range). When $h=0$ the variogram should be zero. However, in most cases this does not occur and usually higher values (nugget effect) are recorded. This is due to two main reasons: measurement errors (both sampling and instrumental) and micro-variations in the measured variable. For mathematical analysis a theoretical variogram model is fitted with the experimental variogram.

The more regular the sampling grid the better the geostatistical analysis; there are indeed more pairs of points to determine the variogram. Similarly, the smaller the distance between points the more accurate the results. It is also recommended to carry out random replication in order to determine the error in sampling and estimate the nugget effect, and also the distance between sampling points should not exceed the range.

The common geostatistical method used to estimate the total efflux is the “sequential Gaussian simulation (sGs)” (De Bortoli et al., 2011; Lewicki et al., 2005b). In our case the simulation was performed with the “R” software applying a trans-gaussian kriging with Box-Cox transformation. In this sense we implemented the functions “krigeTg” and “boxcox” (packages “gstat” and “MASS” respectively (Pebesma, 2004; R Core Team, 2012; Venables and Ripley, 2002). Box-Cox transformation of data (X) with the transformation parameters lambda (λ) is (Box and Cox, 1964):

$$\phi_{\lambda}^{-1}(X) = - \begin{cases} \frac{X^{\lambda} - 1}{\lambda} & \lambda \neq 0 \\ \log(X) & \lambda = 0 \end{cases} \quad (18)$$

The trans-Gaussian kriging predictor of $Y(s_0)$ is (Cressie, 1993; Pebesma, 2004):

$$\begin{aligned} \hat{Y}(s_0) &= \phi(\hat{Z}(s_0)) + \phi''(\hat{\mu}) \left(\frac{\sigma_k^2(s_0)}{2} - m \right) \\ \phi(x) &= \begin{cases} (x \cdot \lambda + 1)^{1/\lambda} & \lambda \neq 0 \\ e^x & \lambda = 0 \end{cases} \\ \phi''(x) &= \begin{cases} \left(\frac{1}{\lambda} - 1 \right) \cdot \lambda \cdot (x \cdot \lambda + 1)^{\left(\frac{1}{\lambda} - 2 \right)} & \lambda \neq 0 \\ e^x & \lambda = 0 \end{cases} \end{aligned} \quad (19)$$

where $\hat{Z}(s_0)$ is the ordinary kriging predictor on the transformed scale data, $\sigma_k^2(s_0)$ the ordinary kriging variance, $\hat{\mu}$ the mean

estimate at each location and m the Lagrange parameter for each location.

The problem is that sGs requires a large computational power, which can be overcome by considering a lower number of observations, while performing the simulations (Bivand et al., 2008). In each simulation an emission rate is estimated and a distribution of the total emission rate is obtained by repeating an appropriate number of times (in our case 1000 times) the simulation. Consequently, we can estimate the average value with a 95% confidence interval (2.5th and 97.5th percentile of the generated estimations).

3. Results

Different CO₂ flux measurements and grid samples were performed in the eight campaigns: from 96 (CA-C1) to 768 (HO-C7) measurements with regular grid size from 20 × 20 m to 100 × 100 m, with the exception of campaign MA-C2 where the terrain prevented a regular sampling. The area covered a surface relatively variable, comprised between 0.05 (CC-C1 and CA-C1) and 7.02 (HO-C2) km² (Table 1). The histograms and probability plots of the CO₂ fluxes are reported in Fig. 4. The highest CO₂ fluxes were obtained at Mt. Amiata (MA-C2) and La Solfatara (SO-C1), with an arithmetic mean of 172 and 2350 g m⁻² d⁻¹, respectively, while the lowest CO₂ fluxes were measured at Hontomín and Campo de Calatrava, with the minimum mean averages of 4.73 (CC-C2) and 4.87 g m⁻² d⁻¹ (HO-C1). A few measurements were under the detection limit (<0.2 g m⁻² d⁻¹).

PDT-Hontomin has typical soil CO₂ flux values of biological signature where soil respiration is the source of CO₂ (Elío et al., 2013; Nisi et al., 2013). The minimum CO₂ fluxes were in the range of 0.15 (<L.D.; HO-C1) to 0.62 (HO-C2) g m⁻² d⁻¹, while the highest values were of 29.46 (HO-C1) to 58.38 (HO-C2) g m⁻² d⁻¹. The average values were between 4.9 (HO-C1) and 13 (HO-C2) g m⁻² d⁻¹, although the great majority was below 20 g m⁻² d⁻¹. Histogram and probability plots (Fig. 4) show that the data follow a log-normal distribution (HO-C1) or have two log-normal mixed populations (HO-C2). It is likely that the dominating mixing process is due to a change in soil respiration and different land use.

In the Campo de Calatrava area, diffuse CO₂ soil fluxes had minimum values of -2.10 (<L.D.; CC-C1) and 0.02 (<L.D.; CC-C2) g m⁻² d⁻¹ and mean averages of 7.39 (CC-C1) and 4.73 (CC-C2) g m⁻² d⁻¹. The maximum values of 141 (CC-C1) and 69 (CC-C2) g m⁻² d⁻¹ were probably related to a deep source (Table 1). As shown in Fig. 4, CO₂ fluxes in the CC-C1 campaign are likely representing a mixture of log-normal populations: background and deep CO₂. The CC-C2 data are log-normally distributed with short-tails. The tail to the left of the diagram is referred to the low fluxes (near detection limit) where the accumulation chamber method has larger errors (ca. 20–25%; according to the brochure of the instrument) and an anomalous low flux value is obtained. The tail to the right corresponds to anomalously high data, likely influenced by a CO₂ deep source. However, it is to mention that there are no enough data to evidence the presence of a new population.

The CO₂ fluxes Mt. Amiata (MA-C1) were from 3.15 to 150 g m⁻² d⁻¹, with a mean value of 19.96 g m⁻² d⁻¹ and an anomalous value of 150.40 g m⁻² d⁻¹, which was recorded close to the Ermeta old mining well, suggesting a possible CO₂ leakage through the well casing. The CO₂ fluxes in CA-C1 were in the same order of magnitude, since they were ranging between 3.93 and 50.09 g m⁻² d⁻¹ with a mean value of 19.81 g m⁻² d⁻¹. The two sites are characterized by the presence of deep CO₂ with leakages in the surrounding areas (e.g. Frondini et al., 2009; Tassi et al., 2009). Nevertheless, we could not distinguish between superficial (biologic) from deep source since the data had a single log-normal

distribution (Fig. 4) and the CO₂ flux values were similar to those recorded from biological activity.

The two campaigns with the highest CO₂ fluxes were MA-C2 and SO-C1 as a consequence of a clear deep source of CO₂ with values of various orders of magnitude higher than those related to soil respiration. In MA-C2 the CO₂ flux ranged from 0.01 (<L.D) to 42,660 g m⁻² d⁻¹ with an average of 271 g m⁻² d⁻¹. The distribution of the CO₂ fluxes shows a mixing of log-normal populations (a background and a deep geothermal source). The CO₂ flux at La Solfatara crater were from 74.81 to 23,220 g m⁻² d⁻¹, following a log-normal distribution, similarly to what observed by Tassi et al. (2013).

The experimental variogram (point), the model fitted (red lines) and the envelope (dotted lines) of all variograms obtained by random permutations of the data are plotted in Fig. 5. If the experimental variogram were within the envelope, it might be considered as the product of a random process and therefore the application of geostatistical techniques is not correct. This is the case for the CC-C1 and MA-C2 campaigns. The parameters used for both normalizing the data (λ) and fitting the experimental variogram (model, nugget, range and sill) are reported in Fig. 5. It is to be pinpointed that for the HO-C1, CC-C2, SO-C1, MA-C1, MA-C2 and CA-C1 campaigns, the best normal transformation is the logarithmic one ($\lambda = 0$) and for those of CC-C2 and HO-C2 the transformation is with a λ value of 0.14 and 0.42, respectively. With this transformation, the range in the model fitted is between 76 (CA-C1) and 225 m (CC-C1).

The different total emission estimation and the confidence intervals are shown in Table 1 (empty cells indicate that the method was not applicable). The emission range is approximately from 0.35 (CC-C1) to 260 t d⁻¹ (SO-C1). The difference between the minimum and the maximum estimation in the same site varies from 0.7 (HO-C1) to 9% (CC-C1). If we calculate the relative standard deviation (RSD%) by dividing the standard deviation of emission estimation by the overall arithmetic mean and multiplying by 100, the maximum variation in the estimation of the emission rate among the various methods is ±4% (CC-C1).

4. Discussion

4.1. Identification of extremes outlier CO₂ flux (hot-spot)

In natural analogs CO₂ leakages are generally found in well-defined and circumscribed areas, with micro-variations in the CO₂ flux. In this study the CO₂ fluxes were occasionally not measured because the IR detector saturated (up to 20,000 ppm of CO₂ were measured inside the accumulation chamber after a few seconds) whereas a few centimeters away from these spots the CO₂ flux abruptly dropped down, reaching values lower than the instrumental detection limit. These effects, called “hot-spots”, have a strong influence in the estimation of the total emission rate and have to be detected to avoid errors.

To detect the hot-spots we defined the extreme upper outlier like any value that was greater than $Q_3 + 3x(Q_3 - Q_1)$ in a normal population (in our case after a log-normal transformation), where Q_1 and Q_3 are the first and third quartile, respectively. After that, we identified whether the extreme outliers were clustering or randomly distributed in the study area and whether the CO₂ flux in their neighbor points were low or high to treat the area like a small high emission zone or only like a punctual emission. In the first case, we assumed that the emission of the hot-spot area was the mean (and standard deviation) of the cluster data. In the second case, we assumed that the area affected by the emission was approximately of 1 m². Thus, the emission was the CO₂ flux measurement and the standard error was the error of the instrument in the range of measurement (approximately 20%).

Table 1

Estimation rates and relative statistical parameters for each campaign considered in the present study.

		CO ₂ storage area		Natural analogs					
		PDT-Hontomin		Campo Calatrava		Monte Amiata		Solfatara	Capresse
		HO-C1	HO-C2	CC-C1	CC-C2	MA-C1	MA-C2	SO-C1	CA-C1
Measurements		233	768	114	524	301	283	138	96
Area (km ²)		1.90	7.02	0.05	0.40	0.79	2.22	0.11	0.05
Sample grid (m)		100 × 100	100 × 100	20 × 20	30 × 30	50 × 50	–	30 × 30	25 × 25
	Min.	0.62	0.15 (<LD)	–2.10 (<LD)	0.02 (<LD)	3.15	0.01 (<LD)	75	3.9
	Q ₁	3.18	7.78	1.46	2.24	1160	9.63	287	11.17
	Median	4.35	11.93	3.76	3.63	16.62	15.69	832	18.51
	Mean	4.87	13.07	7.39	4.73	19.96	271.20	2350	19.81
	Q ₃	5.89	16.80	6.14	5.77	23.84	28.65	2056	25.59
	Max.	29.46	58.38	141.40	69.04	150.4	42660	23220	50.09
	sd	2.95	792	17.15	5.07	14.17	2741	4213	9.57
Method	Emission rate and 95% confidence intervals (t d ^{–1})								
Arithmetic mean		9.2 (8.5–10.0)	92 (88–96)	0.322 (0.259–0.398)	1.91 (1.73–2.08)	16.8 (14.5–17.0)	66 (51–82)	261 (182–339)	1.068 (0.966–1.173)
MVUE		9.2 (8.6–9.8)	–	–	1.95 (1.82–2.10)	15.6 (14.6–16.6)	–	246 (196–309)	1.077 (0.971–1.195)
Bootstrap		9.2 (8.6–10.0)	92 (88–96)	0.329 (0.259–0.395)	1.90 (1.74–2.09)	15.8 (14.6–17.1)	66 (52–81)	261 (188–344)	1.068 (0.967–1.173)
Maximum likelihood		–	92 (88–96)	0.350 (0.267–0.480)	–	–	68 (54–86)	–	–
Sinclair		–	92 (88–95)	0.330 (0.253–0.421)	–	–	65 (56–76)	–	–
sGs		9.0 (8.4–9.6)	92 (90–96)	–	1.97 (1.82–2.12)	15.7 (15.0–16.4)	–	263 (199–327)	1.086 (0.999–1.172)

Source: Hontomin (modified from [Elio et al., 2013](#)), Campo de Calatrava (this work), Mt. Amiata ([Nisi et al., 2014](#)) and La Solfatara and Caprese (this work).

Fig. 4. Histogram and probability plot for each campaign.

We observed this effect in the CC-C1 and MA-C2 campaigns. In CC-C1 there were two outliers (CO_2 flux: 102 and $141 \text{ gm}^{-2} \text{ d}^{-1}$), clustering near a water spring and affecting an area of 401 m^2 . In the MA-C2 campaign there were five outliers, randomly distributed, with low CO_2 flux in the neighborhoods points. The range of the CO_2 flux outlier was from 1440 to $42,660 \text{ gm}^{-2} \text{ d}^{-1}$, while the remaining data were less than $620 \text{ gm}^{-2} \text{ d}^{-1}$.

To evaluate the influence of the extreme data, the emanation rate was calculated by differentiating and without differentiating the hot-spot effect (Table 2). The difference between the minimum

and the maximum estimation with each method and the relative standard deviation (RSD%) were bigger when the hot-spot areas were not differentiated. In CC-C1 and MA-C2 they were 39 and 15% and 100 and 25%, respectively. However, when these areas are studied separately, the emission rates between the different methods are similar, with RSD of 3% (CC-C1) and 1% (MA-C2) and a difference between the minimum and maximum value of 9 and 4% for CC-C1 and MA-C2, respectively. Without differentiating the extreme outliers the CO_2 diffuse emission was computed to be the highest with all the methods, with differences for CC-C1 and MA-C2 from 4 to

Fig. 5. Experimental and fit variograms of CO₂ flux normal transformation.

Table 2Emission rate and 95% confidence intervals (t d^{-1}) by differentiating and without differentiating the hot-spots effect in the CC-C1 and MA-C2 campaigns.

Method	CC-C1		MA-C2	
	Without differentiated Outlier	Differentiated Outlier	Without differentiated Outlier	Differentiated Outlier
Arithmetic mean	0.335 (0.191–0.479)	0.322 (0.259–0.398)	609 (–111 to 1329)	66 (51–82)
Bootstrap	0.335 (0.214–0.493)	0.329 (0.259–0.395)	608 (94–1451)	66 (52–81)
Maximum likelihood	0.387 (0.261–0.622)	0.350 (0.267–0.480)	583 (122–2174)	68 (54–86)
Sinclair	0.464 (0.359–0.608)	0.330 (0.253–0.421)	303 (159–611)	65 (56–76)

Table 3

Results of partitioning in log-normal population using Sinclair and Maximum likelihood.

Campaign	Method	Population	Proportion (%)	Lognormal data ($\text{g m}^{-2} \text{d}^{-1}$)		Back-transformed data (Sichel) ($\text{g m}^{-2} \text{d}^{-1}$)	
				μ	σ	μ	σ
HO-C2	Maximum likelihood	P1	21	1.61	0.93	7.6	8.7521
		P2	79	2.56	0.47	14.5	7.2687
	Sinclair	P1	22	1.33	0.37	4.6	3.0648
		P2	78	2.65	0.16	15.4	6.4702
CC-C1	Maximum likelihood	P1	46	1.28	1.60	12.3	34.5012
		P2	54	1.54	0.48	5.24	2.6442
	Sinclair	P1	17	–0.39	0.62	0.91	0.81
		P2	71	1.54	0.20	5.5	2.44
		P3	12	3.31	0.69	38	35
MA-C2	Maximum likelihood	P1	71	2.7	0.65	18	13
		P2	29	3.2	1.32	59	119
	Sinclair	P1	83	2.55	0.64	16	11
		P2	17	4.31	0.71	95	74

41% and from 240 to 540%, respectively. In this sense if the outliers were not detected the CO_2 output would have been overestimated, regardless of the method used.

4.2. Partitioning of the CO_2 flux data into different log-normal populations

Partitioning of the CO_2 flux data into different log-normal populations can be used to distinguish among different geochemical processes, e.g., in geothermal areas it is frequent to recognize two populations, a background characterized by low CO_2 flux and a deep (hydrothermal, thermometamorphic or mantle) high CO_2 flux connected to degassing processes from deep sources. As a consequence, such a distinction has a fundamental role in CCS programs of monitoring, where the main goal is to demonstrate that there are no leakages from the reservoir to the atmosphere and, if present, they have to be detected and quantified. However, it is reasonable to assume that the magnitude of leakages in CCS projects is smaller than that in geothermal areas. This implies that CO_2 leakage is more difficult to be recognized and more accurate tools are required. Applying the best method to the partitioning of the CO_2 flux data allows to obtain the best approach for recognizing the presence of

different populations and their parameters (mean, standard deviation and proportion). This is the main aim in developing CCS monitoring tools.

To analyze the Sinclair and the Maximum Likelihood (ML) methods, the results obtained in the HO-C2, CC-C1 and MA-C2 campaigns were compared (Table 3, Fig. 6). The advantage in the partitioning with ML is that we can apply the likelihood ratio test, calculating the more likely population mixing and their parameters. The fact that the Sinclair (1974) method describes the methodology on a graphical basis, experience and knowledge of the evaluator are required. Hence, the process involves a considerable degree of subjectivity. In fact, while in the HO-C3 and MA-C2 campaigns the number of the calculated populations is the same with the two methods, the CC-C1 campaign showed ambiguous results: two populations were detected with ML according to the likelihood ratio test, whilst with that of Sinclair (1974) three populations were required (Table 3).

In the HO-C2 and MA-C1 campaigns the same populations were found, although significant differences in the estimation of the parameters were observed (Table 3). In the back-transformation to the original scale the mean estimation in HO-C2 with Sinclair is 40% smaller for P1 and 6% higher for P2 than the ML estimation. For MA-C2, these differences are higher: P1 is 11% smaller and P2

Fig. 6. Partitioning of CO_2 flux data into different lognormal populations with maximum likelihood criteria, (a) campaign HO-C3, (b) CC-C1 and (c) MA-C2.

Fig. 7. Confidence intervals. 1. AM, 2. MVUE, 3. Bootstrap, 4. ML, 5. Sinclair, 6. sGs.

is 61% higher with Sinclair than ML. These results suggest that we can under/over-estimate the population with respect to the likely population mixing.

4.3. Estimation emission rate and confidence intervals

The MA, MVUE, bootstrap, ML and Sinclair estimation methods are based on data independent. Thus, if the data are correlated and a model variogram can be fitted to explain this relationship among the flux data, these methods are not appropriated and geostatistical techniques are to be applied. Therefore, they cannot correctly be applied to the HO-C1, HO-C2, CC-C2, SO-C1, MA-C1 and CA-C1 campaigns. In this sense, until the emission rates in each site with statistical methods are similar to the results obtained with sGs (Fig. 7), CI are bigger.

In the campaign at La Solfatara (SO-C1), the maximum CI with sGs is $\pm 24\%$, this site being characterized by the highest CO_2 emissions related to a deep source (emission of $2373 \text{ t km}^{-2} \text{ d}^{-1}$) among the studied sites. In the remaining areas where sGs was applied, when CO_2 outputs were from 4.7 to $20 \text{ t km}^{-2} \text{ d}^{-1}$, CI was between $\pm 3.5\%$ (HO-C2) to $\pm 8\%$ (CA-C1). These CI values are considered good enough for estimating the CO_2 output, since the error of the instrument is about 20–25% and the CO_2 flux usually had a high local variation due to the surface soil properties. Also, in respect to other estimation methods, the CI obtained with sGs is smaller.

Normally, the CO_2 flux data follow a log-normal distribution. Thus, the Sichel estimation is usually a good estimation of the total output (supposed the independence of the data). Difficulties can be faced when a mixture of populations occurs and the confidence interval of the total emission rate is to be estimated. In Sinclair methods, as described in Chiodini et al. (1998), the total emission rate is the sum of what is emitted from each population (Eq. (10)). However, the confidence intervals are not the sum of the confidence intervals limits (lower and upper) of each population. This problem can be overcome when simulating mix populations and estimating the emanation for each simulation, although a biased confidence interval was observed (e.g., CC-C1 and MA-C2; Table 1). In these cases the smallest value of CI was obtained with the bootstrap method (around $\pm 20\%$). Therefore, bootstrap is to be considered a

good estimation method in the case of mixed populations or when the data are not normal or log-normal distributed.

An important issue in detecting and quantifying CO_2 leakages in CCS projects is that to distinguish the background level and a deep source of CO_2 . This could be achieved by modeling the CO_2 flux on explanatory variables such as soil temperature, moisture and location (e.g. Yang et al., 2011). A comparison between the results computed by the model and those obtained by direct measurements of CO_2 flux can thus be provided. Once a good estimation of accuracy is gathered, the statistical model for background flux can be processed to derive decision rules when leaking detection monitoring programs are to be deployed.

5. Conclusions

Flux measurements of CO_2 at the soil–atmosphere interface are critical in monitoring surveys of geological storage sites particularly when the estimation of the total emission rate is to be computed. The total CO_2 output has high relevance for quantifying a leakage when it has been detected. Therefore, it is of utmost importance to determine the optimum methodology for estimating the total CO_2 emission rate in the injection/leakage area.

Partitioning of CO_2 flux data into different log-normal populations is helpful to distinguish among different CO_2 sources, e.g. geogenic or biological. Thus, the reconnaissance of two or more sources plays a key role in monitoring CCS programs, where the main goals are to demonstrate that there are no CO_2 leakages from the reservoir to the atmosphere or, if occurring, their detection and quantification are required. In this sense, the partitioning of populations is more satisfactorily performed when maximum likelihood criteria are applied, since graphical procedures, as those described by Sinclair (1974), have a degree of subjectivity in the interpretation and the results may not be reproducible.

The MA, MVUE, bootstrap, ML and Sinclair estimation methods are based on data independent. Therefore, if the data are correlated and a model variogram can be fitted to explain this relationship among data these methods are not appropriated. In these cases, geostatistical techniques (sGs) provide more robust estimation values.

Fig. 8. Flow diagram of the procedure for estimating CO₂ Output.

Hence, the procedure to estimate the total diffuse CO₂ soil flux, once anomalous values are detected and studied separately, is firstly to apply a variogram analysis. If the relation between the data can be explained with the variogram, the best technique to calculate the total CO₂ output and its confidence interval is the sequential Gaussian simulation method (sGs). If data are independent (no variogram), the data distribution has to be analyzed. For normal and log-normal distribution the most appropriate methods are AM and MVUE, respectively. If the data are not normal (log-normal) or are a mixture of population the best method is the bootstrap resampling with the whole dataset (Fig. 8).

Following these steps the maximum confidence interval was about $\pm 20/25\%$, with most values comprised between ± 3.5 and $\pm 8\%$. These values are good enough for estimating the CO₂ output, since the error of the accumulation chamber method is about 10–25% and the CO₂ flux usually has high local variations due to significant changes in the soil properties. Therefore, it can be considered a good procedure to quantify a possible seepage in geological CO₂ storage sites. Also, the procedure described in this paper can be applied to other fields where the total emanation rate of gases (e.g., CO₂, CH₄) should be estimated with an accumulation chamber method (e.g., landfills, volcanic and geothermal areas).

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References

Alcalde, J., Martí, D., Calahorrano, A., Marzan, I., Ayarza, P., Carbonell, R., Juhlin, C., Pérez-Estaún, A., 2013. Active seismic characterization experiments of the

- Hontomín research facility for geological storage of CO₂, Spain. *Int. J. Greenh. Gas Control*, <http://dx.doi.org/10.1016/j.ijggc.2013.01.039>.
- Aiuppa, A., Tamburello, G., Di Napoli, R., Cardellini, C., Chiodini, G., Giudice, G., Grassa, F., Pedone, M., 2013. First observations of the fumarolic gas output from a restless caldera: implications for the current period of unrest (2005–2013) at Campi Flegrei. *Geochem. Geophys. Geosyst.*, 14, <http://dx.doi.org/10.1002/ggge.20261>.
- Anelli, L., Gorza, M., Pieri, M., Riva, M., 1994. Subsurface well data in the Northern Apennines (Italy). *Mem. Soc. Geol. Ital.* 48, 461–471.
- Armstrong, M., 1998. *Basic Linear Geostatistics*. Springer-Verlag, Berlin, pp. 155.
- Benaglia, T., Chaveau, D., Hunter, D.R., Young, D.Y., 2009. Mixtools: An R package for analyzing finite mixture models. *J. Stat. Softw.* 32, 1–29.
- Bicocchi, G., Tassi, F., Bonini, M., Capecciacci, F., Ruggieri, G., Bucciatti, A., Burgassi, P., Vaselli, O., 2013. The high pCO₂ Caprese reservoir (Northern Apennines, Italy): relationships between present- and paleo-fluid geochemistry and structural setting. *Chem. Geol.* 351, 40–56.
- Bivand, R.S., Pebesma, E.J., Gómez-Rubio, V., 2008. *Applied Spatial Data Analysis with R*. Springer Science + Business Media LLC.
- Bonini, M., 2009. Structural controls on a carbon dioxide-driven mud volcano field in the Northern Apennines (Pieve Santo Stefano, Italy): relations with pre-existing steep discontinuities and seismicity. *J. Struct. Geol.* 31, 44–54.
- Buil, B., Gómez, P., Peña, J., Garralón, A., Galarza, C., Durán, J.M., Domínguez, R., Escribano, A., Turrero, M.J., Robredo, L.M., Sánchez, L., 2012. Caracterización y monitorización hidrogeoquímica de los acuíferos superiores a la formación almacenamiento de CO₂ (Hontomín, Burgos) y actualización de la caracterización de aguas superficiales. Informe técnico CIEMAT/DMA/2G010/1/2012 (in Spanish).
- Box, G.E.P., Cox, D.R., 1964. An analysis of transformations. *J. R. Stat. Soc. Ser. B (Methodol.)* 26, 211–251.
- Cardellini, C., Chiodini, G., Frondini, F., 2003. Application of stochastic simulation to CO₂ flux from soil: mapping and quantification of gas release. *J. Geophys. Res.* 108, 2425.
- Canty, A., Ripley, B., 2012. *Boot: Bootstrap R (S-Plus) Functions*. R package version 1.3-7.
- Cebriá, J.M., López-Ruiz, J., 1995. Alkali basalts and leucitites in an extensional intracontinental plate setting: the Late Cenozoic Calatrava Volcanic Province (Central Spain). *Lithos* 35, 27–46.
- Chiodini, G., Cardellini, C., Lamberti, M.C., Agosto, M., Caselli, A., Liccioli, C., Tamburello, G., Tassi, F., Vaselli, O., Caliro, S., 2015. Carbon dioxide diffuse emission and thermal energy release from hydrothermal systems at Copahue–Cavihué Volcanic Complex (Argentina). *J. Volcanol. Geotherm. Res.* 304, 294–303.
- Chiodini, G., Cioni, R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO₂ flux measurements in volcanic and geothermal areas. *Appl. Geochem. (Elsevier Science Ltd)* 13 (5), 543–552.
- Cressie, N., 1993. *Statistics for Spatial Data*. Wiley, New York.
- Davison, A.C., Hinkley, D.V., 1997. *Bootstrap Methods and their Applications*. Cambridge University Press, Cambridge.
- De Bortoli, D., Panosso, A.R., Pelegrino, C.E., Pereira, G.T., La Scala, N., 2011. Soil CO₂ emission estimated by different interpolation techniques. *Plant Soil* 345, 187–194.
- De Lary, L., Loschetter, A., Bouc, O., Rohmer, J., Oldenburg, C.M., 2012. Assessing health impacts of CO₂ leakage from a geological storage site into buildings: role of attenuation in the unsaturated zone and building foundation. *Int. J. Greenh. Gas Control* 9, 322–333.
- Elío, J., Ortega, M.F., Nisi, B., Mazadiego, L.F., Vaselli, O., Caballero, J., Grandia, F., 2015. CO₂ and Rn degassing from the natural analog of Campo de Calatrava (Spain): implications for monitoring of CO₂ storage sites. *Int. J. Greenh. Gas Control* 32, 1–14.
- Elío, J., Nisi, B., Ortega, M.F., Mazadiego, L.F., Vaselli, O., Grandia, F., 2013. CO₂ soil flux baseline at the technological development plant for CO₂ injection at Hontomín (Burgos, Spain). *Int. J. Greenh. Gas Control* 18, 224–236.
- Elío, J., Ortega, M.F., Chacón, E., Mazadiego, L.F., Grandia, F., 2012. Sampling strategies using the “accumulation chamber” for monitoring geological storage of CO₂. *Int. J. Greenh. Gas Control* 9, 303–311.
- Etheridge, D., Leuning, R., de Vries, D., Dodds, K., Trudinger, C., Allison, C., Fraser, P., Prata, F., Bernardo, C., Meyer, M., Dunse, B., Luhar, A., 83 pp. 2005. *Atmospheric monitoring and verification technologies for CO₂ storage at geosequestration sites in Australia*. CO2CRC Publication Number RPT05-0134. Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia.
- Evans, W.C., Sorey, M.L., Kennedy, B.M., Stonestrom, B.M., Rogie, J.D., Shuster, D.L., 2001. High CO₂ emissions through porous media: transport mechanisms and implications for flux measurement and fractionation. *Chem. Geol.* 177, 15–29.
- Farrar, D., Neil, J.M., Howle, J.F., 1999. *Mammoth Mountain, California. Water-Resources Investigations, U.S. Geological Survey, Sacramento, California*.
- Förster, A., Norden, B., Zinck-Jørgensen, K., Frykman, P., Kulenkampff, J., Spangenberg, E., Erzinger, J., Zimmer, M., Kopp, J., Borm, G., Juhlin, C., Cosma, C., Hurter, S., 2006. Baseline characterization of the CO2SINK geological storage site at Ketzin, Germany. *Environ. Geosci.* 13, 145–161.
- Frondini, F., Caliro, S., Cardellini, C., Chiodini, G., Morgantini, N., 2009. Carbon dioxide degassing and thermal energy release in the Monte Amiata volcanic-geothermal area (Italy). *Appl. Geochem.* 24, 860–875.
- Granieri, D., Avino, R., Chiodini, G., 2010. Carbon dioxide diffuse emission from the soil: ten years of observations at Vesuvio and Campi Flegrei (Pozzuoli), and linkages with volcanic activity. *Bull. Volcanol.* 72, 103–118.

- Hui Yim, M., Jin Joo, S., Nakane, K., 2002. Comparison of field methods for measuring soil respiration: a static alkali absorption method and two dynamic closed chamber methods. *Forest Ecol. Manag.* (Elsevier) 170, 189–197.
- IGME, 1991. Instituto Geológico y Minero de España. Mapa geológico de España, geological sheet 167/19-9 scale 1:50.000 Montorio.
- IPCC, 2005. In: Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.), *IPCC Special Report on Carbon Dioxide Capture and Storage*. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.
- Klusman, R.W., 2003a. Evaluation of leakage potential from a carbon dioxide EOR/sequestration project. *Energy Convers. Manag.* 44–18, 1921–1940.
- Klusman, R.W., 2003b. Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, Colorado, USA. *Appl. Geochem.* 18, 1825–1838.
- Klusman, R.W., 2003c. Computer modeling of methanotrophic oxidation of hydrocarbons in the unsaturated zone from an enhanced oil recovery-sequestration project, Rangely, Colorado, USA. *Appl. Geochem.* 18, 1839–1852.
- Klusman, R.W., 2005. Baseline studies of surface gas exchange and soil-gas composition in preparation for CO₂ sequestration research: Teapot Dome, Wyoming. In: *The American Association of Petroleum Geologists (Ed.), AAPG Bulletin*, vol. 89-8, pp. 981–1003.
- Klusman, R.W., 2011. Comparison of surface and near-surface geochemical methods for detection of gas microseepage from carbon dioxide sequestration. *Int. J. Greenh. Gas Control* 5, 1369–1392.
- Koch, G.S., Link, R.F., 1970. *Statistical Analysis of Geological Data*. John Wiley and Sons, Inc.
- Korre, A., Imrie, C.E., May, F., Beaubien, S.E., Vandermeijer, V., Persoglia, S., Golmen, L., Fabriol, H., Dixon, T., 2011. Quantification techniques for potential CO₂ leakage from geological storage sites. *Energy Procedia* 4, 3413–3420.
- Laurenzi, M.A., Braschi, E., Casalini, M., Conticelli, S., 2015. New ⁴⁰Ar–³⁹Ar dating and revision of the geochronology of the Monte Amiata Volcano, Central Italy. *Ital. J. Geosci.* 134, 255–265.
- Lewicki, J.L., Hilley, G.E., Oldenburg, C.M., 2005a. An improved strategy to detect CO₂ leakage for verification of geologic carbon sequestration. *Geophys. Res. Lett.*, 32.
- Lewicki, J.L., Bergfeld, D., Cardellini, C., et al., 2005b. Comparative soil CO₂ flux measurements and geostatistical estimation methods on Masaya volcano, Nicaragua. *Bull. Volcanol.* 68, 76–90.
- Minissale, A., Magro, G., Vaselli, O., Verrucchi, C., Perticone, I., 1997. Geochemistry of water and gas discharges from the Mt. Amiata silicic complex and surrounding areas (central Italy). *J. Volcanol. Geotherm. Res.* 79, 223–251.
- Nisi, B., Vaselli, O., Tassi, F., Elío, J., Delgado, A., Mazadiego, L.F., Ortega, M.F., 2013. Hydrogeochemistry of running and spring waters in the Hontomin–Huermeceas area (Burgos Spain). *Int. J. Greenh. Gas Control* 14, 151–168.
- Nisi, B., Vaselli, O., Tassi, F., Elío, J., Ortega, M., Caballero, J., Rappuoli, D., Mazadiego, L.F., 2014. Origin of the gases released from the Acqua Passante and Ermeta wells (Mt. Amiata, central Italy) and possible environmental implications for their closure. *Ann. Geophys.* 57 (4), S0438, <http://dx.doi.org/10.4401/ag-6584>.
- Pebesma, E.J., 2004. Multivariable geostatistics in S: the gstat package. *Comput. Geosci.* 30, 683–691.
- Pérez, N.M., Nakai, S., Wakita, H., Albert-Bertan, J.F., Redondo, R., 1996. Preliminary results on the ³He/⁴He isotopic ratios in terrestrial fluids from Iberian Peninsula: seismotectonic and neotectonic implications. *Geogaceta* 20, 830–833.
- R Core Team, 2012. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, <http://www.R-project.org/>.
- Raco, B., Battaglini, R., Lelli, M., 2010. Gas emission into the atmosphere from controlled landfills: an example from Legoli landfill (Tuscany, Italy). *Environ. Sci. Pollut. Res.* 17, 1197–1206.
- Scandone, R., Giacomelli, L., Fattori Speranza, F., 2006. The volcanological history of the volcanoes of Naples: a review. In: De Vivo, B. (Ed.), *Volcanism in the Campania Plain*, pp. 1–26 (Chapter 1).
- Sinclair, A.J., 1974. Selection of threshold values in geochemical data using probability graphs. *J. Geochem. Explor.* 3, 129–149.
- Strutt, M., Beaubien, S., Beaubron, J., et al., 2003. In: Gale, J., Kaya, Y. (Eds.), *Soil gas as a monitoring tool of deep geological sequestration of carbon dioxide: preliminary results from the EnCana EOR project in Weyburn, Saskatchewan (Canada)*, vol. I. Greenhouse Gas Control Technologies, pp. 391–396.
- Tassi, F., Nisi, B., Cardellini, C., Capecchiacci, F., Donnini, M., Vaselli, O., Avino, Y., Chiodini, G., 2013. Diffuse soil emission of hydrothermal gases (CO₂, CH₄, and C₆H₆) at Solfatara crater (Campi Flegrei, southern Italy). *Appl. Geochem.*, <http://dx.doi.org/10.1016/j.apgeochem.2013.03.020>.
- Tassi, F., Vaselli, O., Cuccoli, F., Buccianti, A., Nisi, B., Lognoli, E., Montegrossi, G., 2009. A geochemical multi-methodological approach in hazard assessment of CO₂-rich gas emissions at Mt. Amiata volcano (Tuscany, central Italy). *Water Air Soil Pollut. Focus* 9, 117–127, <http://dx.doi.org/10.1007/s11267-008-9198-2>.
- US-EPA, 2002. Calculating upper confidence limits for exposure point concentrations at hazardous waste sites. Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, D.C., 20460, OSWER 9285.6-10.
- US-EPA, 2007. ProUCL Version 4.0 Technical Guide. U.S. Environmental Protection Agency Office of Research and Development, Washington, DC, 20460, EPA/600/R-07/041.
- Vaselli, O., Nisi, B., Tassi, F., Darrah, T., Bruno, J., Elío, J., Grandia, F., Del Villar, L.P., 2013a. Gas discharges for continental Spain: geochemical and isotopic features. *Mineral. Mag.* 77 (5), 2401.
- Vaselli, O., Nisi, B., Tassi, F., Giannini, L., Grandia, F., Darrah, T., Capecchiacci, F., Pérez del Villar, L., 2013b. Water and gas geochemistry of the Calatrava Volcanic Province (CVP) hydrothermal system (Ciudad Real, central Spain). *Geophysical Research Abstracts* Vol. 15, EGU2013-12020, 2013 EGU General Assembly 2013, 7–12 April, 2013, Wien. (Austria).
- Venables, W.N., Ripley, B.D., 2002. *Modern Applied Statistics with S*, Fourth edition. Springer, New York, ISBN 0-387-95457-0.
- Welles, J.M., Demetriades-Shah, T.H., McDermitt, D.K., 2001. Considerations for measuring ground CO₂ effluxes with chambers. *Chem. Geol.* (Elsevier), 3–13.
- West Systems, 2009. *Portable diffuse flux meter*. Handbook, release 8.0. Pontedera, Pisa.
- Yang, Y.M., Small, M.J., Junker, B., Bromhal, G.S., Strazisar, B., Wells, A., 2011. Bayesian hierarchical models for soil CO₂ flux and leak detection at geologic sequestration sites. *Environ. Earth Sci.* 64, 787–798.
- Young, D.S., Hunter, D.R., 2010. Mixtures of regression with predictor-dependent mixing proportions. *Comput. Stat. Data Anal.* 54–10, 2253–2266.