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### **CO<sub>2</sub> and Rn degassing from the natural analog of Campo de Calatrava (Spain): Implications for monitoring of CO<sub>2</sub> storage sites**

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

*Original Citation:*

CO<sub>2</sub> and Rn degassing from the natural analog of Campo de Calatrava (Spain): Implications for monitoring of CO<sub>2</sub> storage sites / Orlando Vaselli. - In: INTERNATIONAL JOURNAL OF GREENHOUSE GAS CONTROL. - ISSN 1878-0148. - ELETTRONICO. - 32:(2015), pp. 1-14. [10.1016/j.ijggc.2014.10.014]

*Availability:*

The webpage <https://hdl.handle.net/2158/1231499> of the repository was last updated on 2021-03-24T15:15:12Z

*Published version:*

DOI: 10.1016/j.ijggc.2014.10.014

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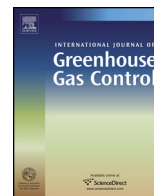
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## CO<sub>2</sub> and Rn degassing from the natural analog of Campo de Calatrava (Spain): Implications for monitoring of CO<sub>2</sub> storage sites



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### ARTICLE INFO

#### Article history:

Received 8 July 2014

Received in revised form 17 October 2014

Accepted 23 October 2014

Available online 13 November 2014

#### Keywords:

CO<sub>2</sub> storage

Geochemical monitoring

CO<sub>2</sub> leakages

Radon isotopes

Natural analogs

Soil gases

### ABSTRACT

Natural analogs offer a valuable opportunity to investigate the long-term impacts associated with the potential leakage in geological storage of CO<sub>2</sub>.

Degassing of CO<sub>2</sub> and radon isotopes (<sup>222</sup>Rn–<sup>220</sup>Rn) from soil, gas vents and thermal water discharges was investigated in the natural analog of Campo de Calatrava Volcanic Field (CCVF; Central Spain) to determine the CO<sub>2</sub>–Rn relationships and to assess the role of CO<sub>2</sub> as carrier gas for radon. Furthermore, radon measurements to discriminate between shallow and deep gas sources were evaluated under the perspective of their applicability in monitoring programs of carbon storage projects.

CO<sub>2</sub> flux as high as 5000 g m<sup>-2</sup> d<sup>-1</sup> and <sup>222</sup>Rn activities up to 430 kBq m<sup>-3</sup> were measured; <sup>220</sup>Rn activities were one order of magnitude lower than those of <sup>222</sup>Rn. The <sup>222</sup>Rn/<sup>220</sup>Rn ratios were used to constrain the source of the Campo de Calatrava soil gases since a positive correlation between radon isotopic ratios and CO<sub>2</sub> fluxes was observed. Thus, in agreement with previous studies, our results indicate a deep mantle-related origin of CO<sub>2</sub> for both free and soil gases, suggesting that carbon dioxide is an efficient carrier for Rn. Furthermore, it was ascertained that the increase of <sup>222</sup>Rn in the soil gases was likely produced by two main processes: (i) direct transport by a carrier gas, i.e., CO<sub>2</sub> and (ii) generation at shallow level due to the presence of relatively high concentrations of dissolved U and Ra in the thermal aquifer of Campo de Calatrava.

The diffuse CO<sub>2</sub> soil flux and radon isotopic surveys carried out in the Campo de Calatrava Volcanic Fields can also be applicable to geochemical monitoring programs in CCS (Carbon Capture and Storage) areas as these parameters are useful to: (i) constrain CO<sub>2</sub> leakages once detected and (ii) monitor both the evolution of the leakages and the effectiveness of subsequent remediation activities. These measurements can also conveniently be used to detect diffuse leakages.

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### 1. Introduction

Carbon Capture and Storage (CCS) is one of the most feasible techniques to reduce anthropogenic greenhouse gas emissions into the atmosphere, allowing fossil fuels combustion to be environmentally sustainable (IEA, 2008; IPCC, 2005). In 2011 the United Nations Framework Convention on Climate Change of Durban (UNFCCC, 2011) defined CCS as a clean development mechanism. However, its commercial application still requires further (theoretical and practical) investigations in order to make this technology

economically viable and environmentally safe. Moreover, a proper evaluation of the costs (Kühn et al., 2013; Lupion and Herzog, 2013; Nataly Echevarria Huaman and Xiu Jun, 2014; Romanak et al., 2013) is needed since CCS can be difficult to sustain by private companies without financial support by governmental authorities unless carbon sequestration with enhanced gas recovery and oil recovery is applied (CSEGR and CSEOR; e.g., Oldenburg, 2003; Solomon et al., 2008). Eventually, as recently suggested, e.g., Oldenburg, 2012 and references therein, anthropogenic CO<sub>2</sub> can be used to improve the economic viability by increasing the use of this greenhouse gas for different (e.g., industrial, agricultural, food and beverages, pharmaceutical, chemical, healthcare) purposes. Thus, it has been suggested to include the term of “utilization of CO<sub>2</sub>” in the CCS process, i.e., carbon capture, utilization and storage (CCUS).

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The study of natural systems hosting CO<sub>2</sub>-rich gas reservoirs can help to interpret the different stages of the CO<sub>2</sub> storage processes, which normally require long periods of time and can only partially be reproduced in the laboratory (Pearce, 2006). Consequently, in the recent years a large number of studies addressed to the evaluation of leakage processes from CO<sub>2</sub>-rich natural analogs and the implications for the geological storage of CO<sub>2</sub> has been performed (e.g., Gal et al., 2012; Holloway et al., 2007; Jeandel et al., 2010; Lewicki et al., 2007; Voltattorni et al., 2009).

Surface monitoring methods (e.g., water and dissolved gas chemistry and soil-gas investigations) are relevant in the monitoring, verification and accounting (MVA) of CO<sub>2</sub> geosequestration to assess the environmentally safe storage (Klusman, 2011), during both site characterization and injection and post-injection phases. These methods have been oriented to detect and quantify possible CO<sub>2</sub> leakages to the atmosphere and cover a large range of techniques (e.g., IPPC, 2006; NETL, 2009).

Measurements of radon activity (<sup>222</sup>Rn–<sup>220</sup>Rn) in soil gases are considered useful in monitoring programs of geological storage for two main reasons: (i) CO<sub>2</sub> is often regarded as the main carrier gas for radon (e.g., Etiope and Martinelli, 2002; Etiope et al., 2005; Voltattorni et al., 2009), and then CO<sub>2</sub> leakages from deep sources may produce significant anomalies in radon activity, and (ii) radon, similarly to CO<sub>2</sub>, can be used to detect fracture/fault systems since they represent the preferential pathways for gas leakage (e.g., Ioannides et al., 2003; Walia et al., 2010). Radon measurements at the soil–atmosphere interface for leakage detection were applied in some projects of CO<sub>2</sub> geological storage, such as the IEA GHG Weyburn CO<sub>2</sub> Monitoring and Storage Project (Riding and Rochelle, 2005; Strutt et al., 2003; Wilson and Monea, 2004) and the Frio Brine Pilot Project (Nance et al., 2005).

The detection of radon emission is also significant in terms of its effect on human health. USEPA has estimated that radon is the second cause of lung cancer after smoking (e.g., EPA, 2003; Field et al., 2000; Rosario and Wichmann, 2006). Thus, recognizing positive correlations between Rn and CO<sub>2</sub> and defining Rn abundances from permeable zones are critical and would allow the definition of potential hazard areas to be taken into consideration in the risk assessment of geological storage.

This research article describes and discusses the results obtained on free- and soil-gases from the Campo de Calatrava Volcanic Field (CCVF) natural analog, which is located in the Neogene Granátula – Moral de Calatrava Basin (central Spain). The main goals of this study were to (i) determine the relationships between CO<sub>2</sub> fluxes and activity of radon isotopes (<sup>222</sup>Rn and <sup>220</sup>Rn) in the soil gas and (ii) to assess the possible use of radon measurements as monitoring tool in CCS projects.

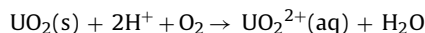
### 1.1. Radon physical-chemical background

Radon has four main isotopes, <sup>218</sup>Rn, <sup>219</sup>Rn, <sup>220</sup>Rn and <sup>222</sup>Rn, which are decay products of <sup>218</sup>At, <sup>223</sup>Ra, <sup>224</sup>Ra and <sup>226</sup>Ra, respectively, all belonging to the U and Th decay series. Radon isotopes are characterized by relatively short half-lives being <sup>222</sup>Rn ( $t_{1/2} = 3.8$  days) and <sup>220</sup>Rn ( $t_{1/2} = 55$  seconds) with the longest half-lives (e.g., Fleischer, 1997). The decay products of <sup>220</sup>Rn (commonly named thoron) and <sup>222</sup>Rn are the radioactive isotopes of polonium, bismuth, lead and thallium. While <sup>220</sup>Rn has no long-lived progeny, <sup>222</sup>Rn has <sup>214</sup>Pb, <sup>214</sup>Bi and <sup>214</sup>Po (e.g., Ramachandan and Sathish, 2011).

Radon (<sup>222</sup>Rn–<sup>220</sup>Rn) activity has extensively been used in the earth sciences as tracer of U deposits (e.g., Sutton and Soonwala, 1975), precursor of seismic and volcanic activity (e.g., Cox, 1980; Dueñas and Fernández, 1987; Fleischer and Mogro-Campero, 1978; Nielson, 1978), tracer of subsurface fracture systems (Walia et al., 2010), oil/gas reservoirs (Klusman and Voorhees, 1983; Morse et al.,

1982; Mazadiego, 1994) and subsurface hydrocarbon pollution (Davis et al., 2003; García-González et al., 2008; Schubert et al., 2001). Recently, radon isotopes have been applied to distinguish CO<sub>2</sub> emission from deep and shallow (biogenic) sources (Etiope et al., 2005; Etiope and Martinelli, 2002; Giammanco et al., 2007; Michel-Le Pierres et al., 2010; Voltattorni et al., 2009).

A schematic cycle of <sup>220</sup>Rn and <sup>222</sup>Rn isotopes is reported in Fig. 1. The mobility of radon isotope parents, including uranium and radium, is limited. Uranium (an element with long-lived isotopes) is found in minerals and chemical alteration favors its transfer to surface and ground waters (e.g., Bonotto and Andrews, 1999; Mazadiego, 1994). Aqueous dissolution of uranium minerals (e.g., uraninite) can be represented by the following reaction:



Additionally, if water contains HCO<sub>3</sub><sup>−</sup> and CO<sub>3</sub><sup>2−</sup> the mobility of uranium tends to increase due to the formation of carbonate complexes (Casas et al., 1998; Gorman-Lewis et al., 2008; Majumdar et al., 2003). Under oxidizing conditions, uranium in solution is preferentially present as uranyl ion (UO<sub>2</sub><sup>2+</sup>), whereas U<sup>4+</sup> prevails in reducing conditions and UO<sub>2</sub> can precipitate (e.g., Bonotto and Andrews, 1999; García-González et al., 2008).

The uranyl ion may also be trapped in clay minerals and iron oxy-hydroxides by adsorption/absorption processes (e.g., Hsi and Langmuir, 1985; Langmuir, 1978). Conversely, radium (with shorter-lived isotopes than uranium) is exclusively present in solution as Ra<sup>2+</sup> (Langmuir and Riese, 1985) and is rather recalcitrant to form salts under reducing and oxidizing environments. Thus, in surface and ground waters radium is maintained in solution. Neutral or anionic (e.g., SO<sub>4</sub>) complexes are formed for pH approaching 10 (Langmuir and Riese, 1985). Nevertheless, according to Langmuir and Melchoir (1985) and Martin and Akber (1999), Ra<sup>2+</sup> can coprecipitate with barite (BaSO<sub>4</sub>), witherite (BaCO<sub>3</sub>) and celestite (SrSO<sub>4</sub>). Consequently, spring waters and related salts may represent a source of radon (<sup>222</sup>Rn–<sup>220</sup>Rn), whose values can be higher than those of the background signals.

In the vadose zone, Rn may also have a deep origin although, due to its relatively fast decay, radon is expected to have small mobility from its source by diffusion processes (Cothorn and Smith, 1987; Martinelli, 1998; Rose et al., 1979). Thus, underground long migration of radon from deeper sources to the surface requires advective transport driven by major gases such as CO<sub>2</sub> and CH<sub>4</sub> (the “geogas” theory, Etiope and Martinelli, 2002).

As Rn migrates, the radon isotopic ratios change due to significant differences in the <sup>222</sup>Rn and <sup>220</sup>Rn half-lives. The latter is thus preferentially found close to the parent isotope source (Huxol et al., 2012, 2013). The <sup>222</sup>Rn/<sup>220</sup>Rn ratios can be used to define the depth at which free- and soil-gases retrieved at the surface were formed (e.g., Giammanco et al., 2007). The relationship between <sup>222</sup>Rn and <sup>220</sup>Rn in soil gases is clearly dependent on the concentration of their parents in the substrate (<sup>238</sup>U and <sup>232</sup>Th, respectively). Thus, leaking of deep-seated gases at the surface is expected to result in reduced <sup>220</sup>Rn concentrations, while the <sup>222</sup>Rn/<sup>220</sup>Rn ratios increase. Relatively low <sup>222</sup>Rn/<sup>220</sup>Rn ratios are generally associated with the production of radon in shallow environments (e.g., Giammanco et al., 2007).

Radon concentrations in soil gases are affected by a number of factors, such as meteorological, geological and pedological (e.g., De Jong et al., 1994; Vaupotic et al., 2007) and major seismic events (e.g., King and Minissale, 1994; Toutain and Baubron, 1999; Virk and Walia, 2001). According to Tanner (1980), radon can be released from soils and rocks by molecular diffusion, direct recoil and molecular diffusion after indirect recoil. Molecular and convection processes influence soil radon activity concentrations, which

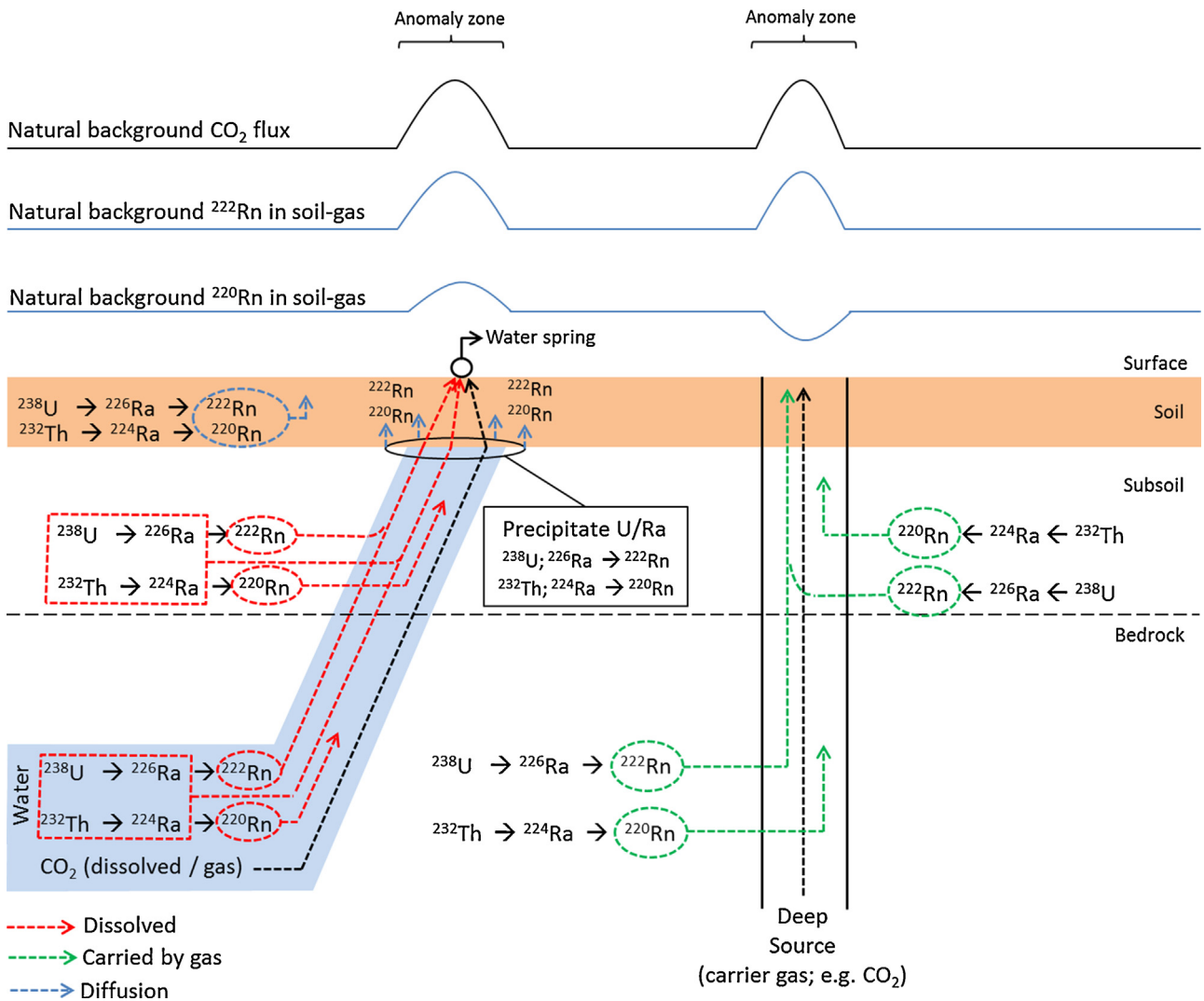


Fig. 1. Sketch of radon transport in liquid and gas phase.

increase with depth until when an equilibrium concentration is achieved (Nazaroff and Nero, 1988; Szabó et al., 2013).

Radon ( $^{222}\text{Rn}$ ) concentration ( $C_{\text{Rn}}$  in  $[\text{Bq m}^{-3}]$ ) in soil gases depends on  $^{226}\text{Ra}$  concentration ( $C_{\text{Ra}}$   $[\text{Bq kg}^{-1}]$ ), emanation coefficient ( $\varepsilon$ ; adimensional), soil density ( $\rho$   $[\text{kg m}^{-3}]$ ) and effective porosity ( $n$ ; adimensional) (Guerra and Lombardi, 2001; Schubert et al., 2001), as follows:

$$C_{\text{Rn}} = C_{\text{Ra}} \cdot \varepsilon \cdot \rho \cdot n^{-1} \quad (1)$$

Soil water (saturation in pore space,  $0 \leq S_F \leq 1$ ) increases radon concentration in soil gas (Schubert et al., 2001). Such an increase is defined by Eq. (2) ( $K_{\text{w/air}} = 0.25$ , radon partitioning coefficients between water and air) and plotted in Fig. 2. It can be seen that the  $^{222}\text{Rn}$  concentration can increase up to 300% ( $S_F = 1$ ) with respect to radon equilibrium in dry soil ( $S_F = 0$ ).

$$\frac{1}{1 - S_F + S_F \cdot K_{\text{w/air}}} \quad (2)$$

## 2. Geological outlines

The Campo de Calatrava Volcanic Field (CCVF) is located in the province of Ciudad Real (central Spain) (Ancochea, 1983; Hernández-Pacheco, 1932; Fig. 3a). The study area consists of a

Hercynian basement 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 km<sup>2</sup>. A complex fracture pattern (E–W to ENE–WSW, NW–SE and NE–SW) controls the basins geometries (Crespo, 1992). At least three different Neogene tectonic episodes were recognized in the CCVF (IGME, 1988). A first extensional phase of late Miocene age, which resulted in the initial opening of the sedimentary basins, was followed in time by two Pliocene tectonic episodes: the opening of the so-called La Mancha basin and a final regional-scale weak compressional phase. The Miocene-Quaternary CCVF consists of volcanic deposits of alkaline composition (e.g., Cebriá et al., 2009; Cebriá and López-Ruiz, 1995; López-Ruiz et al., 2002). The area is characterized by several gas and water discharges (e.g., Melero Cabañas, 2007; Piedrabuena, 1992; Vaselli et al., 2013) that are distributed almost throughout the whole CCVF. It is interesting to point out that the geochemical and isotopic features of the gas seeps indicate a high purity of CO<sub>2</sub> (up to 98.5% by vol.), while the helium isotopic ratio suggests a mantle-related source for these gases (Pérez et al., 1996; Vaselli et al., 2013). The CCVF, along with La Selva-Empordà (NE Spain), likely represents the highest CO<sub>2</sub> discharge area in the whole continental Spain (Vaselli et al., 2013).

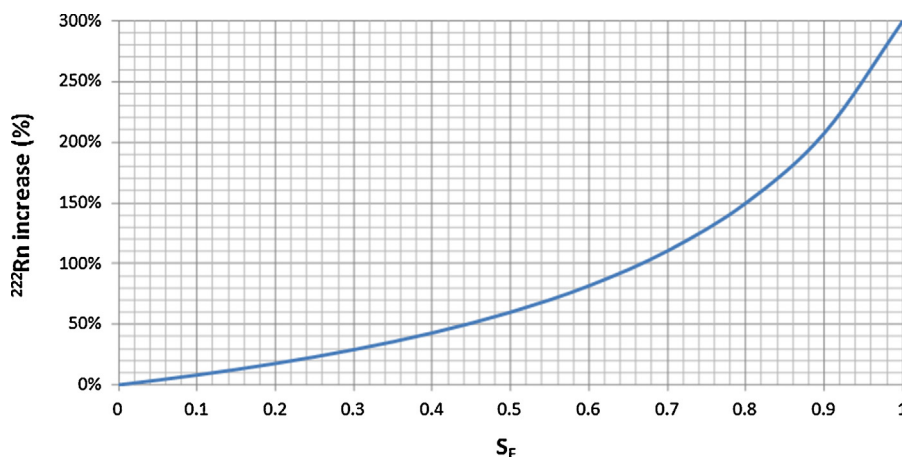


Fig. 2. Water influence in the equilibrium radon ( $^{222}\text{Rn}$ ) concentration of the soil-gas.

### 3. Materials and methods

#### 3.1. Area of study

More than 25  $\text{CO}_2$  seepages from CCVF, mainly associated to fracture systems, were investigated from June 2010 to February 2012. Gas leakages were commonly found as small ( $<1\text{ m}^2$ ) leakage points. Considering the elevated number of  $\text{CO}_2$  emissions, this study focused on two areas that were considered representative of the  $\text{CO}_2$  seepage in CCVF, namely La Sima (dry gas vents) and Jabalón River (degassing pools and springs) (Fig. 3a).

La Sima is a  $\text{CO}_2$ -rich gas discharge (up to  $2\text{ t d}^{-1}$ ), which has a surface of a few square meters. The emission is restricted to a small ( $\approx 5\text{ m}$  in diameter) depression, where small dead animals are frequently found. The Jabalón River area is located 6 km from the village of Granátula de Calatrava (Fig. 3a). Four subareas were considered: (i) Jabalón, (ii) NH-1, (iii) Fontecha and (iv) NH-2. In the Jabalón River, an elevated number of  $\text{CO}_2$ -rich manifestations, bubbling into warm water ( $<30\text{ }^\circ\text{C}$ ) springs, occur, likely aligned along a fault system parallel (NW–SE) to the river bed (12 emission points in a profile of approximately 2 km). The location of the studied sites where  $\text{CO}_2$  flux and radon measurements were carried out is shown in Fig. 3.

#### 3.2. $\text{CO}_2$ flux measurements

Carbon dioxide soil fluxes were measured in 70 stations (Table 2, Fig. 3) using the accumulation chamber method (e.g., Cardellini et al., 2003; Chiodini et al., 1998), which is based on the continuous measurement of the  $\text{CO}_2$  concentrations with time by using an inverted chamber placed on the ground. The accumulation chamber device consists of: (i) a metal cylindrical chamber with an inlet net area and inner volume of  $3.14 \times 10^{-2}\text{ m}^2$  and  $3.06 \times 10^{-3}\text{ m}^3$ , respectively, (ii) an Infra-Red (IR) Spectrophotometer (Licor<sup>®</sup> Li-820, infra-red sensor detector, measuring range of 0–20,000 ppm, accuracy of 4% of readings), (iii) an analog–digital (AD) converter, and (iv) a palmtop computer (PC).

#### 3.3. Radon measurements

The recording of the radon activity (70 points for  $^{222}\text{Rn}$  and 31 for  $^{220}\text{Rn}$ , respectively; Table 2, Fig. 3) was performed with two SARAD<sup>®</sup> RTM-2100 devices and one ionization chamber RADON V.O.S., model RM-2. Soil gases were collected with a stainless-steel hollow probe, which was hammered into the soil, down to a depth of 0.75–1.00 m in order to minimize the influence of atmospheric factors (e.g., King and Minissale, 1994). At La Sima, the probe was

inserted at the depth of 0.15–0.20 m due to the thin soil layer, which covered the bedrock. The radon monitor was fitted with a canister filled with drierite (97%  $\text{CaSO}_4 + 3\% \text{CoCl}_2$ ) and a hydrophobic Teflon filter to minimize the humidity content within the instrument and preventing fine particles entering the ionization chamber (García-González et al., 2008). In the bubbling sites, radon measurements were carried out directly in the airflow, with a collector into which the bubbling gas was trapped.

The radon ( $^{222}\text{Rn}$ – $^{220}\text{Rn}$ ) measurements were performed with a SARAD<sup>®</sup> RTM-2100 by analyzing the radon daughter isotopes ( $^{218}\text{Po}/^{214}\text{Po}$  and  $^{216}\text{Po}$ ). The subsequent radioactive decay of these isotopes was recorded with a multichannel analyzer (alpha spectrometry). Soil gases were driven into the ionization chamber by an internal pump at the rate of  $3\text{ L min}^{-1}$ . Measurements were carried out with the instrument in “thoron” mode and with integration time of 1 min.  $^{222}\text{Rn}$  activity was assigned to the value of “radon” after 15 min and those of thoron after 5 min. After each series of measurements, the internal pump was set at high flow ( $3\text{ L min}^{-1}$ ) for 20–30 min to clean the ionization chamber before starting a new measurement. The detection limit of the instrument was  $1\text{ kBq m}^{-3}$ , and the statistical error at  $1\sigma$  was defined as  $100\%/\sqrt{N}$ , where  $N$  is the number of registered counts of the relevant nuclides ( $^{218}\text{Po}/^{214}\text{Po}$  and  $^{216}\text{Po}$ ) within the time interval. For an Equivalent Radon Concentration of  $1\text{ kBq m}^{-3}$  or higher the statistical error was below 10%.

The RM-2 system was designed for the determination of soil gas radon ( $^{222}\text{Rn}$ ) concentrations. The detection principle consists in an ionization chamber where a potential difference between a positively charged metal outer shell and an electrode located along the longitudinal axis (0V) was applied. When radon emits alpha particles, ions were detected by the electrode. The ion current was then measured and converted to Rn concentration, expressed as  $\text{Bq m}^{-3}$ . The soil gas was collected with a 150 mL syringe, connected to the top of a stainless-steel hollow probe and transferred into a pre-evacuated ionization chamber (250 mL). Pressure inside the chamber was equalized to the ambient atmospheric pressure by opening the valve. Measurements were carried out after 15 min. The delay of 15 min ensured that the activity of  $^{220}\text{Rn}$  was practically negligible due to its short half-life. The detection limit was  $5\text{ kBq m}^{-3}$ . The uncertainty of radon concentration ( $1\sigma$ ) was  $0.33(C_{\text{rn}})^{0.5}$ , where  $C_{\text{rn}}$  is the radon concentration ( $C_{\text{rn}} \pm \sigma$ ). The RM-2 error of the radon concentration was below 15%.

Radon concentrations ( $^{222}\text{Rn}$  [ $\text{Bq m}^{-3}$ ]) obtained with the two instrumentation (SARAD<sup>®</sup> RTM-2100 and RM-2) did not significantly differ (relative standard deviation – RSD – around 10%). Thus, the  $^{222}\text{Rn}$  concentrations were analyzed independently of the instrument, and will not be discussed further.

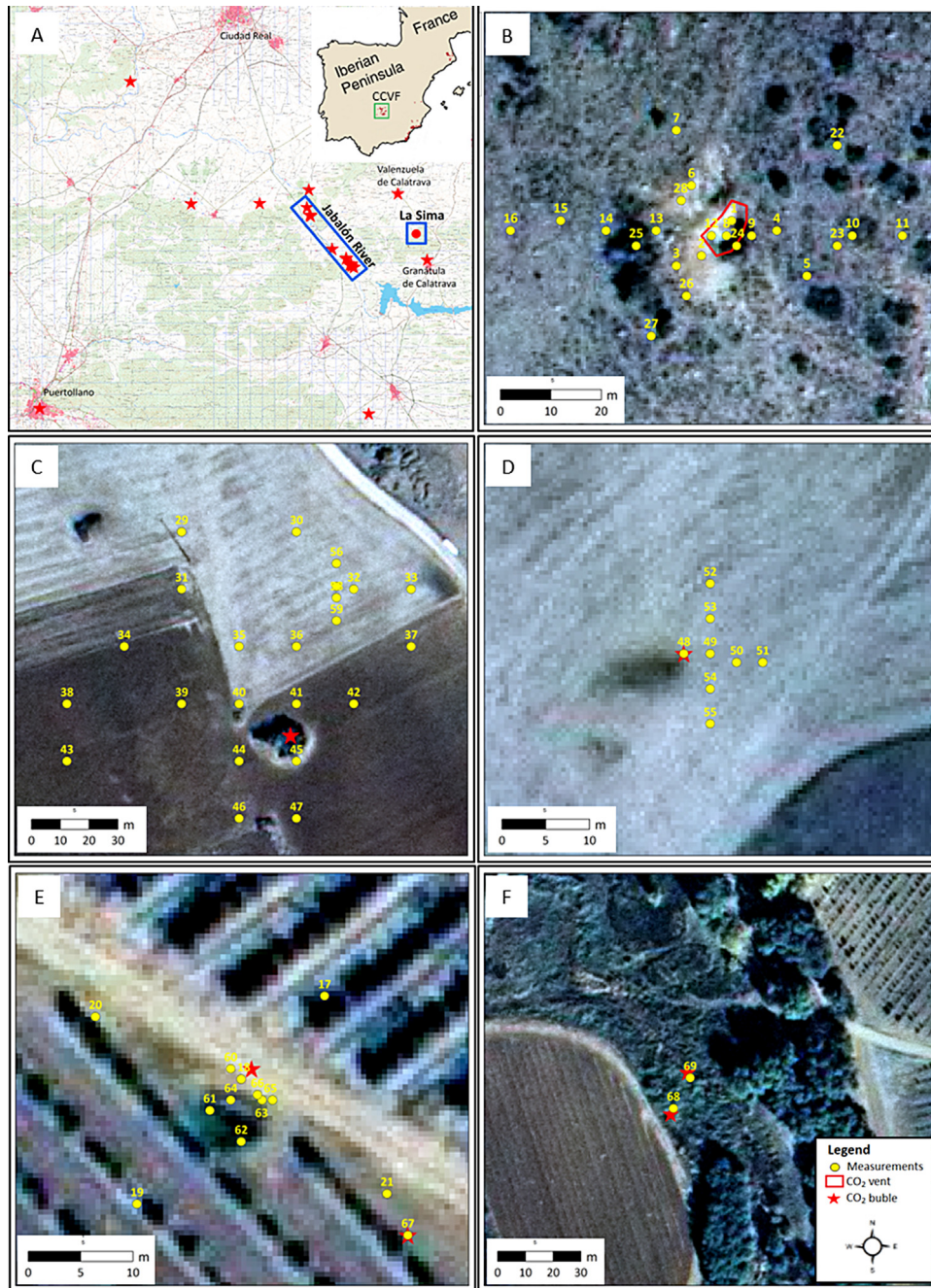


Fig. 3. Sampling zones: (a) CCVF area, (b) La Sima, (c) Jabalón, (d) NH-1, (e) Fontecha and (f) NH-2.

### 3.4. Soil sampling

Eight soil samples (Table 3; Fig. 3) were collected to measure the concentration of the radon parent radionuclides (U–Ra) and to assess whether radon was originated by the soil cover or was transferred from deep sources by advective circulation. Sampling was carried out with an Edelman auger at the same depth where the soil-gases were measured: two at La Sima gas vent (inside and outside the degassing site) and six at the Jabalón River area (2 close to the CO<sub>2</sub> seepage, i.e., where CO<sub>2</sub> was bubbling in water, and 4 at a distance of 10–30 m). Samples were analyzed by gamma-ray spectrometry (Quindós et al., 2006) at the Department of Medical Physics, Faculty of Medicine (University of Cantabria, Spain). The <sup>226</sup>Ra concentrations in soils provided the theoretical <sup>222</sup>Rn concentrations, which were estimated according to Eq. (1).

Since  $\varepsilon$ ,  $\rho$  and  $n$  were not measured, the distribution of the theoretical concentration of <sup>222</sup>Rn was estimated by Monte Carlo simulation, assuming that  $\varepsilon$ ,  $\rho$  and  $n$  were normally distributed with the typical values of gravel, sand and clay (Table 1; Yu et al., 1993). The theoretical concentration was interpreted as a geochemical threshold. Hence, in the case that the soil was the only source

Table 1  
Typical  $\varepsilon$ ,  $\rho$  and  $n$  values in soil.

Parameter	Minimum	Mean	Maximum
$\varepsilon$	0.18	0.29	0.40
$\rho$ (kg m <sup>-3</sup> )	1200	1350	1500
$n$	0.01	0.30	0.50

Source: Yu et al. (1993).

of  $^{222}\text{Rn}$ , which was related to the presence of  $^{226}\text{Ra}$ , the measured activity was expected to be similar to the calculated content. If  $^{222}\text{Rn}$  activity was higher than this threshold radon was interpreted to be deep-sourced.

#### 4. Results

To avoid possible interpretation errors originated by the influence of water to the activity of radon in the soil-gas, the geochemical analyses were divided into two types of emissions: (i) La Sima (dry gas vent) and (ii) Jabalón River ( $\text{CO}_2$ -rich gases bubbling in water).

##### 4.1. La Sima

The soil  $\text{CO}_2$  flux ranged from 0.20 to  $5379 \text{ g m}^{-2} \text{ d}^{-1}$ , although inside the morphological depression of La Sima the  $\text{CO}_2$  flux was not measured as the IR detector saturated in a few seconds (i.e.,  $>20,000 \text{ ppm s}^{-1}$  of  $\text{CO}_2$ ). The  $^{222}\text{Rn}$  activity in soil also showed a relatively wide range, between 0.64 and  $138 \text{ kBq m}^{-3}$ . The  $^{220}\text{Rn}$  contents were more constant and ranged between 7.6 and  $51.7 \text{ kBq m}^{-3}$  (Table 2).

Five out of the 23  $\text{CO}_2$  flux measurements at La Sima (Table 2, Fig. 3b) were considered anomalous [higher than  $Q_3 + 1.5 \times (Q_3 - Q_1)$ , being  $Q_1$  and  $Q_3$  the first and the third quartile, respectively], i.e., #13 ( $45 \text{ g m}^{-2} \text{ d}^{-1}$ ), #12 ( $196 \text{ g m}^{-2} \text{ d}^{-1}$ ), #8 ( $566 \text{ g m}^{-2} \text{ d}^{-1}$ ), #24 ( $3322 \text{ g m}^{-2} \text{ d}^{-1}$ ) and #1 ( $5379 \text{ g m}^{-2} \text{ d}^{-1}$ ). These anomalous points were located inside the depression of La Sima (# 1, 8 and 24) or very close (# 12) to it, suggesting that the  $\text{CO}_2$  seepage was well restricted to very small area (red zone in Fig. 3b).

Radium activity ( $^{226}\text{Ra}$ ) was similar inside and outside the emission site, with an average value clustering around  $40 \text{ Bq kg}^{-3}$  (Table 3). From Eq. (1), the theoretical concentration of radon ( $^{222}\text{Rn}$ ), inside and outside the  $\text{CO}_2$  emission, was estimated to be  $55 \text{ kBq m}^{-3}$  (Table 4), with 95% of the data below  $82 \text{ kBq m}^{-3}$  (Table 4).

##### 4.2. Jabalón River

All studied subareas along the Jabalón River were related to spring water discharges ( $T < 30^\circ\text{C}$ ) where a  $\text{CO}_2$ -rich gas phase was gently-to-vigorously bubbling. The  $\text{CO}_2$  fluxes were from  $<0.2$  ( $<\text{D.L.}$ ) to  $1 \times 10^6 \text{ g m}^{-2} \text{ d}^{-1}$ . In some cases the  $\text{CO}_2$  flux was not measured as the IR detector instantly saturated. Occasionally, high  $\text{CO}_2$  fluxes (up to  $1 \text{ t m}^{-2} \text{ d}^{-1}$  or even higher) were measured, although at a short distance, even at the scale of few decimeters, a dramatic decrease was recorded, and the  $\text{CO}_2$  fluxes, typical of biologic respiration ( $0.02\text{--}18 \text{ g m}^{-2} \text{ d}^{-1}$ ; Elío et al., 2013 and reference therein; Fig. 4), were determined. The lowest activity of  $^{222}\text{Rn}$  was  $2.3 \text{ kBq m}^{-3}$  whilst the highest one was  $428 \text{ kBq m}^{-3}$ . The concentrations of  $^{220}\text{Rn}$  ranged from 9.0 to  $44.5 \text{ kBq m}^{-3}$  (Table 2).

The results by gamma-ray spectrometry (Table 3) showed that there was a difference in the  $^{226}\text{Ra}$  concentration between the sites close to the leaking points (#41 and #45) and away from them (#30, #42, #A and #B). While near the main  $\text{CO}_2$ -rich sources the  $^{226}\text{Ra}$  concentration was approximately  $70 \text{ Bq kg}^{-1}$ , in the distal zones its content abruptly decreased down to  $30 \text{ Bq kg}^{-1}$ . The difference in radium concentration produced two theoretical  $^{222}\text{Rn}$  activities for the soil gas due to the presence of  $^{226}\text{Ra}$  in the Jabalón River area. The  $^{222}\text{Rn}$  activity for those soil gas located far from the water springs was around  $40 \text{ kBq m}^{-3}$ , with 95% of the data below  $60 \text{ kBq m}^{-3}$ . This value increased up to  $95 \text{ kBq m}^{-3}$ , with 95% of the data below  $140 \text{ kBq m}^{-3}$ , near the water springs (Table 4).

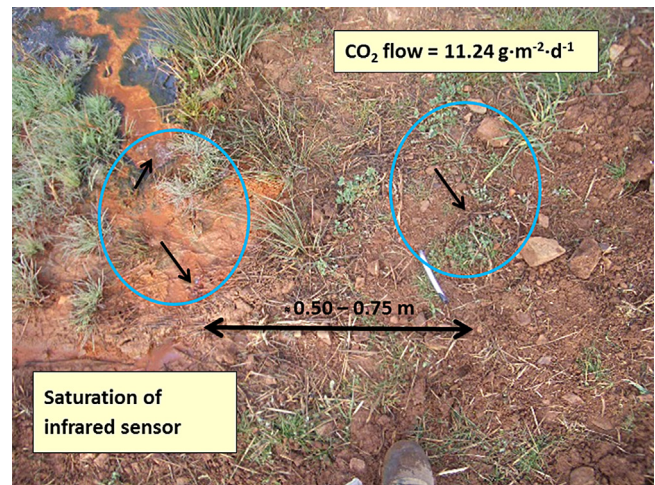


Fig. 4. Example of very high  $\text{CO}_2$  flow through very small spots. To the left, the IR detector saturated in a few seconds; a few centimeters to the right, the  $\text{CO}_2$  soil flux showed values, which can be related to a background emission, i.e., biological activity.

#### 5. Discussion

##### 5.1. La Sima

###### 5.1.1. Theoretical $^{222}\text{Rn}$ concentration in soil-gas

At La Sima, most  $^{222}\text{Rn}$  measurements were between 0.6 and  $37.2 \text{ kBq m}^{-3}$ , i.e., slightly lower than the theoretical estimation (approximately  $55 \text{ kBq m}^{-3}$ ; Table 4). As previously mentioned, the lack of a developed soil cover partly prevented the radon measurement, which was made at the depth of 0.15–0.20 cm, where the influence of the atmospheric parameters can significantly affect the radon concentrations. However, despite the discrepancy between the theoretical and measured values and the uncertainty of the field measurements (below 10–15%) and the theoretical estimations, it is reasonable to assume that the threshold in this zone was of  $45\text{--}60 \text{ kBq m}^{-3}$ . Such high concentrations cannot be explained with the presence of  $^{226}\text{Ra}$  in the soil and consequently, a deep Rn source is required. This value was exceeded in four points (#12:  $63 \text{ kBq m}^{-3}$ ; #1:  $117 \text{ kBq m}^{-3}$ ; #8:  $118 \text{ kBq m}^{-3}$  and #24:  $138 \text{ kBq m}^{-3}$ ).

###### 5.1.2. Correlation between $\text{CO}_2$ flux and radon ( $^{222}\text{Rn}\text{--}^{220}\text{Rn}$ ) activity in soil-gas

Setting aside #13, which had a  $\text{CO}_2$  flux value of  $45 \text{ g m}^{-2} \text{ d}^{-1}$ , four anomalous data were measured at La Sima, #12 ( $196 \text{ g m}^{-2} \text{ d}^{-1}$ ), #8 ( $566 \text{ g m}^{-2} \text{ d}^{-1}$ ), #24 ( $3322 \text{ g m}^{-2} \text{ d}^{-1}$ ) and #1 ( $5379 \text{ g m}^{-2} \text{ d}^{-1}$ ), likely associated with the occurrence of a deep-seated flow that affects the soil degassing in this area. When comparing the  $\text{CO}_2$  flux and the  $^{222}\text{Rn}$  activity data, we observed that the higher the  $\text{CO}_2$  flux the higher the Rn activities (#1, #24, #8 and #12; Fig. 5a). These sites are those whose  $^{222}\text{Rn}$  concentrations cannot be explained without invoking a deep radon source. Conversely, where low  $\text{CO}_2$  fluxes were measured the  $^{222}\text{Rn}$  values can be associated with the presence of  $^{226}\text{Ra}$  in the soil.

The  $^{220}\text{Rn}$  concentrations are inversely correlated with the  $\text{CO}_2$  flux values (Fig. 5b). The relatively high  $^{222}\text{Rn}/^{220}\text{Rn}$  ratios (up to 20; Fig. 5c) are likely associated with a deep origin of radon. This is also supported by the  $\delta^{13}\text{C}\text{--CO}_2$  and  $^3\text{He}/^4\text{He}$  isotopic values, which suggest a deep (mantle) root for the CCVF gas discharges (Pérez et al., 1996; Vaselli et al., 2013).

The relationship between the highest  $\text{CO}_2$  fluxes and  $^{222}\text{Rn}$  concentrations is well illustrated when plotting the W–E oriented

**Table 2**Soil CO<sub>2</sub> gas flux (in g m<sup>-2</sup> d<sup>-1</sup>) and <sup>222</sup>Rn and <sup>220</sup>Rn (in kBq m<sup>-3</sup>) measurements. Coordinates are in UTM-WGS84 projection, zone 30N.

Site	Data	Sample	Est	North	CO <sub>2</sub> flux (g m <sup>-2</sup> d <sup>-1</sup> )	<sup>222</sup> Rn (kBq m <sup>-3</sup> )	<sup>220</sup> Rn (kBq m <sup>-3</sup> )	Observation
La Sima	June 10	1	434,419	4,297,245	5379	116.8	7.6	Soil-gas
La Sima	June 10	2	434,413	4,297,238	0.4	0.64		Soil-gas
La Sima	June 10	3	434,408	4,297,236	0.3	1.2		Soil-gas
La Sima	June 10	4	434,428	4,297,243	4.3	1.7		Soil-gas
La Sima	June 10	5	434,434	4,297,234	2.1	6.6		Soil-gas
La Sima	June 10	6	434,411	4,297,252	1.3	9.7		Soil-gas
La Sima	June 10	7	434,408	4,297,263	1.5	5.7		Soil-gas
La Sima	August 10	8	434,418	4,297,242	567	118.4	13.3	Soil-gas
La Sima	August 10	9	434,423	4,297,242	5.4	3.1	31.1	Soil-gas
La Sima	August 10	10	434,443	4,297,242	0.2	11.1	34.0	Soil-gas
La Sima	August 10	11	434,453	4,297,242	0.6	6.6	26.7	Soil-gas
La Sima	August 10	12	434,415	4,297,242	196	63.2	10.4	Soil-gas
La Sima	August 10	13	434,404	4,297,243	45	10.5		Soil-gas
La Sima	August 10	14	434,394	4,297,243	7.1	10.2	23.0	Soil-gas
La Sima	August 10	15	434,385	4,297,245	0.2	13.0	32.7	Soil-gas
La Sima	August 10	16	434,375	4,297,243	0.5	11.5	51.7	Soil-gas
Fontecha	May 11	17	428,709	4,295,194	7.3	58.0		Soil-gas
Fontecha	May 11	18	428,701	4,295,186	192	428.0		Soil-gas
Fontecha	May 11	19	428,691	4,295,174	12.3	3.0		Soil-gas
Fontecha	May 11	20	428,687	4,295,192	17.9	39.7		Soil-gas
Fontecha	May 11	21	428,715	4,295,175	15.8	2.3		Soil-gas
La Sima	May 11	22	434,440	4,297,260	7.6	9.8		Soil-gas
La Sima	May 11	23	434,440	4,297,240	4.2	3.0		Soil-gas
La Sima	May 11	24	434,420	4,297,240	3322	138.0		Soil-gas
La Sima	May 11	25	434,400	4,297,240	5.5	37.2		Soil-gas
La Sima	May 11	26	434,410	4,297,230	5.7	16.7		Soil-gas
La Sima	May 11	27	434,403	4,297,222	18.0	34.0		Soil-gas
La Sima	May 11	28	434,409	4,297,249	3.1	11.5		Soil-gas
Jabalón	September 11	29	429,130	4,294,625	1.4	32.4		Soil-gas
Jabalón	September 11	30	429,170	4,294,625	44	83.1	27.0	Soil-gas
Jabalón	September 11	31	429,130	4,294,605	5.3	29.1	9.0	Soil-gas
Jabalón	September 11	32	429,190	4,294,605	21.9	28.2		Soil-gas
Jabalón	September 11	33	429,210	4,294,605	12.3	24.5	28.5	Soil-gas
Jabalón	September 11	34	429,110	4,294,585	<0.2	25.6	15.5	Soil-gas
Jabalón	September 11	35	429,150	4,294,585	5.1	12.2	17.8	Soil-gas
Jabalón	September 11	36	429,170	4,294,585	11.6	47.0	10.5	Soil-gas
Jabalón	September 11	37	429,210	4,294,585	9.6	49.7		Soil-gas
Jabalón	September 11	38	429,090	4,294,565	<0.2	18.6	11.2	Soil-gas
Jabalón	September 11	39	429,130	4,294,565	2.9	22.7	12.3	Soil-gas
Jabalón	September 11	40	429,150	4,294,565	25.7	34.2	30.8	Soil-gas
Jabalón	September 11	41	429,170	4,294,565	45	182.5	35.2	Soil-gas
Jabalón	September 11	42	429,190	4,294,565	102	91.1	31.6	Soil-gas
Jabalón	September 11	43	429,090	4,294,545	<0.2	24.2	19.4	Soil-gas
Jabalón	September 11	44	429,150	4,294,545	5.7	13.2	24.0	Soil-gas
Jabalón	September 11	45	429,170	4,294,545	141	183.5	18.4	Soil-gas
Jabalón	September 11	46	429,150	4,294,525	5.2	7.8		Soil-gas
Jabalón	September 11	47	429,170	4,294,525	0.5	17.3	13.9	Soil-gas
NH-1	February 12	48.5	429,137.5	4,294,759	913,887	118.0		Bubbling pool
NH-1	February 12	48	429,137	4,294,759	523,140	130.0		Bubbling pool
NH-1	February 12	49	429,140	4,294,759	4.6	171.0	11.5	Soil-gas
NH-1	February 12	50	429,143	4,294,758	7.1	56.1		Soil-gas
NH-1	February 12	51	429,146	4,294,758	8.9	37.8		Soil-gas
NH-1	February 12	52	429,140	4,294,767	0.3	39.7	44.5	Soil-gas
NH-1	February 12	53	429,140	4,294,763	1.6	60.6	23.5	Soil-gas
NH-1	February 12	54	429,140	4,294,755	0.9	55.6	39.5	Soil-gas
NH-1	February 12	55	429,140	4,294,751	7.4	42.2	38.2	Soil-gas
Fontecha	February 12	56	429,184	4,294,614	3.2	23.2		Soil-gas
Fontecha	February 12	57	429,184	4,294,606	9.0	8.9		Soil-gas
Fontecha	February 12	58	429,184	4,294,602	1.4	59.0		Soil-gas
Fontecha	February 12	59	429,184	4,294,594	241	15.6	10.8	Soil-gas
Fontecha	February 12	60	428,700	4,295,187	1.2	75.1		Soil-gas
Fontecha	February 12	61	428,698	4,295,183	8.6	82.6		Soil-gas
Fontecha	February 12	62	428,701	4,295,180	6.6	421.9	27.9	Soil-gas
Fontecha	February 12	63	428,704	4,295,184	8.1	154.0		Soil-gas
Fontecha	February 12	64	428,700	4,295,184	7.1	218.0		Soil-gas
Fontecha	February 12	65	428,703	4,295,184	918,290	129.0		Bubbling pool
Fontecha	February 12	66	428,703	4,295,185	548,485	92.4		Bubbling pool
Fontecha	February 12	67	428,717	4,295,171	35,821	54.1		Bubbling pool
NH-2	February 12	68	427,578	4,295,993	684	13.5		Bubbling pool
NH-2	February 12	69	427,584	4,296,004	180	15.5		Bubbling pool

**Table 3**  
Results of gamma-ray spectrometry in soil samples.

Site	Sample	$^{238}\text{U}$ ( $^{234}\text{Th}$ )	$^{226}\text{Ra}$ ( $^{214}\text{Bi}$ )	$^{232}\text{Th}$ ( $^{228}\text{Ac}$ )	$^{40}\text{K}$	$^{137}\text{Cs}$
La Sima	Outside	$79.0 \pm 10.8$	$40.2 \pm 1.5$	$70.4 \pm 4.5$	$775.5 \pm 32.2$	<D.L. (1.2)
	Inside	$86.3 \pm 11.5$	$40.9 \pm 1.6$	$117.3 \pm 7.2$	$694.8 \pm 29.9$	$31.6 \pm 1.0$
Jabalón River	30	$26.2 \pm 3.9$	$34.0 \pm 1.4$	$64.5 \pm 4.4$	$984.9 \pm 40.2$	<D.L. (1.4)
	A	<D.L. (25.4)	$23.0 \pm 1.2$	$79.2 \pm 5.0$	$776.3 \pm 33.0$	<D.L. (1.7)
	42	$39.5 \pm 8.5$	$26.5 \pm 1.3$	$71.1 \pm 4.9$	$871.8 \pm 35.6$	<D.L. (1.8)
	41	$137.8 \pm 14.9$	$76.0 \pm 2.2$	$72.9 \pm 4.9$	$962.3 \pm 39.7$	<D.L. (1.8)
	45	<D.L. (27.6)	$69.5 \pm 2.1$	$71.0 \pm 4.7$	$935.4 \pm 39.2$	<D.L. (1.8)
	B	<D.L. (24.9)	$35.4 \pm 1.4$	$57.6 \pm 3.9$	$742.6 \pm 30.9$	<D.L. (1.6)

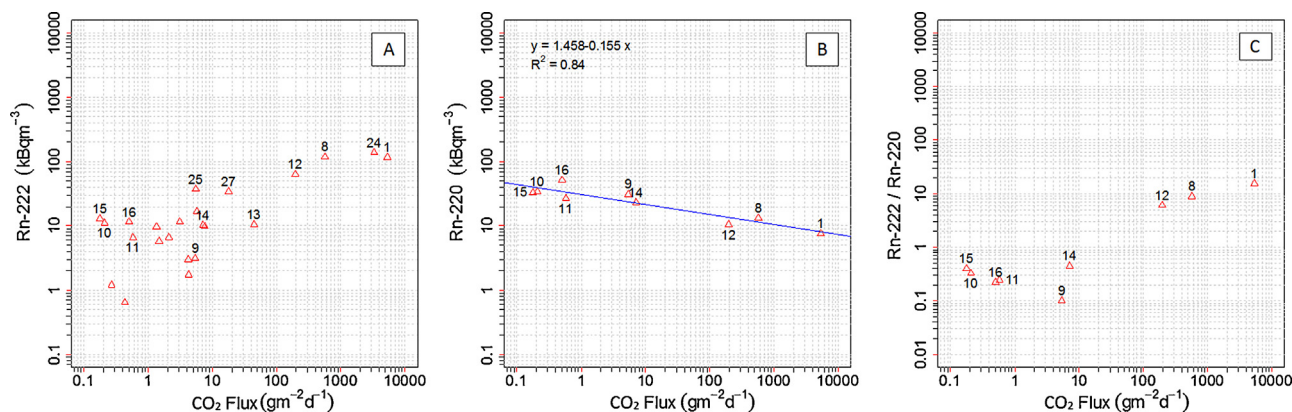
Concentrations are in  $\text{Bq kg}^{-1}$ . Points A and B not shown in Fig. 3.

**Table 4**  
Theoretical concentrations of  $^{222}\text{Rn}$  (in  $\text{Bq m}^{-3}$ ) in soil gas as calculated by  $^{226}\text{Ra}$  decay in the soil.

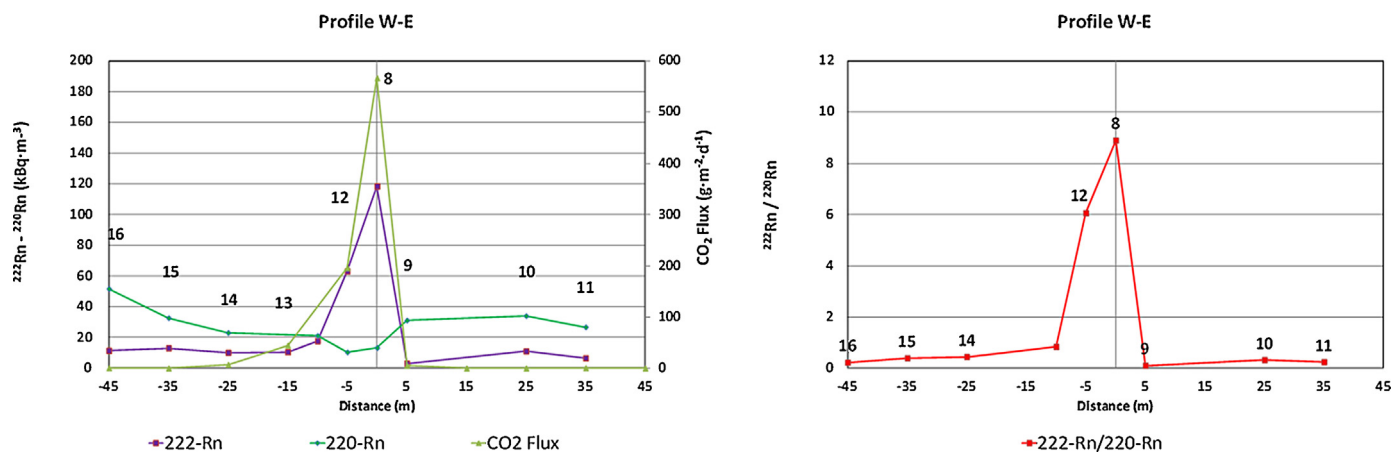
Site	$^{226}\text{Ra}$ ( $\text{Bq kg}^{-1}$ )	$^{222}\text{Rn}$ ( $\text{kBq m}^{-3}$ )						
		Min.	$Q_1$	Median	Mean	$Q_3$	95th percentile	Max.
La Sima	40	23	44	51	54	61	82	452
Jabalón River (away bubbling)	30	17	33	38	41	46	61	339
Jabalón River (near bubbling)	70	40	77	90	95	107	143	791

profile (Fig. 6) as a function of the distance from La Sima gas vent. Another relevant result was that at #8 (distance 0 m) the highest concentration of  $^{222}\text{Rn}$  was recorded while that of  $^{220}\text{Rn}$  was among the lowest measured values. This might be explained with the dilution of a  $^{220}\text{Rn}$ -free deep gas as it rises to the surface. Furthermore, the amount of  $^{220}\text{Rn}$  generated at the surface was promptly released

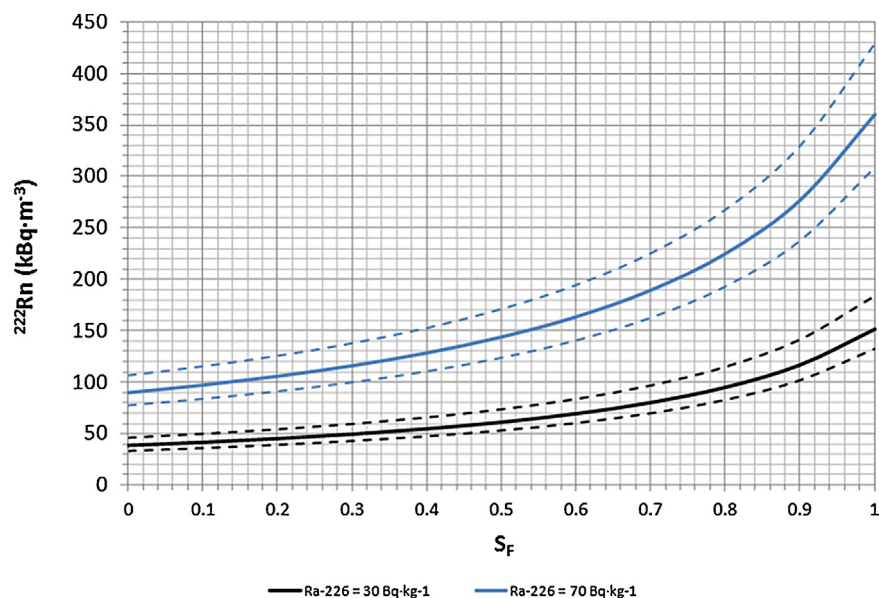
once produced because of the elevated  $\text{CO}_2$ -rich gas flux and, consequently, the recorded data were smaller than those really produced. The highest  $^{222}\text{Rn}/^{220}\text{Rn}$  ratios were at #8 (La Sima) and #12, suggesting a predominance of the highest half-life isotope ( $^{222}\text{Rn}$ ). These results demonstrate that  $\text{CO}_2$  acts as a carrier gas for radon in a regime of advective transport.



**Fig. 5.** Relationship between  $\text{CO}_2$  flux and  $^{222}\text{Rn}/^{220}\text{Rn}$  in the La Sima zone (Table 2, Fig. 3).



**Fig. 6.** Spatial correlation between  $^{222}\text{Rn}/^{220}\text{Rn}$  and  $\text{CO}_2$  flux in the La Sima zone (Table 2, Fig. 3). Horizontal axis is the distance (m) from the sample point to the center of the  $\text{CO}_2$  leak.



**Fig. 7.** Equilibrium  $^{222}\text{Rn}$  activity of the soil-gas in the area of Jabalón River versus  $^{226}\text{Ra}$  activity. Black and blue lines represent a radium activity of  $30\text{ Bq}\cdot\text{kg}^{-1}$  and  $70\text{ Bq}\cdot\text{kg}^{-1}$ , respectively. Continuous lines are the median of theoretical radon concentration and dotted lines are referred to the first ( $Q_1$ ) and the third ( $Q_3$ ) quantile (Table 4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 5.2. Jabalón River

### 5.2.1. Theoretical $^{222}\text{Rn}$ activity in soil-gas

The increase of  $^{226}\text{Ra}$  activity between the sites located away from the thermal waters ( $30\text{ Bq}\cdot\text{kg}^{-1}$ ) and those close to them ( $70\text{ Bq}\cdot\text{kg}^{-1}$ ) could be produced by a process of transport of dissolved U and Ra and their precipitation at the spring. Thus, two theoretical  $^{222}\text{Rn}$  concentrations were carried out, although in this case the influence of soil water saturation ( $S_F$ ; Eq. (2)) are to be taken into account for the interpretation of the gas  $^{222}\text{Rn}$  origin. The radon activity equilibrium of the soil gas is plotted in Fig. 7. In order to evaluate the influence on the radon measurements produced by the water contained in the soil, a distinction between the Ra concentrations was made. In those points located far from the water springs, the soil is expected to be relatively dry or slightly moist ( $S_F \approx 0.1\text{--}0.5$ ). This would imply that the increase of  $^{222}\text{Rn}$  from the water contained in the soil should not exceed more than 50% of the theoretical concentration for dry soil ( $\approx 70\text{ kBq}\cdot\text{m}^{-3}$ ; black lines in Fig. 7). Thus, the concentration of Ra in the soil does not account for the  $^{222}\text{Rn}$  concentrations in soil gases when they are much higher than  $40\text{--}70\text{ kBq}\cdot\text{m}^{-3}$ . Close to the water springs, where soils are expected to be relatively moist ( $S_F \approx 0.5\text{--}0.8$ ), the radon concentration can increase of 50–150% with respect to dry conditions; therefore the theoretical activity of  $^{222}\text{Rn}$  could be around  $120\text{ kBq}\cdot\text{m}^{-3}$  (black lines in Fig. 7). If the transport of radium is driven by ground water, the  $^{222}\text{Rn}$  content is expected to increase up to  $270\text{ kBq}\cdot\text{m}^{-3}$  (blue lines in Fig. 7).

In these areas, the points located at a distance from the water springs were commonly characterized by radon activity values less than  $70\text{ kBq}\cdot\text{m}^{-3}$ , which are in agreement with those calculated with the presence of  $^{226}\text{Ra}$  in the relatively dry soil, e.g., #17, #20, #32 and #35 (Table 2; Fig. 3). However, this threshold was exceeded at two points: #30 ( $83\text{ kBq}\cdot\text{m}^{-3}$ ) and #42 ( $91\text{ kBq}\cdot\text{m}^{-3}$ ), which are unlikely values for dry/moderately moist soils. This would imply a more efficient advective transport and/or a deep gas source.

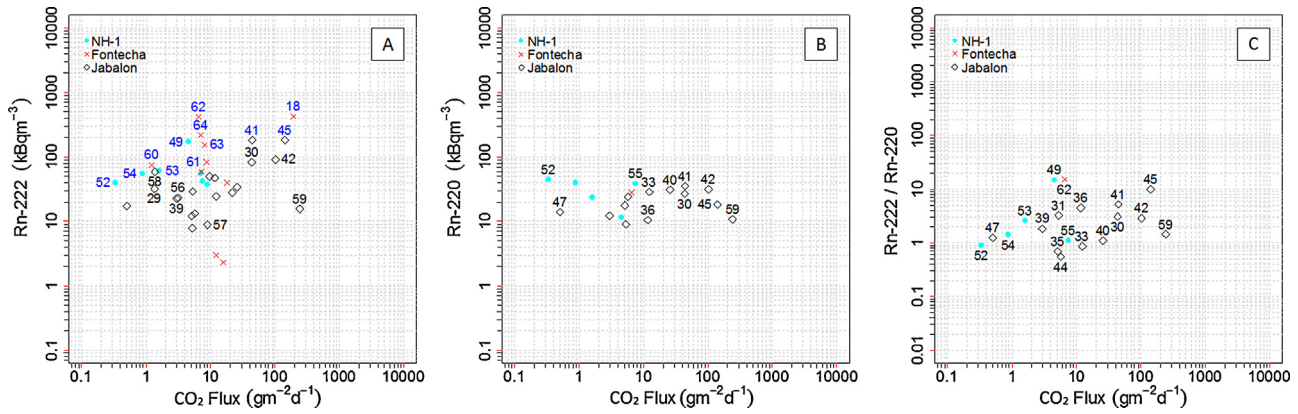
In proximity to the water springs (#18, #41, #45, #49–55, #60–64; Table 2 and Fig. 3), the  $^{222}\text{Rn}$  activity was between 38 (#51) and  $428\text{ kBq}\cdot\text{m}^{-3}$  (#18). As previously described, the radon activity can increase to  $120\text{ kBq}\cdot\text{m}^{-3}$  due to presence of water in the soil. Actually, some high  $^{222}\text{Rn}$  values (from 56 to  $83\text{ kBq}\cdot\text{m}^{-3}$ ,

e.g., #50, #53, #60 and #61) could be related to the increase in water saturation. Nevertheless, very high values were also measured at #63 ( $154\text{ kBq}\cdot\text{m}^{-3}$ ), #49 ( $171\text{ kBq}\cdot\text{m}^{-3}$ ), #41 ( $182\text{ kBq}\cdot\text{m}^{-3}$ ), #45 ( $183\text{ kBq}\cdot\text{m}^{-3}$ ), #64 ( $218\text{ kBq}\cdot\text{m}^{-3}$ ), #62 ( $421\text{ kBq}\cdot\text{m}^{-3}$ ) and #18 ( $428\text{ kBq}\cdot\text{m}^{-3}$ ). Radon activity at #63, #49, #41, #45 and #64 can be attributed to soil moisture when the radium content are up to  $70\text{ Bq}\cdot\text{kg}^{-1}$  (blue line in Fig. 7). However, radon activities higher than  $270\text{ kBq}\cdot\text{m}^{-3}$  are unlikely when increases in radium content and soil moisture are considered. Consequently, also in this case, the contribution by a deep source can be invoked (e.g., #62 and #18). We may speculate that in addition to the increase of radon concentration by water saturation in the soil, an excess of  $^{222}\text{Rn}$  is likely occurring and favored by the presence of parent radionuclides (U and Ra) dissolved in the ground water system.

### 5.2.2. Correlation between $\text{CO}_2$ flux and radon ( $^{222}\text{Rn}\text{--}^{220}\text{Rn}$ ) activity in soil-gas

At Jabalón River the highest activities of  $^{222}\text{Rn}$  and  $\text{CO}_2$  fluxes are not apparently closely correlated (Fig. 8a). Nevertheless,  $^{222}\text{Rn}$  contents higher than those estimated by the presence of  $^{226}\text{Ra}$  in the soil were detected in sites close to the thermal springs (e.g., #18 and #62) and away from them (e.g., #30 and #42), suggesting the presence of a deep  $^{222}\text{Rn}$  source. However,  $^{222}\text{Rn}$  activity near the spring waters (blue-colored numbers in Fig. 8a) was always higher than those measured in the distal points (black-colored numbers in Fig. 8a), although  $\text{CO}_2$  fluxes were relatively low (e.g., #62 and #64 versus #30, #42 or #59). An inverse correlation between  $^{220}\text{Rn}$  and  $\text{CO}_2$  was not observed (Fig. 8b). On the other hand,  $^{220}\text{Rn}$  had a small increase (Fig. 9), which could be interpreted in terms of shallow origin of radon, at least more superficial than that of La Sima. This could likely be accounted for the transport and precipitation of U and Ra. In relation to the  $^{222}\text{Rn}/^{220}\text{Rn}$  ratio (Fig. 8c) there was not a clear increase with the  $\text{CO}_2$  flux in contrast to what observed at La Sima. Despite the relatively high isotopic ratio (e.g., #49, #62, #45), no correlation with the  $\text{CO}_2$  flux was highlighted since in some cases the  $^{222}\text{Rn}/^{220}\text{Rn}$  ratio decreased (e.g., #59 vs #36 or #49). Similar features can be produced by either deep or shallow origin for radon and by the soil water saturation.

These results suggest that the increase of radon activity in the Jabalón River with respect to the background is likely related to two

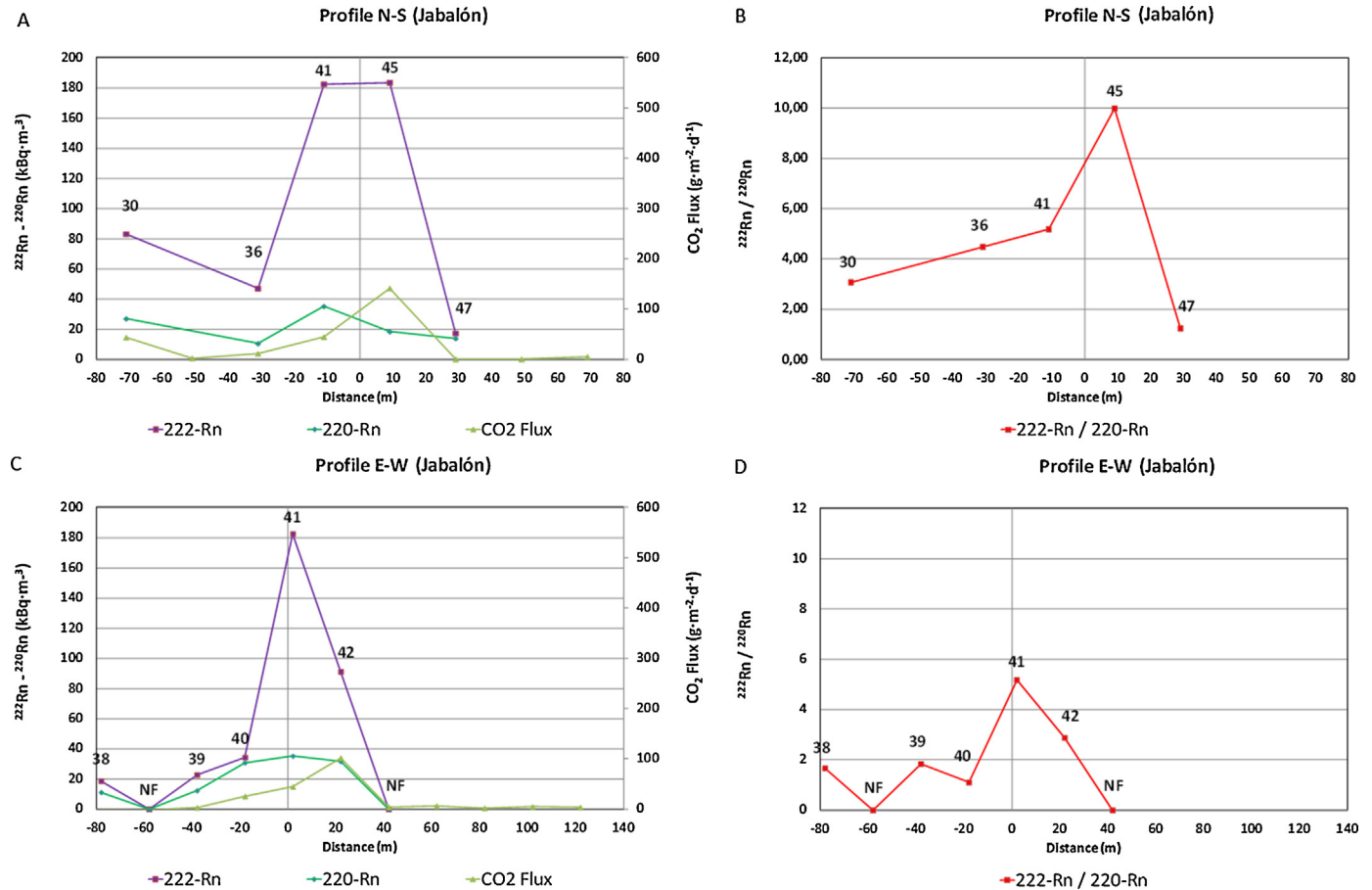


**Fig. 8.** Relationship between CO<sub>2</sub> flux and <sup>222</sup>Rn/<sup>220</sup>Rn ratios in the Jabalón River (blue texts in A indicate the points near water spring, Table 2, Fig. 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contributions: (i) a deep-seated source carried by CO<sub>2</sub>, supported by the higher concentrations of <sup>222</sup>Rn with respect to those theoretically estimated by <sup>226</sup>Ra in soil, and (ii) a source related to the decay of parent radionuclides (U–Ra), dissolved and transported by groundwater system as supported by the highest radium activities when approaching the spring water discharges.

The profiles of the CO<sub>2</sub> flux as a function of the distance with respect to the CO<sub>2</sub>-rich gas emission sites and those of the Rn isotopic concentration and <sup>222</sup>Rn/<sup>220</sup>Rn ratios for the Jabalón River are plotted in Figs. 9 and 10. In Fig. 9a and b (profile N–S for Jabalon, Fig. 3c, Table 2), the highest value of CO<sub>2</sub> flux (#45, 141 g m<sup>-2</sup> d<sup>-1</sup>) is

coupled with that of <sup>222</sup>Rn (184 kBq m<sup>-3</sup>), although at #41 the CO<sub>2</sub> flux sharply decreases down to 45 g m<sup>-2</sup> d<sup>-1</sup> while the Rn activity was found to be constant (182 kBq m<sup>-3</sup>). Moving to the north of the CO<sub>2</sub>-bearing spring (#36) both activity of <sup>222</sup>Rn and CO<sub>2</sub> flux (47 kBq m<sup>-3</sup> and 12 g m<sup>-2</sup> d<sup>-1</sup>, respectively) decrease. Then, the <sup>222</sup>Rn activity achieves a secondary peak (#30: 83 kBq m<sup>-3</sup>), which is not related to any increase of <sup>226</sup>Ra in the soil (Table 3), while the CO<sub>2</sub> flux increases (44 g m<sup>-2</sup> d<sup>-1</sup>). In contrast, in the E–W profile (Fig. 9c and d) the highest recorded CO<sub>2</sub> flux (#42; 102 g m<sup>-2</sup> d<sup>-1</sup>) does not match with that of the <sup>222</sup>Rn activity (#41; 182 kBq m<sup>-3</sup>). The activity of <sup>220</sup>Rn in both profiles shows an increase associated



**Fig. 9.** Spatial correlation between <sup>222</sup>Rn/<sup>220</sup>Rn and CO<sub>2</sub> flux along the Jabalón River (Table 2, Fig. 3; NF: no flow, soil-gas could not be sampled due to the extremely low permeability). Horizontal axis is the distance (m) from the sample point to the center of the CO<sub>2</sub> leak.

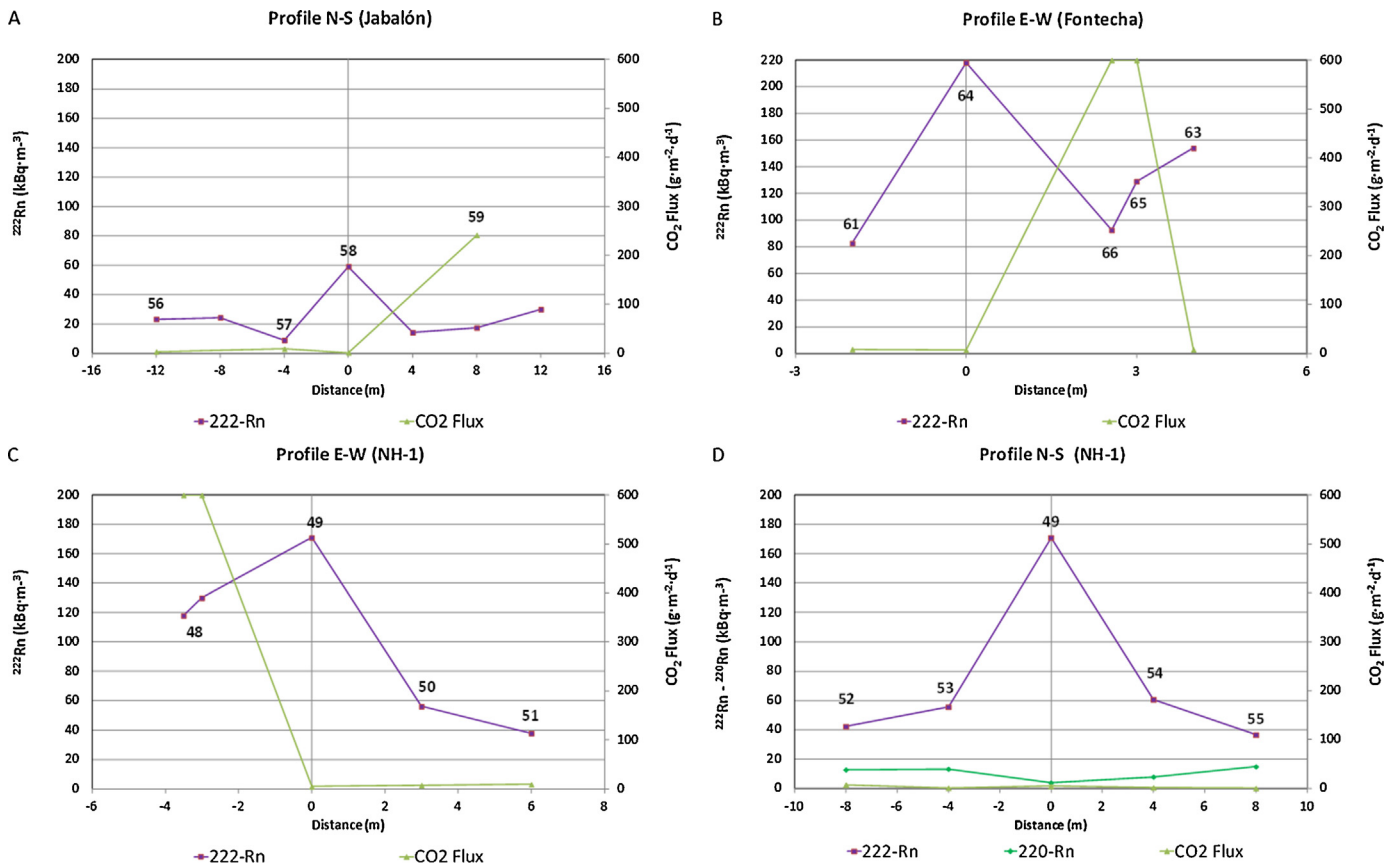


Fig. 10. Spatial correlation between  $^{222}\text{Rn}/^{220}\text{Rn}$  and  $\text{CO}_2$  flux along the Jabalón River (Table 2, Fig. 3). Horizontal axis is the distance (m) from the sample point to the center of the  $\text{CO}_2$  leak.

with the  $\text{CO}_2$  flux, although the highest  $^{220}\text{Rn}$  concentration (#41) does not completely match with respect to the site where the highest  $\text{CO}_2$  flux (#45 in profile N-S and #42 in profile E-W in Fig. 9a and b) is found.

In Fig. 10, the lack of correlation between the highest values of  $^{222}\text{Rn}$  concentration and  $\text{CO}_2$  flux for the same spot is more evident. Nevertheless, despite the fact that a linear correlation between  $\text{CO}_2$  and  $^{222}\text{Rn}$  is not detected, there is a direct influence in radon ( $^{222}\text{Rn}$ ) activity associated with the  $\text{CO}_2$  leakage. This is supported by the presence of  $^{222}\text{Rn}$  concentrations near the seepage zones much higher than those calculated by considering the Ra concentrations in the soil or the increase related to soil water saturation.

In the springs with bubbling  $\text{CO}_2$  (#48, #65 to #68; Table 2, Fig. 11) the  $^{222}\text{Rn}$  activity is lower with respect to that measured in the surrounding sites. This discrepancy can likely be due to the different sampling methods since in these spots radon measurements were carried out directly in the airflow, with a collector on the bubbling gas phase due to the presence of water. Consequently, these measurements can be related to the amount of  $^{222}\text{Rn}$  carried by  $\text{CO}_2$  and not to the content of U and Ra in the thermal waters or the presence of soil water saturation ( $S_F$ ). Nevertheless, in the soil-gas near the degassing sites all effects could be detected and therefore the radon concentration in the gas is higher. The positive linear correlation between the  $\text{CO}_2$  flux and concentration of  $^{222}\text{Rn}$  in the gas vent is supporting this hypothesis (Fig. 11).

Another significant observation was that at La Sima the  $\text{CO}_2$  fluxes in the  $\text{CO}_2$ -rich gas emission sites were higher than those recorded along the Jabalón River, with the exception of the water-degassing points, whereas the  $^{222}\text{Rn}$  activities showed an opposite behavior. At La Sima the highest  $\text{CO}_2$  fluxes were from 3000 to 5000 g·m<sup>-2</sup> d<sup>-1</sup> and the  $^{222}\text{Rn}$  concentrations were clustering

around 120 kBq m<sup>-3</sup> (Table 1; #1, #8 a#24). Conversely, at Jabalón River the  $\text{CO}_2$  flux was 200 g·m<sup>-2</sup> d<sup>-1</sup> (e.g., #18 and #59) and the  $^{222}\text{Rn}$  concentration was around 400 kBq m<sup>-3</sup> (e.g., #18 and #62). This would support the hypothesis that along the Jabalón River a radon source derived from dissolved U and Ra adds to that

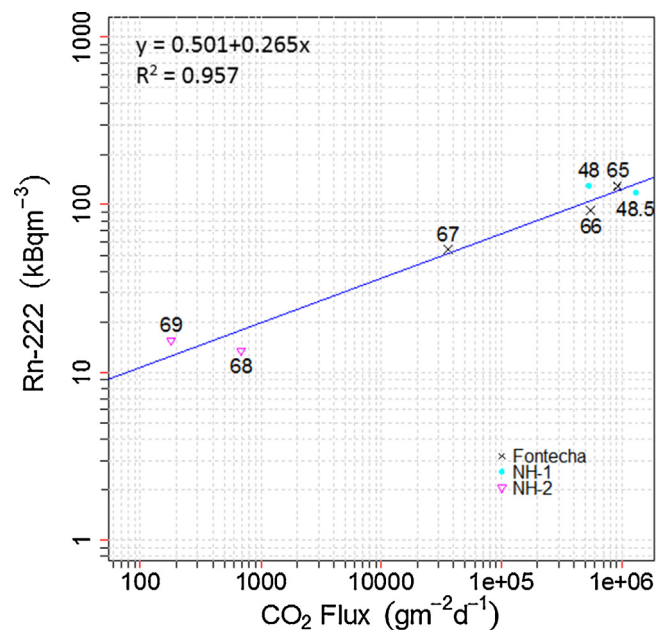


Fig. 11. Correlation between  $\text{CO}_2$  flux and  $^{222}\text{Rn}$  in the degassing pools (Table 2, Fig. 3).

transported by CO<sub>2</sub>. While at La Sima the only cause that leads to the increase in radon is the CO<sub>2</sub> flux, in the Jabalon River contributions from soil water, U and Ra and CO<sub>2</sub> flux are to be added. Thus, this would explain why at La Sima we measured high CO<sub>2</sub> fluxes while the <sup>222</sup>Rn activities were relatively lower than that in the Jabalon River area.

### 5.3. Implication for monitoring CO<sub>2</sub> storage sites

The CO<sub>2</sub>-rich emissions at CCFV are mainly associated with fracture systems and the gas discharges are regarded as point-source seepage, being occasionally characterized by relatively high flow: 1 t m<sup>-2</sup> d<sup>-1</sup> or even higher. In the vicinity of these sites, the CO<sub>2</sub> fluxes approach values, which are typical of soil respiration. In the perspective of assessing gas leakages in areas selected for geological carbon storage, the observation of the point-source seepage reveals that the detection of leakage sites can pose serious difficulties given the large area potentially affected by the leakage of injected CO<sub>2</sub> (hundreds km<sup>2</sup>). It is worth mentioning that the amount of CO<sub>2</sub> emitted from these points can be of the order of magnitude of the maximum leakage rate considered acceptable (0.1% of the total amount in storage per year; Van der Zwaan and Smekens, 2006) for a commercial storage project (i.e., approximately 1 Mt year<sup>-1</sup>; such as in Snohvit: 0.73 Mt year<sup>-1</sup>, Sleipner: 0.98 Mt year<sup>-1</sup> and In Salah: 1.28 Mt year<sup>-1</sup>; Michael et al., 2010). Thus, conventional approaches might not be able to detect small-scale emissions.

In this regards, in the framework of CCS projects significant variations in terms of soil diffuse CO<sub>2</sub> flux may be occurring at the scale of few meters or even centimeters and CO<sub>2</sub> leakages cannot be detected until clear evidences (e.g., impacts on the vegetation, newly formed bubbling sites) are visible in the field, even when small sample grids, e.g., 10–20 m (e.g., Elío et al., 2013 and references therein) are considered. Besides, natural analogs (e.g., geothermal or volcanic areas) have gas fluxes, which are by far higher than those expected for a sequestration project. Furthermore, in the case of seepages small geographic changes and moderate seasonal changes in the CO<sub>2</sub> fluxes are expected to be detected with respect to the background levels. This makes the reconnaissance of seepages real challenging.

The application of other cost-effective monitoring/detection techniques able to cover larger areas, such as Eddy covariance, open-path laser and remote sensing, need to be improved and properly evaluated for their applicability to CCS projects (e.g., Klusman, 2011; Lewicki et al., 2009; Ortega et al., 2014). Long-term continuous soil gas surveys can help to identify leakages (e.g., Schlömer et al., 2014), although these might also be undetectable when occurring in very localized and small areas.

Concerning radon measurements in the CCFV areas, an increase in the <sup>222</sup>Rn soil-gas concentration was detected and correlated to the CO<sub>2</sub> flux. The influence of this <sup>222</sup>Rn anomaly zone, though small, seems to be of larger extent with respect to that of CO<sub>2</sub>. Consequently, radon isotopes can be considered as good tracers to discriminate leakage areas, providing useful information about the (biological or deep-seated) origin of CO<sub>2</sub>. Radon isotope measurements can overcome the limitations of others geochemical methods, which are commonly used to interpret the origin of the soil gases, e.g., δ<sup>13</sup>C–CO<sub>2</sub> or helium isotope ratios. Another advantage of radon measurements is that to avoid “false positives”. Radon activity in soil-gas is indeed related to lithological and geostructural (faults and fractures) features. This means that when an increase “deep” CO<sub>2</sub> fluxes with respect to the background values occurs, radon activity is also expected to increment. Conversely, if CO<sub>2</sub> fluxes increase in response of an enhanced biological activity, radon activity should not suffer any particular variation.

At CCFV, the <sup>222</sup>Rn activity in the soil gas was occasionally as high as 430 kBq m<sup>-3</sup>, i.e., much higher than the threshold value

(>50 kBq m<sup>-3</sup>; Cothorn and Smith, 1987) for which a certain site is considered with a high-risk potential. Such high concentrations need to be taken into account when CCS risk assessment plans are to be designed, particularly when CO<sub>2</sub> leakages may affect residential areas and working environments. Consumption of CO<sub>2</sub>-rich waters is also a risk since they may potentially contain high concentrations of dissolved <sup>222</sup>Rn, and U and Ra.

In this study, correlations between <sup>220</sup>Rn concentrations and CO<sub>2</sub> fluxes were not as clear as observed for those of <sup>222</sup>Rn and CO<sub>2</sub>. In the dry gas vent of La Sima, a significant reduction of the <sup>220</sup>Rn concentrations was detected and likely related to an increase in the CO<sub>2</sub> flux. However, in the emission sites associated with water springs <sup>222</sup>Rn and CO<sub>2</sub> were not correlated while a slight increase in <sup>220</sup>Rn concentrations with the CO<sub>2</sub> flux was recorded. This effect is likely due to different source of <sup>222</sup>Rn and <sup>220</sup>Rn isotopes.

## 6. Conclusions

The Campo de Calatrava Volcanic Field is a relevant natural analog where gas leakages in the framework of geological CO<sub>2</sub> storage projects can be investigated. A large number of CO<sub>2</sub>-rich emissions, predominantly associated with fracture/fault systems occur, although they mainly discharge as punctual manifestations. The results suggest a deep origin of CO<sub>2</sub>, in agreement with previous geochemical and isotopic analyses of the gas leaks, which indicate that CO<sub>2</sub> is mantle sourced.

According to our data, the increase of <sup>222</sup>Rn in the soil gases is likely produced by two mechanisms, (i) advective transport where CO<sub>2</sub> acts as carrier gas and (ii) generation at shallow level due to the presence of U and Ra in both thermal waters and soils.

Geochemical surveys of CO<sub>2</sub> flux and radon isotopic measurements are very useful to: (i) define and quantify CO<sub>2</sub> leakages once detected and (ii) monitor the evolution of the leakages and the effectiveness of subsequent remediation activities. These techniques can also be successfully applied to detect diffuse leakages.

## Acknowledgements

We wish to thank C. Jenkins and Nunzia Voltattorni and an anonymous reviewer who greatly improved an early version of the manuscript. This work was funded by the Ciudad de la Energía Foundation (CIUDEN), through the ALM-08-006 contract, and co-financed by the European Union (European Energy Programme for Recovery). The sole responsibility of this publication lies with the authors. The European Union is not responsible for any use that may be made of the information contained therein.

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