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# The “Escarot” gas seep, French Massif Central: CO<sub>2</sub> discharge from a quiescent volcanic system – Characterization and quantification of gas emissions

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1 The “Escarot” gas seep, French Massif Central: CO<sub>2</sub> discharge from a quiescent volcanic  
2 system – Characterization and quantification of gas emissions.

3

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10 **Abstract**

11 Natural CO<sub>2</sub> emissions from the volcanic rocks of the French Massif Central are poorly  
12 constrained. It is of interest better to assess the emission of such non-anthropogenic gases  
13 that may significantly contribute to the global carbon budget. We quantified the CO<sub>2</sub>  
14 emissions to the atmosphere in a small area (0.052 km<sup>2</sup>) located in the Massif Central close  
15 to Lake Pavin, the most recent volcanic edifice in metropolitan France. The specific character  
16 of this area, known as the Escarot mofette, was earlier studied for soil-gas concentrations  
17 only. In June 2017, we used the accumulation chamber method for measuring CO<sub>2</sub> flux and  
18 related O<sub>2</sub> depletion in the gases emitted at the soil/atmosphere interface, resulting in 176  
19 data acquisitions over four days. In addition, 44 soil-gas concentration measurements were  
20 made at selected locations. CO<sub>2</sub> emission rates are estimated at 8,100±1,800 tons/year of  
21 deep-seated CO<sub>2</sub> and at 660±440 tons/year of biologically produced CO<sub>2</sub>. The uncertainty on  
22 these evaluations comes from the high-frequency variability of CO<sub>2</sub> efflux in the more  
23 emissive areas and from the occurrence of heavy precipitation events. Though unexpected,  
24 these events were used for quantifying the decreases in CO<sub>2</sub> efflux, which were as high as  
25 500% over a few hours or even days in some locations. However, repeat acquisitions  
26 performed under more favourable weather conditions showed errors of commonly accepted  
27 amplitude (±15%). The area showed several degassing centres aligned along a NNW-SSE  
28 direction that correlates well with known geological structures, proving the ability of soil-gas  
29 methods to map hidden faults. The whole area is characterized by strong CO<sub>2</sub> enrichment  
30 and related O<sub>2</sub> depletion, but it is nonetheless possible to detect areas influenced by the rise  
31 of deep-seated gases and a few peripheral areas where biological processes dominate (CO<sub>2</sub>  
32 up to 10% vol.). This study of gas emissions in a non-urban area also provides  
33 complementary information that is of use when extrapolated to similar structures in urban

34 areas, where the occurrence of such gas releases, and its potential hazard may be more  
35 difficult to assess.

36 **Highlights**

- 37 - Spatial and geochemical characterizations of a CO<sub>2</sub> gas seep in the French Massif Central.
- 38 - Magmatic CO<sub>2</sub> gas emissions into the atmosphere evaluated at around 8,100 tons/year.
- 39 - CO<sub>2</sub> gas flux is successfully used for mapping hidden faults.
- 40 - Decrease in gas flux of up to 500% after the occurrence of heavy precipitation events.
- 41 - Use of the O<sub>2</sub>-decrease parameter in gas efflux better to assess the strength of gas
- 42 emissions to the surface.

43

44 **Keywords**

45 Carbon dioxide – gas flux – released amounts – meteorological parameters – degassing

46 structures

## 47 **1. Introduction**

48 The Earth's natural degassing induces the release into the atmosphere of many gas species,  
49 including some "greenhouse gases" (e.g. N<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub> or H<sub>2</sub>O). Volcanic structures  
50 obviously play an important role in this degassing process, either during explosive (eruptive)  
51 phases, or during quiescent (non-eruptive) periods (e.g. Halmer *et al.*, 2002). Such degassing  
52 may be diffuse, or focused through volcanic edifices, hydrothermal manifestations, or gas  
53 vents, the last two commonly being related to faults (e.g. Judd, 2005; Burton *et al.*, 2013;  
54 Etiope, 2015). The budgets of carbon emissions into the atmosphere have been assessed  
55 since the 1980s (e.g. Werner *et al.*, 2000; Kerrick, 2001; Mörner and Etiope, 2002 and  
56 references therein) and are regularly refined (e.g. Holloway *et al.*, 2007; Lewicki *et al.*, 2007),  
57 or the ongoing investigations on French active volcanoes by Boudoire *et al.*, 2017 and Liuzzo  
58 *et al.*, 2015). Such carbon-emission budgets should include the release of CO<sub>2</sub> as a gas phase  
59 as well as the amounts of CO<sub>2</sub> dissolved in aquifers or lakes that may represent a non-  
60 negligible contribution (e.g. Sorey *et al.*, 1998).

61 Even during periods of quiescence, the release of gases, especially CO<sub>2</sub>, can be high (e.g.  
62 Werner *et al.*, 2009). Volcanic structures are not only characterized by the presence of  
63 degassing structures, such as fumaroles or gas vents, and diffuse degassing processes, but  
64 commonly also by the existence of thermal anomalies in the soil and of hot springs or steam  
65 emissions (e.g. Frondini *et al.*, 2004). This is often the case when the quiescence period has  
66 been relatively short at a geological scale, such as around 130 years at Pantelleria Island,  
67 Sicily (Favara *et al.*, 2001), around 400 years at Furnas volcano, Azores (Pedone *et al.*, 2015)  
68 and around 600 years at Mammoth Mountains, California (Sorey *et al.*, 1998). Nevertheless,  
69 some volcanic edifices that have been quiescent for a similar duration will have no thermal

70 anomalies or fumarolic activity (Hakkoda, Japan; Hernández-Perez *et al.*, 2003) and even no  
71 gas emissions into the atmosphere (Mount Fuji, Japan; Notsu *et al.* (2006). The longer the  
72 duration of the quiescent period, the fewer thermal anomalies there will be, such as in the  
73 West European rift and its associated volcanic structures in France and Germany.

74 Here, however, the absence of high-temperature manifestations does not mean that there  
75 are no gas releases, but these are less commonly quantified. When they are, quantification  
76 may refer to the gas flux in water bodies, such as a flux of  $1450\pm 350 \text{ g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$  of magmatic  
77  $\text{CO}_2$  in the German Laacher See (Aeschbach-Hertig *et al.*, 1996), or a flux of  $170\pm 60 \text{ g}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$   
78 of magmatic  $\text{CO}_2$  in the French Lake Pavin (Aeschbach-Hertig *et al.*, 1999). In the French  
79 Massif Central, little is known on  $\text{CO}_2$  emissions from the numerous carbogaseous springs  
80 that are part of the West European rift system, though several studies deal with the origin of  
81 such  $\text{CO}_2$  (e.g. Batard *et al.*, 1982; Blavoux and Dazy, 1990; Czernochowski-Lauriol *et al.*,  
82 2003). Only a rough estimate of the  $\text{CO}_2$  emissions associated with quiescent volcanism in  
83 the French Massif Central is reported by Mörner and Etiope (2002) – citing Hermansson *et*  
84 *al.* (1991) – as being over  $6 \text{ kg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ . And only one study quantified the  $\text{CO}_2$  emissions into  
85 the atmosphere at the Sainte-Marguerite site (Battani *et al.*, 2010).

86 The present study thus aimed at quantifying the gas emissions related to quiescent  
87 volcanism in the French Massif Central near Lake Pavin (France *et al.*, 2016). Here, the  $\text{CO}_2$   
88 percolation is not associated with mineral water, thus leading to the appearance of mofette  
89 structures ( $\text{CO}_2$  dry-gas vents), such structures commonly being related to Cenozoic rifting  
90 (Pearce *et al.*, 2004). In Europe, dry  $\text{CO}_2$  vents occur, e.g., in the Pannonian basin (Bräuer *et*  
91 *al.*, 2016), in the Eger rift zone (Kämpf *et al.*, 2013), in the Eifel volcanic district (Gal *et al.*,  
92 2011; Krüger *et al.*, 2011). A large number is reported from Italy, though gas vents there can

93 be related to both magmatic CO<sub>2</sub> emissions and emissions of CO<sub>2</sub> accumulated in carbonated  
94 reservoirs (Rogie *et al.*, 2000; Chiodini *et al.*, 2007; Beaubien *et al.*, 2008; Roberts *et al.*,  
95 2011). In the French Massif Central, the only occurrence reported so far is the Escarot  
96 mofette (Gal and Gadalia, 2011; Braüer *et al.*, 2017).

97 Our new investigations around this mofette used the complementary approaches of  
98 measuring soil-gas concentrations (*e.g.* Fleischer and Mogro-Campero, 1978; Toutain and  
99 Baubron, 1999) and soil-gas flux (*e.g.* Chiodini *et al.*, 1998). The data were used to quantify  
100 the range of annual CO<sub>2</sub> emissions, to evaluate their relationship with geological structures  
101 and to evaluate their contribution to the long-term global carbon cycle (*e.g.* Werner and  
102 Brantley, 2003). Another part of the study was the assessment of changes in gas-emission  
103 rates linked to the occurrence of major precipitation events, as fieldwork cannot always be  
104 done under favourable weather conditions. Finally, we envisaged the consequences such gas  
105 emissions may have in more populated areas.

106

## 107 **2. Settings**

### 108 **2.1. Hydro(geo)logical setting**

109 The study area is located 2 kilometres west of Lake Pavin, a maar lake characterized by its  
110 meromictic character (Meybeck, 2015) that was formed around 7,000 years ago. The  
111 volcanic system today is non-active, though some magma may still be present at depth  
112 (France *et al.*, 2016). Compared to the duration of volcanic rest periods in the neighbouring  
113 Chaîne des Puys (10,000 years or more), the system must be seen as quiescent (or dormant),  
114 but not extinct. The dissolved CO<sub>2</sub> in the lake water is attributed to organic-matter  
115 degradation (70% of total input) and to seepage of magmatic CO<sub>2</sub> and/or CO<sub>2</sub> from

116 methanogenesis (Jézéquel, 2015). Deep-CO<sub>2</sub> input becomes dominant in the deeper part of  
117 the lake (Aeschbach-Hertig *et al.*, 1999). The presence of magmatic CO<sub>2</sub> from the sub-  
118 continental lithospheric mantle was reported from the Fontaine Goyon mineral spring and  
119 the Escarot mofette (Bräuer *et al.*, 2016, 2017). Meybeck (2015) reports that other degassing  
120 spots seem to have been identified in the past.

121 The study area is small (about 200x300 m) close to the Escarot degassing zone (*Figure 1*).  
122 The Escarot site was earlier described by Gal and Gadalia (2011) and by Bräuer *et al.* (2017).  
123 A distinction has to be made between the location of the mofette as defined in 2011 (*Figure*  
124 *1*) and the location of the data reported by Bräuer *et al.* (2017) that concerned samples  
125 mostly taken around the Escarot piezometer (*Figure 1*). This observation well is part of a  
126 network of several boreholes that were drilled in the late 2000s to resolve a controversy  
127 about potential renewal of degassing activity (Meybeck, 2015).

128 The gas phase released at Escarot is dominated by CO<sub>2</sub> (>99.2% vol.) with a minor proportion  
129 of permanent gases (N<sub>2</sub> <0.65%; O<sub>2</sub> <0.09%; Ar <0.007%) and traces of CH<sub>4</sub> (360 to 500 ppm)  
130 and of He (27 to 30 ppm; Bräuer *et al.*, 2017). Higher helium concentrations in soil gas, up to  
131 47 ppm were reported by Gal and Gadalia (2011). Isotope data on CO<sub>2</sub> ( $\delta^{13}\text{C}_{\text{CO}_2}$ ), from the  
132 piezometer or the mofette (*Figure 1*), fall in a narrow range (-3.6 to -3.8‰ VPDB, Bräuer *et*  
133 *al.*, 2017; -3.1 to -4‰, unpublished BRGM data) and so do the <sup>3</sup>He/<sup>4</sup>He ratios (6 to 6.3 R/Ra,  
134 Bräuer *et al.*, 2017; 6.09 R/Ra, BRGM unpublished data). Similar values are reported  
135 regionally for magmatic CO<sub>2</sub> (e.g. Battani *et al.*, 2010; Gal *et al.*, 2017).

136 The new data were mostly acquired to the west of a road near the Escarot piezometer; here,  
137 the ground level is approximately 3 m below the road and flooding occurs frequently. Near  
138 the Escarot mofette, the ground level is approximately 2 m above the road. Several zones of

139 bubbling exist along the road and can be seen each time there is some stagnant water in the  
140 road shoulders (after precipitation events). As will be described later, these areas, which are  
141 frequently flooded, were investigated at the start of the fieldwork and were not accessible  
142 after large precipitation events. To the east of the road, there is a large area of peat land,  
143 where flux measurements were made on only unflooded clumps of grass as the soil is nearly  
144 saturated all year long. To the south of the monitoring area lie some meadows, but they,  
145 too, were almost saturated with water on the day they were investigated.

146 Figure 1

147

## 148 **2.2. Methods**

149 In June 2017, 44 soil-gas concentration measurements and 176 soil-gas flux measurements  
150 were made in the 200x300 m area (*Figure 1*). The objective was to obtain a more detailed  
151 description of the degassing area that was highlighted by 53 earlier soil-gas concentration  
152 measurements over a 250x400 m area (Gal and Gadalia, 2011). The new sampling aimed at  
153 lowering the uncertainty in the estimate of CO<sub>2</sub> emissions from the Escarot area (Werner *et*  
154 *al.*, 2000). As emissions of chemical species into the atmosphere from mofette structures are  
155 not restricted to just the gas phases, complementary data on soil gas and dissolved elements  
156 in snow cover, acquired in February 2009, are presented as Supplementary Material.

157 In order to reduce the uncertainty in soil-gas flux evaluations caused by the use of relatively  
158 small flux chambers (Parkin and Venterea, 2010), we used a 10-m-square grid close to the  
159 mofette and a 25-m-square grid farther away from the mofette (*Figure 1*). Flux  
160 measurements were done first, followed by soil-gas concentration measurements if

161 warranted by the flux results. Such soil-gas concentration measuring points were shifted  
162 20 cm away from the flux chamber, to avoid wrong estimates on later flux acquisitions at the  
163 same location. All sampling points were marked in the field so that a repeat acquisition could  
164 be done in exactly the same place; in addition, the trace of the flux chamber often remains  
165 visible.

166 Soil-gas concentrations were measured with the same method as used before (Gal and  
167 Gadalia, 2011). Small holes (1 cm diameter) were drilled down to 1 m depth, and then a  
168 sampling probe was inserted that was plugged into an Infra-Red Gas Analyser equipped with  
169 a moisture filter (LFG20, ADC Gas Analysis Ltd., UK). Pumping was at a low flow rate of  
170 200 ml.min<sup>-1</sup>. Steady-state conditions were reached within tens of seconds. No  
171 concentration changes over a few minutes were noted. CO<sub>2</sub> and O<sub>2</sub> concentrations were  
172 directly monitored. The monitoring of CH<sub>4</sub> concentrations was not technically feasible  
173 (detection limit of 200 ppm at best), but the Escarot mofette is not CH<sub>4</sub>-rich (Bräuer *et al.*,  
174 2017). Analytical precision for CO<sub>2</sub> was ±0.5% of the reading for low concentrations (0.01–  
175 10% vol.), ±3% of the reading for higher concentrations (10 to 50% vol.) and ±5% of the  
176 reading when CO<sub>2</sub> was >50%. The precision for oxygen was ±0.4% of the full scale reading (0–  
177 25% vol.). Samples were stored in Tedlar® bags and analysed by the end of the day for <sup>4</sup>He  
178 with mass spectrometry (Adixen ASM102S leak detector, France) with reference to  
179 atmospheric content (5.24 ppm). Precision of the measurement was better than 4% at full  
180 scale.

181 Soil-gas flux measurements used the accumulation chamber method with external  
182 recirculation (*e.g.* Chiodini *et al.*, 1998; Inguaggiato *et al.*, 2013). The flux-chamber system  
183 was a customized version of the Echo Instruments (Slovenia) soil-gas flux system. The

184 aluminium chamber has a semi-spherical shape with a basal area of 0.0289 m<sup>2</sup> and a volume  
185 of 0.0018 m<sup>3</sup>-(soft ground). The chamber was directly put on the soil surface, which is mainly  
186 grassland with some gravel patches close to the road. No soil was removed except in case  
187 (point C9). A fan with variable speed ensured the mixing of the headspace gas as required  
188 for such sampling (Parkin and Venterea, 2010). The flow rate of the recirculation flux was set  
189 to 0.5-0.6 l.min<sup>-1</sup>, to avoid possible underestimations of the CO<sub>2</sub> flux when lower  
190 recirculation flow rates are used, as well as to avoid possible CO<sub>2</sub> flux overestimations when  
191 using higher recirculation flow rates (Camarda *et al.*, 2009). Pressure, temperature and  
192 relative humidity inside the chamber, as well as pumping rate, were continuously monitored  
193 thus constraining the possible influence of external parameters on the data. The following  
194 gas species were monitored after the gas passed through a moisture filter: CO<sub>2</sub> and CH<sub>4</sub> by  
195 Non-Dispersive Infra-Red (NDIR) detectors (0 to 5000 ppmv ±2% and 0 to 10000 ppmv ±5%,  
196 respectively), and O<sub>2</sub> by electrochemical cells (0 to 25% vol. ±2% of the reading).

197 Some examples of field-data acquisitions are given in *Figure 2*. The flux calculation was  
198 based on the rate of CO<sub>2</sub> increase (positive flux; *e.g.* point A15, *Figure 2*) and potential O<sub>2</sub>  
199 decrease in the chamber (*e.g.* points BZ8, E12, *Figure 2*). The flux was calculated by  
200 considering the linear build-up of gas concentration in the chamber during 3 minutes and by  
201 determining the initial slope of the gas-concentration vs. time relationship (*e.g.* Chiodini *et*  
202 *al.*, 1998; Werner *et al.*, 2000). Flux was normalized to take into account the influence of  
203 pressure and temperature (Lewicki *et al.*, 2005). Normalized CO<sub>2</sub> flux generally was 4.5%  
204 higher than raw flux values.

205 Not all fluxes were calculated using the initial slope of the build-up of gas concentrations.  
206 Short time-scale variations of the CO<sub>2</sub> flux (gas flush) were sometimes observed (*Figure 2*)

207 and were used to evaluate the uncertainty on the gas release. Increases of 10 times of the  
208 flux over some seconds were noticed in points A8 (once) and Z16 (several times). Such multi-  
209 linear increases were also reported from the Yellowstone area (Werner *et al.*, 2000).

210 Figure 2

211

### 212 **2.3. Weather parameters**

213 It is well established that soil-gas concentrations and fluxes can be affected by, among  
214 others, meteorological parameters such as temperature, atmospheric pressure, wind or  
215 precipitation (*e.g.* Hinkle, 1994; Toutain and Baubron, 1999; Viveiros *et al.*, 2008, 2009;  
216 Werner *et al.*, 2014). Unexpectedly for late June, the weather was strongly variable. No  
217 precipitation was reported during the week preceding fieldwork at a nearby weather station  
218 (*Figure 3*). Air temperatures were quite high and pressure showed little variability. The  
219 situation changed the weekend before the fieldwork. Temperature and pressure steadily fell  
220 between 24 and 29 June, and large precipitation events occurred during late afternoon on  
221 26 and 27 June (31 mm and 34.6 mm, respectively). June 28<sup>th</sup> and 29<sup>th</sup> were rainy days, with  
222 intermittent precipitation events on the 28<sup>th</sup> (10.8 mm) and continuous precipitation events  
223 on the 29<sup>th</sup> (14.8 mm).

224 The gas-concentration and -flux dataset was acquired as follows: 45 flux measurements prior  
225 the rainfall (26 June), 56 flux and 22 concentration measurements after 31 mm of rain on  
226 27 June, 42 flux and 15 concentration measurements after >65.6 mm of precipitation on  
227 28 June, and 33 flux and 7 concentration measurements after >76.4 mm of rain on 29 June.

228 The temperature and pressure data recorded during flux acquisitions are in good agreement  
229 with the weather station data (*Figure 3*). Temperature during the first two days rose during  
230 the day as a consequence of sunshine thermal forcing, the humidity of the gas at the  
231 soil/atmosphere interface thus decreasing during the day. During the last two days, the  
232 situation was reversed as there was no sunshine; the soil-gas humidity was high and further  
233 rose during the day after the rain.

234 Because of these large precipitation events, there was a strong correlation between  
235 temperature and pressure (Pearson's coefficient of 0.88), relative humidity and temperature  
236 of the atmosphere (coefficient of -0.89), and relative air humidity and atmospheric pressure  
237 (coefficient of -0.82) during flux measurements.

238 Figure 3

239

### 240 **3. Results and discussion**

#### 241 **3.1. Statistical parameters**

242 The main statistical characteristics of the soil-gas concentrations and fluxes measured in  
243 2017 are shown on *Figure 4*. Former concentration data measured near the Escarot mofette,  
244 between 2008 and 2012, are also shown; the location of these data is shown on the bottom  
245 map of *Figure 1*.

246 As may be expected from a survey designed for highlighting the behaviour of soil-gas species  
247 near a gas vent, the data distribution of soil-gas concentrations shows a very high mean CO<sub>2</sub>  
248 concentration ( $72.6 \pm 36.1\%$  - arithmetic mean  $\pm$  standard deviation), a very low mean O<sub>2</sub>  
249 concentration ( $5.8 \pm 6.8\%$ ) and a strong enrichment in helium-4 in the soil ( $19.9 \pm 13$  ppm as a

250 mean). By comparison, data from the 2008 to 2012 surveys in the Escarot area showed mean  
251 CO<sub>2</sub> and helium enrichments ( $47.3 \pm 43.7\%$  and  $17.3 \pm 9.6$  ppm, respectively) and O<sub>2</sub> depletion  
252 ( $11.1 \pm 8.5\%$  as a mean), suggesting that the degassing pattern of the Escarot area has  
253 remained stable over several years.

254 No CH<sub>4</sub>-flux was measured during the survey, but this is not really surprising. Even on active  
255 volcanoes, the diffuse CH<sub>4</sub> flux may only represent trace releases compared to diffuse CO<sub>2</sub>  
256 degassing (Hernández *et al.*, 1998).

257 As the variation coefficient of CO<sub>2</sub> flux shows a skewed distribution, which is common in  
258 high-flux areas, we refer to the arithmetic mean as explained by Werner and Brantley (2003)  
259 and references therein. Three evaluations are presented in *Figure 4*. The first corresponds to  
260 the data calculated using the linear fit prevailing during most of the sampling and  
261 considering the normalization to standard temperature and pressure (STP) conditions. The  
262 second evaluation corresponds to the flux calculated from the gas flush(es) that may occur  
263 along the 3-minute-long flux acquisition (*Figure 2*), called “maximum value”. The third  
264 evaluation combines the previous two datasets in order to account for the short-term  
265 variability induced by the occurrence of gas flushes. The STP values are thus corrected to  
266 include these potential short-term increases, the “maximum value” being integrated as a  
267 function of the number and duration of the increases observed during the acquisition. The  
268 ponderated flux value deriving from this last calculation thus represents the best estimate of  
269 the gas emission over 3 minutes.

270 Such gas flushes can have a noticeable influence: they were observed for 59 of the 176  
271 acquisitions. The minimum duration of a gas flush over 3 minutes was 5 seconds (one event)  
272 and the maximum was 75 seconds (several events of up to 15 seconds duration each).

273 Maximum fluxes that may be calculated during these short events are shown at least by an  
274 increase of 20% of STP-flux, a value similar to the error reported for flux measurements  
275 ( $\pm 15\%$ ; Chiodini *et al.*, 1996). At most, the increase corresponds to a multiplication by a  
276 factor of 20 of the flux. As a mean, gas flushes induced a short-term increase of the flux by a  
277 factor of 7 (*e.g.* for point A8, *Figure 2*). Only few points showed a decrease in CO<sub>2</sub> flux during  
278 the acquisition (*e.g.* point Z32, *Figure 2*), which can lower the flux by up to 40% and is only  
279 noted at low emissive points. Consequently, the initial mean value of the uncorrected STP-  
280 flux data ( $500 \pm 2,080 \text{ g.m}^{-2}.\text{d}^{-1}$ ) is re-evaluated at  $575 \pm 2,100 \text{ g.m}^{-2}.\text{d}^{-1}$  (*Figure 4*).

281 *Figure 4*

282

## 283 **3.2. Data analysis**

### 284 **3.2.1. Relations between gas species**

285 The CO<sub>2</sub>-O<sub>2</sub> relationship for soil gas is presented in *Figure 5A* and interpreted using the  
286 process-based approach of Romanak *et al.* (2012). Three main relationships are plotted. The  
287 first is the respiration line (in blue), characteristic of aerobic respiration in soil that consumes  
288 1 mole of O<sub>2</sub> to produce 1 mole of CO<sub>2</sub>. The second relation corresponds to the CH<sub>4</sub> oxidation  
289 line (in green) in near-surface environments, where 2 moles of O<sub>2</sub> are needed to produce  
290 CO<sub>2</sub>+H<sub>2</sub>O. The last relationship (red lines) corresponds to the dilution process occurring  
291 when a deep (magmatic) CO<sub>2</sub> endmember dilutes the O<sub>2</sub>+N<sub>2</sub> pool in a near-surface  
292 environment (relative abundance: 20.9% of O<sub>2</sub> and 78.1% of N<sub>2</sub>). Different dilution lines can  
293 be plotted, depending on the CO<sub>2</sub>/O<sub>2</sub> initial ratio: *Figure 5* illustrates three cases at 0.03%,  
294 5% and 10% of biologically produced CO<sub>2</sub>.

295 Only few data lie on the respiration line and these have a CO<sub>2</sub> concentration below 5%. Most  
296 of the data plot close to the dilution line with a possible influence of respiration processes.  
297 This kind of data distribution confirms previous data that reported a threshold value around  
298 10% of CO<sub>2</sub> in soil (Gal and Gadalia, 2011). Below this value, CO<sub>2</sub> mainly originates from  
299 biological processes; above it, a supply of deep-seated CO<sub>2</sub> is required. The area investigated  
300 around the Escarot mofette (*Figure 1*) is thus largely influenced by the degassing of  
301 magmatic CO<sub>2</sub>, as shown by the general relationship between CO<sub>2</sub> and O<sub>2</sub> concentrations  
302 (slope of -0.20). Biological processes, though existing, have little influence on the relation  
303 between these two gas species.

304 Strong helium enrichment (>10 ppm) was earlier measured when the CO<sub>2</sub> concentrations  
305 were over 10% (Gal and Gadalia, 2011). *Figure 5B* links <sup>4</sup>He data to CO<sub>2</sub> data and similar  
306 conclusions arise from the <sup>4</sup>He-O<sub>2</sub> relationship in the present study. In 2017, there still was a  
307 good correlation between <sup>4</sup>He and CO<sub>2</sub> as shown by the overlapping fits in *Figure 5B*, even if  
308 the helium enrichment of soil gas seems to be lower in 2017 for CO<sub>2</sub> concentrations below  
309 80%. However, for a nearly pure CO<sub>2</sub> gas phase, <sup>4</sup>He concentrations were higher than  
310 previously measured. Despite a less sensitive character, the new data still suggest that  
311 helium is a good proxy for detecting the presence of deep-seated CO<sub>2</sub>.

312 The variability of the helium signal in soil gas may have at least three different origins. First,  
313 it may have been a result of the poor weather conditions during the 2017 fieldwork, with  
314 their potential impact on pressure and temperature gradients in soil that govern advective  
315 transport (*e.g.* Werner *et al.*, 2000; Etiope and Martinelli, 2002; Rinaldi *et al.*, 2012). Second,  
316 such variability may be caused by demixtion phenomena that are variable over time (Gal and

317 Gadalia, 2011). Third, such variability in the helium signal this may also be caused by long-  
318 term variability of the deep-seated gas efflux (e.g. Chiodini *et al.*, 2010; Werner *et al.*, 2014).

319 Finally, our data show a good correlation between CO<sub>2</sub> flux and O<sub>2</sub> depletion. *Figure 5C*  
320 presents this relation with reference to the domain of biological CO<sub>2</sub> efflux as recently  
321 established in France by Pokryszka *et al.* (2017). The maximum efflux mentioned by these  
322 authors is close to 84 g.m<sup>-2</sup>.d<sup>-1</sup> (or 30 cm<sup>3</sup>.min<sup>-1</sup>.m<sup>-2</sup>) for summer acquisitions and close to  
323 34 g.m<sup>-2</sup>.d<sup>-1</sup> (or 12 cm<sup>3</sup>.min<sup>-1</sup>.m<sup>-2</sup>) for winter acquisitions, the last value being closer to  
324 maximum values for biogenic flux reported in other areas (e.g. Werner and Brantley, 2003:  
325 30 g.m<sup>-2</sup>.d<sup>-1</sup>). Any CO<sub>2</sub> flux over 84 g.m<sup>-2</sup>.d<sup>-1</sup> strongly suggests a relation with deep-seated  
326 processes. *Figure 5C* shows a fairly good relationship between the CO<sub>2</sub> flux and O<sub>2</sub> depletion,  
327 with large depletions associated with strong emission of CO<sub>2</sub> into the atmosphere. This is the  
328 translation on the flux parameter of the flush effect existing for soil-gas concentrations, this  
329 effect being induced by the intrusion of deep CO<sub>2</sub> in the soil that sweeps away the naturally  
330 existing O<sub>2</sub>+N<sub>2</sub> pool in soil. When the strength of the CO<sub>2</sub> efflux is high, then the sweeping of  
331 O<sub>2</sub> can also be monitored using the depletion of O<sub>2</sub> concentrations at the soil/atmosphere  
332 interface. Such monitoring may be an interesting – and complementary – tool for testing the  
333 strength of deep-seated gas emissions.

334 Correlation-matrix calculation fails to suggest the existence of other relations between the  
335 different gas phases. It is nonetheless important to assess if CO<sub>2</sub> flux is related to CO<sub>2</sub> or <sup>4</sup>He  
336 soil-gas concentrations, markers of deep-seated processes in the present case (*Figure 6*).

337 Four groups are defined in *Figure 6A*. Group A has typical CO<sub>2</sub>-flux values overlapping the  
338 ones of biological sources, though the CO<sub>2</sub> concentrations may be much higher than those of  
339 biologically produced CO<sub>2</sub> in soil gas. Group B marks a clear departure from this biological

340 pool, especially when considering the high CO<sub>2</sub> concentration values, and group C is only  
341 related to CO<sub>2</sub> leaks from depth. There is a graphical trend from Group A to Group C, which  
342 suggests that the higher the CO<sub>2</sub> concentration, the higher will be the CO<sub>2</sub> flux. Group D  
343 corresponds to high CO<sub>2</sub> concentration in the soil, but low flux at the surface. *Figure 6B*  
344 shows that this 'low CO<sub>2</sub> flux' group is He-rich too, suggesting that the soil structure has an  
345 influence on gas emission to the surface (June 26<sup>th</sup> acquisitions) and that an additional  
346 influence of precipitation may be invoked for acquisitions made on June 27<sup>th</sup>.

347 The difficulty of monitoring low fluxes over soils that only have CO<sub>2</sub> as a soil-gas phase may  
348 be linked to several reasons. One reason is the presence of variable amounts of clay in the  
349 soil in the area (*Figure 7*). Because of changing weather conditions and large precipitation  
350 events, the upper part of the soil can reach near-saturation conditions (low CO<sub>2</sub> flux), but at  
351 1-m depth the soil may allow efficient gas advection. Another reason may be the distance  
352 from the main CO<sub>2</sub> supplying areas, *i.e.* from highly permeable fault zones. Above a  
353 degassing structure, high flux and high CO<sub>2</sub> concentrations are supposed to occur conjointly  
354 (Gal *et al.*, 2011, 2012, and references therein), but at some distance of such structures, the  
355 strength of advection processes may be lower, thus lowering the efflux at the  
356 soil/atmosphere interface.

357 This reasoning can be extended to the helium concentrations in soil gas. Tendency (1) in  
358 *Figure 6B* is found close to or above a deep-rooted degassing structure where a strong  
359 ascent of gas causes combined strong CO<sub>2</sub> and <sup>4</sup>He enrichment (>30 ppm). Nonetheless, as  
360 highlighted by Tendency (2), the higher <sup>4</sup>He values in soil are not found in high CO<sub>2</sub> flux zones  
361 (*i.e.* they are found with some distance to the degassing structures), but they correspond to  
362 100% of CO<sub>2</sub> in the soil. In that case, soil permeability may play a role even if some authors

363 consider permeability to be of secondary importance (Camarda *et al.*, 2006). More precisely,  
364 the presence of water in the upper part of the soil may be the cause. If the first 10-20 cm are  
365 saturated after precipitation, then the emissivity of the soil will be low (low CO<sub>2</sub> flux), but  
366 farther down in the soil, the soil-gas concentrations can be high: the data shown on *Figure 4*  
367 suggest that high CO<sub>2</sub> concentrations are widespread at the scale of the Escarot site so that  
368 having 100% CO<sub>2</sub> in soil gas is a common phenomenon. Helium has a larger diffusive capacity  
369 than CO<sub>2</sub> (*e.g.* Jähne *et al.*, 1987), as well as a much lower solubility in water (*e.g.* Weiss,  
370 1971, 1974). If a saturated horizon is present in the upper part of the soil, then the barrier  
371 effect (“soil capping”, Werner *et al.*, 2000) induced by this horizon may not be noticed when  
372 considering CO<sub>2</sub> concentrations (high background), but it may cause an increase in <sup>4</sup>He  
373 concentration as the leaking of helium to the atmosphere is considerably reduced because  
374 of the presence of a water-saturated horizon. Lateral diffusion of <sup>4</sup>He may also contribute to  
375 local enrichment.

376 Figure 5

377 Figure 6

378

### 379 **3.2.2. Relationship with meteorological parameters**

380 *Figure 3* illustrates the changing weather conditions during sampling. This offered an  
381 opportunity further to evaluate the influence these parameters may have on flux  
382 quantification, even it is preferred to sample soil gases during periods of dry weather.  
383 Correlation-matrix calculations highlight a good correspondence between the changes in  
384 temperature and relative humidity (Pearson’s coefficient of correlation  $r$  of -0.887), of

385 temperature and pressure ( $r$  of +0.876), and thus of pressure and relative humidity ( $r$  of -  
386 0.816). The amounts of precipitation also negatively correlated with the relative humidity ( $r$   
387 of -0.830). Huge amounts of rain fell during the strong precipitation events, increasing the  
388 humidity at the soil/atmosphere interface. By the end of the sampling period, the amount of  
389 precipitation was much lower, but the cumulative amount was high and thus the rise of  
390 relative humidity continued. Nonetheless, these calculations fail to illustrate if there is a  
391 global influence of these meteorological parameters onto the soil-gas and soil-flux data. For  
392 instance, correlation coefficients are  $<0.1$  ( $r$ ) when comparing  $\text{CO}_2$ -flux data with  
393 temperature, pressure or relative humidity. This suggests that external parameters exert  
394 little to insignificant influence on degassing processes; this is congruent with a deep-seated  
395 origin of the gases and with the low variability of the degassing strength that is expected for  
396 a monitoring period of short duration (*e.g.* Werner *et al.*, 2014).

397 However, it is well established that external parameters can have a strong influence on the  
398 acquisitions (*e.g.* Oertel *et al.*, 2016), and especially on flux data when considering the  
399 duration of our survey. A time span of three days may be too short to allow the percolation  
400 of water to 1-m depth, particularly during summer when water is easily taken up by the  
401 vegetation. For instance, Werner *et al.* (2014) report a decrease of emission rates by a factor  
402 of 2-3 over several days after the passage of a weather front associated with high winds and  
403 strong precipitation: they highlight the influence of wind in this decrease as this may change  
404 the pressure gradient in soil. This may be less obvious for our dataset because the wind  
405 speed measured during the survey (maximum  $3.33 \text{ m}\cdot\text{s}^{-1}$ ) and far below the  $14 \text{ m}\cdot\text{s}^{-1}$  reported  
406 by Werner *et al.* (2014). As temperature, pressure, amount of precipitation and relative  
407 humidity are interdependent, it is not easy to designate the most influent parameter, though  
408 rain and its consequences on soil moisture are of primary importance (*e.g.* Viveiros *et al.*,

409 2014, and references therein). We will thus use the generic term “precipitation event” to  
410 describe the influence of external parameters on flux evaluation.

411 Some examples are shown in *Figure 7* to illustrate different aspects. Short-term variations  
412 under consistent weather conditions were assessed through repeat acquisitions at points  
413 Z13, Z18 and Z19 before precipitation events (grey and blue dots on *Figure 7*) and at point  
414 E12 after several precipitation events, in order to evaluate the bias that may exist for high  
415 CO<sub>2</sub> fluxes. Under dry weather conditions, the variability in CO<sub>2</sub> flux was between 2.5% and  
416 12% for points showing similar degassing properties (points Z13 and Z18). This 2.5-12%  
417 variability is in reasonable agreement with the standard error of this method (*e.g.* Chiodini *et al.*,  
418 1996; Evans *et al.*, 2001). This is also similar to what is reported for the amplitude of flux  
419 variation even under stable weather conditions (10% to 20%; Viveiros *et al.*, 2014). The  
420 variability can be much higher when gas flushes exist (300% of variability for point Z19). High  
421 intrinsic variability may thus be caused by these flushes of unpredictable variability, which  
422 were common during our acquisitions and represent fluctuations of the advective  
423 component (Werner *et al.*, 2000). For point E12, the reduction of flux was around 150% and  
424 associated with increased soil moisture, but no acquisition was done before precipitation  
425 events so that the decrease between dry and wet conditions may be much larger.

426 The occurrence of a precipitation event may not always points to a decrease in CO<sub>2</sub> flux. An  
427 increase of the flux was monitored at point Z13 after the first precipitation event (*Figure 7*).  
428 As shown on the three photographs above the plot, the area of point Z13 was bare and the  
429 soil was humid (31 mm precipitation, evening of 26 June). Surprisingly, this had no influence  
430 on the gas emission as the flux was 25% higher. This is certainly due to the location of this  
431 point Z13, as shown by the strong bubbling on 28 June after another large precipitation

432 event. The monitoring point was just above a degassing centre and soil saturation had  
433 almost no influence on this process at least over a short period. Though not frequent, such  
434 an increase of gas flux after rainfall may also occur in areas where water taken up by the  
435 vegetation, such as point EZ12. General flux was low, in the range of biological CO<sub>2</sub> flux  
436 (Pokryszka et al, 2017), but an increase of +60% was measured after the second precipitation  
437 event. Some of this variability may also be linked to the daily variability of biological soil-gas  
438 efflux (e.g. Parkin and Kaspar, 2003).

439 Normally, flux (e.g. Werner *et al.*, 2000) and soil-gas concentrations (e.g. Hinkle, 1994)  
440 decrease after precipitation events. This is illustrated for flux by repeat acquisitions at points  
441 CZ4, Z18 and Z19 (Figure 7); a decrease by a factor 5 or 10 occurred after 31 mm of rain  
442 (respectively, points Z18 and Z19). Werner *et al.* (2000) reported a decrease by a factor 2  
443 after 21 mm rain in the Yellowstone area. Further decrease may occur as the cumulative  
444 precipitation increases (-15% at Z18, 8-fold decrease at CZ4). Such huge decreases are the  
445 direct result of soil capping, which is maximized when acquisitions occur during precipitation  
446 events. It is thus recommended to wait for two days without any precipitation to get rid of  
447 the potential effects of water saturation in the soil pores (e.g. Fridriksson *et al.*, 2006), but  
448 this was not possible during our survey.

449 Soil properties must be considered as well. In volcanic areas, high degassing zones are  
450 generally located on or near faults, meaning that soil permeability will have only minor  
451 influence on flux values (Camarda *et al.*, 2006), and a shallow soil cover may only slightly  
452 affect the shape and size of the soil degassing anomalies. However, this general statement  
453 has to be verified for each study (Viveiros *et al.*, 2014), and in our case the influence of the  
454 soil cover is shown by the increase in CO<sub>2</sub> flux at point C9 (Figure 7). Here, a first direct  
455 measurement was followed by the removal of the uppermost few centimetres; the second

456 measurement, 15 minutes after the first, then showed a 6-fold increase in CO<sub>2</sub> flux. This  
457 delay may be too short to reach stability of the gas efflux; Fridriksson *et al.* (2006) indeed  
458 mentioned a duration of 30 minutes to reach steady-state conditions. Nevertheless, the  
459 amplitude of the increase also suggests that the clayey topsoil strongly reduced the gas  
460 emission, especially when rain fell before the acquisitions. This may explain some of the  
461 discrepancies between soil-gas concentrations and soil-gas flux, the second being far more  
462 affected by the humidity and type of soil. There may be exceptions to this rule as shown by  
463 the data from point E12, which is close to a road on gravel banks that are highly permeable  
464 even under wet conditions. Some variability (40%) was noted between repeat acquisitions,  
465 but this was largely due to uncertainty on the rate of CO<sub>2</sub> enrichment in the chamber in the  
466 case of very high emissions.

467 Precipitation events were common during this survey, more or less affecting three quarters  
468 of the acquisitions. Direct use of these field acquisitions to calculate the CO<sub>2</sub> budget into the  
469 atmosphere would probably underestimate this budget. We thus corrected the dataset to  
470 arrive at a better assessment of the gas emissions, based on relationships established  
471 between the data points that were measured before and after precipitation events.

472 Based on the above-described data, this underestimate can be evaluated at up to 500% for a  
473 flux range of 96-720 g.m<sup>-2</sup>.d<sup>-1</sup> just after a large precipitation event, whereas higher fluxes  
474 (>1440-1920 g.m<sup>-2</sup>.d<sup>-1</sup>) that are found in areas with potential bubbling manifestations are not  
475 really modified. When precipitation events are less intense but last for several hours, an  
476 additional drop of the flux by approximately 15% is seen. We thus propose the following  
477 empirical correction procedure: 1) 45 data from 26 June: no correction; 2) Data from 27  
478 June: if CO<sub>2</sub> flux is <240 g.m<sup>-2</sup>.d<sup>-1</sup> the value is multiplied by 5 (49 data); if the flux is 240 to

479 1440 g.m<sup>-2</sup>.d<sup>-1</sup> the value is multiplied by 2 (5 data); if CO<sub>2</sub> flux >1440 g.m<sup>-2</sup>.d<sup>-1</sup> there is no  
480 correction (2 data); 3) Data from 28 and 29 June: similar correction as for 27 June data and  
481 an additional correction of +15% (multiplied by 5 +15%: 28 data; multiplied by 2 +15%: 2  
482 data; no correction: 3 data). Data corrected only for pressure and temperature effects and  
483 those including further correction steps (gas flush and precipitation events) are compared in  
484 *Figure 8* (data shown in Supplementary table). The effect of this correction procedure is  
485 greatest for low fluxes considered as extreme. Some low CO<sub>2</sub> flux values after precipitation  
486 correction are still less than 40 g.m<sup>-2</sup>.d<sup>-1</sup>, but most are much higher and point to CO<sub>2</sub> flux  
487 values far above biological ones. Even if this procedure likely represents an over-correction  
488 of the data, it should still be used when evaluating CO<sub>2</sub> release at site scale, to give a range  
489 indication of the maximum expected gas release.

490 *Figure 7*

491 *Figure 8*

492

### 493 **3.3. Spatial distribution**

#### 494 **3.3.1. Background values and threshold levels**

495 Soil-gas and soil-flux data are usually processed in order to determine threshold values from  
496 the data distribution. Such threshold levels help in better distinguishing between a pure  
497 biological, deep-seated, or mixed origin (*e.g.* Bloomberg *et al.*, 2014), using the procedure  
498 proposed by Sinclair (1974) that relies on probability plot calculations. This procedure may  
499 be adapted when the dataset is skewed, as is the case here with neither a normal nor log-

500 normal distribution, except for helium data that range under normal law with a p-value of  
501 0.20. Some inflections in the cumulative probability plot may exist (*Figure 9*).

502 In our case, the acquisitions were oriented towards definition of the mofette structure and  
503 not towards a characterization of the background population, which may correspond to soil-  
504 respired CO<sub>2</sub> emissions. Nevertheless, an upper limit for biologically sourced CO<sub>2</sub> in the soil,  
505 close to 10% may be deduced from the 2017 CO<sub>2</sub> data (blue on *Figure 9*) and from the  
506 previous dataset (red on *Figure 9*). A similar result derives from the earlier described CO<sub>2</sub>-O<sub>2</sub>  
507 relationship. An upper threshold of 80-90% CO<sub>2</sub> may be defined, but its sole significance is to  
508 help locating potential gas vents that show strong emission into the atmosphere as a  
509 function of meteorological and soil parameters.

510 The helium data showed a similar distribution in 2017 (Escarot area) and in 2008-2012 (over  
511 a much larger area), suggesting some representativeness. A lower threshold of 5.5 ppm can  
512 be defined and corresponds to near-atmospheric values accounting for a measuring error of  
513 5% ( $5.24 \times 1.05 = 5.5$ ). The upper threshold is around 24 ppm and any value above this  
514 threshold will indicate the presence of deep-seated gas phases.

515 Finally, depending on which CO<sub>2</sub> flux data are considered (*Figure 9*), the biological  
516 background value can range from  $<33.6 \text{ g.m}^{-2}.\text{d}^{-1}$  (precipitation correction taken into  
517 account) to  $<74.4 \text{ g.m}^{-2}.\text{d}^{-1}$  (data normalized to STP conditions). The higher value is close to  
518 the upper limit defined by Pokryszka *et al.* (2017) for French soils. Higher flux values are  
519 typical of strong gas emissions with a growing influence of deep-seated CO<sub>2</sub> feeding. Mixed  
520 sources (biological and deep-seated) may exist until the  $240 \text{ g.m}^{-2}.\text{d}^{-1}$  threshold level is  
521 reached.

522 Figure 9

523

524 **3.3.2. Data interpolation**

525 As may be expected from the skewed data that were acquired near the gas seeps, all gas  
526 data show an anisotropic behaviour as pointed out by variogram calculations. Variograms for  
527 soil-gas data (data not shown) are best fitted using a preferential distribution along a N60°  
528 axis, whereas soil-gas flux data rather show a preferential distribution along a N25° axis. The  
529 lag distances were calculated between 50 and 60 m except for helium (35 m). This agrees  
530 with the size of emitting areas reported elsewhere for CO<sub>2</sub> or CH<sub>4</sub> degassing structures (e.g.  
531 Battani *et al.*, 2010; Etiope *et al.*, 2010). These data were used to construct interpolated  
532 maps for an area of about 310 m N-S by 170 m E-W.

533 The interpolated maps for CO<sub>2</sub> flux and correlative O<sub>2</sub> depletion (*Figure 10A and B*) show  
534 several degassing centres that seem to be aligned along a roughly NNW-SSE direction.  
535 Several seeps of secondary degassing power occur in the north of the area, between the  
536 piezometer and the first mofette centre (as defined by Gal and Gadalia, 2011), releasing  
537 2,400 to 3,600 g.m<sup>-2</sup>.d<sup>-1</sup> of CO<sub>2</sub> into the atmosphere. Interestingly, this NNW-SSE direction is  
538 also revealed by O<sub>2</sub> depletion data at the soil/atmosphere interface, indicating the most  
539 efficient degassing centres. Two main such centres are located in the south of the area. The  
540 less emissive one releases about 6,000 g.m<sup>-2</sup>.d<sup>-1</sup> of CO<sub>2</sub>, whereas the most active can reach  
541 over 14,000 g.m<sup>-2</sup>.d<sup>-1</sup> of CO<sub>2</sub> (Point E12, *Figure 7*). This most active area, set close to the road  
542 over a gravel bed, shows no traces in the vegetation (grass) that might suggest the existence  
543 of such strong CO<sub>2</sub> release. Compared, e.g. to the Latera gas vents, of lower release strength  
544 (2,000 to 3,000 g.m<sup>-2</sup>.d<sup>-1</sup>; Beaubien *et al.*, 2008) but without vegetation, the absence of  
545 visible effects at Escarot is probably related to the absence of reducing gas species such as

546 H<sub>2</sub>S or CH<sub>4</sub>, which are released at Latera. Based on the maps constructed from STP-  
547 normalized flux or that corrected for precipitation effects, an inner structuring of these high  
548 release seeps seems to exist. This potential structure is oriented NE-SW, but, as the map  
549 built using the flux accounting from gas flushes does not reveal the same secondary  
550 structuring, this may be an artefact from kriging calculations and thus little confidence is  
551 given to this feature.

552 The soil-gas concentration measurements shown on *Figure 10C* include all the available  
553 (2008-2012 and 2017) data. The resulting interpolated maps show a good spatial agreement  
554 between these data, as was expected from probability-plot results (*Figure 9*). The data  
555 define several structures in the soil where CO<sub>2</sub> and <sup>4</sup>He enrichment and the correlative O<sub>2</sub>  
556 depletion may be very high. The mofette and the piezometer are located on two of these  
557 structures that are also aligned along a NNW-SSE direction. Helium enrichment appears to  
558 be less important to the southeast, but this effect may be caused by a lack of data in this  
559 area.

560 At site scale, the soil-gas and soil flux measurements correlate. Areas where CO<sub>2</sub> flux is high  
561 are rich in CO<sub>2</sub> in the soil, but not all areas rich in CO<sub>2</sub> in the soil show high CO<sub>2</sub> release into  
562 the atmosphere. Similar spatial correlations were reported by Battani *et al.* (2010) and  
563 highlight the role of soil in the shape and size of degassing (Camarda *et al.*, 2006).

564 The structure and surface arrangement of degassing centres perfectly match the known  
565 regional tectonic structures. Brousse *et al.* (1990) reported the existence of NE-SW to NNE-  
566 SSW faults whose directions were inherited from pre-existing fractures in the Hercynian  
567 basement. Locally, these authors also mention the existence of a recent NNW-SSE fault  
568 (*Figure 10B*) that separates two series of the Mont-Dore volcanism (3 to 1.2 Ma-old basalt to

569 the west and 1.2 to 0.3 Ma-old benmoreite to the east). Hydrothermal traces exist along this  
570 fault over some tens of metres across the fault trace. This fault becomes invisible about  
571 300 m north of the Escarot piezometer after offsetting the surficial formations filling the  
572 valley. Farther south this fault has no surface expression, but our data show that its trace  
573 can be extended as it still has some permeability for gas phases.

574 Figure 10

575

### 576 **3.4. Quantifying gas release to the atmosphere**

577 The strength of degassing and thus the permeability of the fault to gas flow can be assessed  
578 using the interpolated maps described above (*Figure 10*). Such evaluation is based on  
579 volume calculations functionalities that are found in *e.g.* Surfer software (Goldensoftware),  
580 provided the coordinates are in metric scale (*e.g.* Werner *et al.*, 2000). *Table 1* shows some  
581 results.

582 The CO<sub>2</sub> that is released into the atmosphere may not all be of deep-seated origin (*Figure 5*).  
583 Three different levels of background biological flux are considered: 30 g.m<sup>-2</sup>.d<sup>-1</sup>, the common  
584 upper limit for biological flux; 48 g.m<sup>-2</sup>.d<sup>-1</sup>, the upper limit for grassland and agricultural soil;  
585 and 84 g.m<sup>-2</sup>.d<sup>-1</sup>, the upper limit reported for French soils. Each increase of the biological CO<sub>2</sub>  
586 flux induces a decrease of the deep-seated CO<sub>2</sub> component.

587 The first evaluation refers to the STP-normalized CO<sub>2</sub> flux, without considering any further  
588 correction. The second evaluation includes a correction to take gas flush into account. The  
589 third evaluation adds a correction to consider the effect of precipitation events, as earlier  
590 mentioned. Finally, a basic estimate is given, simply using the surface of the monitored area

591 (52,000 m<sup>2</sup>) and the mean CO<sub>2</sub> flux (576 g.m<sup>-2</sup>.d<sup>-1</sup>). The end result is an emission of 30 tons  
592 per day (tpd) of CO<sub>2</sub> into the atmosphere.

593 The first two evaluations gave quite similar results: the area affected by degassing is smaller  
594 than 32,000 m<sup>2</sup> (60% of the investigated area) and larger than 17,000 m<sup>2</sup> (33% of the  
595 investigated area). The amount of biologically produced CO<sub>2</sub> for a 52,000 m<sup>2</sup> area is between  
596 1.6 and 4.4 tpd (depending on soil productivity). Interpolation calculations show that some  
597 areas may not be as productive as expected, so the biological CO<sub>2</sub> flux was re-estimated at  
598 between 0.7 and 2 tpd. This correction could only be a calculation bias linked to the  
599 procedure itself, but it may also be representative: biological flux can naturally vary and may  
600 be low in areas where deep CO<sub>2</sub> escapes. The resulting quantity of such deep-seated CO<sub>2</sub> is  
601 evaluated between 17.3 and 20.8 tpd. The third evaluation, including the flux decrease  
602 related to precipitation events, leads to quantities of emitted CO<sub>2</sub> very close to that of the  
603 basic estimate (27 to 30 tpd), suggesting that even the most basic assumption can lead to a  
604 realistic result, where the role of biological CO<sub>2</sub> flux is higher but nearly all the area appears  
605 to be affected by diffuse degassing. This may be an optimistic appraisal, but we nevertheless  
606 used it for proposing an overall estimate of the CO<sub>2</sub> budget, based on the mean value of all  
607 estimates presented in *Table 1*. The CO<sub>2</sub> degassing over 0.052 km<sup>2</sup> at Escarot is thus  
608 estimated at between 8100±1800 tons per year with an additional biological contribution of  
609 660±400 tons per year, or respectively 22.2±4.9 and 1.8±1.1 tpd.

610 This amount of deep-seated CO<sub>2</sub> is three times larger than that reported regionally from  
611 Sainte-Marguerite, 35 km to the north-east, where a CO<sub>2</sub> release of 8.5 tpd over 0.06 km<sup>2</sup>  
612 was estimated (Battani *et al.*, 2010). This quantity is similar to that emitted by diffuse  
613 degassing in volcanic environments, such as in Greece (25 tpd, 0.346 km<sup>2</sup>; Brombach *et al.*,

614 2001), in Italy (Stromboli Island: 20 tpd on the flanks; Inguaggiato *et al.*, 2013), in Japan  
615 (74 tpd of hydrothermal CO<sub>2</sub> reported over 0.58 km<sup>2</sup> by Hernández-Perez *et al.*, 2003), or in  
616 New-Zealand (Taupo Volcanic Zone: from 8±3 tpd over 0.3 km<sup>2</sup> to 72±13 tpd over 0.19 km<sup>2</sup>;  
617 Bloomberg *et al.*, 2014). Far higher emissions are nevertheless known from other volcanic  
618 areas (e.g. Viveiros *et al.*, 2010; Burton *et al.*, 2013; and references therein) and also for  
619 other mofettes in Europe (1566 tpd over 0.075 km<sup>2</sup> in the Czech Republic; Kämpf *et al.*,  
620 2013).

621 Table 1

622

### 623 **3.5. Links to risk assessment**

624 The second aspect of this study relates to risk assessment, of interest to the populated areas  
625 that exist a few dozen kilometres to the north-east. The Escarot area is not inhabited, but  
626 cattle grazing close to, or over, the seep apparently is unaffected by the strong gas  
627 emissions. However, this situation can be different when transposed to urban areas. Gas-  
628 emission occurrences are known from the French Massif Central, especially in its capital city  
629 Clermont-Ferrand, where some degassing spots release as much as 18 to 100 tons CO<sub>2</sub> per  
630 year over 1 m<sup>2</sup> (Gal *et al.*, 2017). In an urban context, buildings and other constructions often  
631 hamper and modify natural degassing pathways, thus focusing and/or enhancing the  
632 release, possibly causing gas accumulations in foundations or cellars. For comparison, the  
633 highest emission rate measured at Escarot leads to a release of 'only' 7.5 tons CO<sub>2</sub> per year  
634 over 1 m<sup>2</sup>. As a result, the population could be exposed to a gas hazard, but there may be no  
635 warning signal, such as H<sub>2</sub>S, in the gas phase or damage to the vegetation. The Escarot case  
636 study can be seen as an analogy to the situation prevailing before human occupation. It

637 strongly suggests that further investigations are needed in (future) urban areas, to evaluate  
638 the potential hazard and, if yes, to assess the composition and volume of gas releases, as is  
639 done in Italy (e.g. Carapezza *et al.*, 2012).

640

#### 641 4. Concluding remarks

642 With the aim of better evaluating emissions of non-anthropogenic gas and their influence on  
643 the global carbon cycle, the 2017 fieldwork on the Escarot site revealed that CO<sub>2</sub> emissions  
644 into the atmosphere are not of minor importance compared those reported from  
645 volcanically more active environments. At ground level, a NNW-SSE elongated structure was  
646 revealed, marked by several degassing centres that are located as a function of soil  
647 properties and their relative permeability to gas transport. In the soil, the presence of CO<sub>2</sub> is  
648 even more common, and a clear relationship with local and regional fault directions was  
649 established. Local biological CO<sub>2</sub> production can be high (up to 10% of soil-gas), thus  
650 contributing to a total mean CO<sub>2</sub> release into the atmosphere of 660 tons per year (tpy) for  
651 the 52,000 m<sup>2</sup> area. This agrees with the magnitude of CO<sub>2</sub> emissions reported by  
652 Hermansson *et al.* (1991), when extrapolated to a similar scale (310 tpy). The present case  
653 highlights the need for better understanding the CO<sub>2</sub> emissions at the scale of the French  
654 Massif Central, because existing evaluations may have missed far higher CO<sub>2</sub> emission rates  
655 associated to mineral springs and/or gas vents. The existence of structures emitting CO<sub>2</sub> in  
656 populated areas should also be taken into account in risk scenarios.

657 The deep-seated contribution is evaluated at over 8,000 tpy of CO<sub>2</sub> and compares well with  
658 gas emissions reported for diffuse degassing in some active volcanic areas. However, gas  
659 emissions may vary throughout the year, depending on the season and on meteorological

660 conditions. Very strong, though temporary, decreases of flux into the atmosphere (up to a  
661 factor 5) are caused by precipitation that saturates the upper soil horizons, and the presence  
662 of snow cover during winter may further reduce the yearly CO<sub>2</sub> budget. In addition, the rise  
663 of deep-seated CO<sub>2</sub> is not a linear process and high-frequency changes in gas-emission rates  
664 have been noted. The result is a quite high uncertainty as to the quantification of such gas  
665 emissions ( $\pm 1,800$  tpy), or about one quarter of the overall estimated amount of CO<sub>2</sub>.

666

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674 **References**

- 675 Aeschbach-Hertig W., Kipfer R., Hofer M., Imboden D.M., Wieler R., Signer P., 1996,  
676 Quantification of gas fluxes from the subcontinental mantle: The example of Laacher See, a  
677 maar lake in Germany, *Geochimica et Cosmochimica Acta*, 60(1), 31-41.
- 678 Aeschbach-Hertig W., Hofer M., Kipfer R., Imboden D.M., Wieler R., 1999, Accumulation of  
679 mantle gases in a permanently stratified volcanic lake (Lac Pavin, France), *Geochimica et*  
680 *Cosmochimica Acta*, 63(19/20), 3357-3372.
- 681 Batard F., Baubron J.C., Bosch B., Marcé A., Risler J.J., 1982, Isotopic identification of gases of  
682 a deep origin in French thermomineral waters, *Journal of Hydrology* 56, 1-21.
- 683 Battani A., Deville E., Faure J.L., Noirez S., Tocqué E., Jeandel E., Benoît Y., Schmitz J.,  
684 Parlouar D., Gal F., Le Pierrès K., Brach M., Braibant G., Bény C., Pokryszka Z., Charmoille A.,  
685 Bentivegna G., Pironon J., de Donato P., Garnier C., Cailteau C., Barrès O., Radilla G., Bauer  
686 A., 2010, Geochemical study of the natural CO<sub>2</sub> emissions in the French Massif Central: How  
687 to predict origin, processes and evolution of CO<sub>2</sub> leakage, *Oil and Gas Science Technology*,  
688 65, 615-633.
- 689 Beaubien S.E., Ciotoli G., Coombs P., Dictor M. C., Krüger M., Lombardi S., Pearce J.M., West  
690 J.M., 2008, The impact of a naturally occurring CO<sub>2</sub> gas vent on the shallow ecosystem and  
691 soil chemistry of a Mediterranean pasture (Latera, Italy), *International Journal of Greenhouse*  
692 *Gas Control*, 2(3), 373-387.
- 693 Blavoux B., Dazy J., 1990, Caractérisation d'une province à CO<sub>2</sub> dans le bassin du Sud-Est de  
694 la France, *Hydrogéologie* 4, 241-252.

- 695 Bloomberg S., Werner C., Rissmann C., Mazot A., Horton T., Gravley D., Kennedy B., Oze C.,  
696 2014, Soil CO<sub>2</sub> emissions as a proxy for heat and mass flow assessment, Taupo Volcanic  
697 Zone, New Zealand, *Geochemistry Geophysics Geosystems*, 15, 4885–4904,  
698 doi:10.1002/2014GC005327.
- 699 Boudoire G., Liuzzo M., DiMuro A., Ferrazzini V., Michon L., Grassa F., Derrien A., Villeneuve  
700 N., Bourdeu A., Brunet C., Giudice G., Gurrieri S., 2017, Investigating the deepest part of a  
701 volcano plumbing system: Evidence for an active magma path below the western flank of  
702 Piton de la Fournaise (La Réunion Island), *Journal of Volcanology and Geothermal Research*  
703 341, 193–207.
- 704 Bräuer K., Geissler W.H., Kämpf H., Niedermann S., Rman N., 2016, Helium and carbon  
705 isotope signatures of gas exhalations in the westernmost part of the Pannonian Basin (SE  
706 Austria/NE Slovenia): Evidence for active lithospheric mantle degassing, *Chemical Geology*,  
707 422, 60–70.
- 708 Bräuer K., Kämpf H., Niedermann S., Wetzel H.-U., 2017, Regional distribution pattern of  
709 carbon and helium isotopes from different volcanic fields in the French Massif Central:  
710 Evidence for active mantle degassing and water transport, *Chemical Geology*, 469, 4–18.
- 711 Brombach T., Hunziker J.C., Chiodini G., Cardellini C., Marini L., 2001, Soil diffuse degassing  
712 and thermal energy fluxes from the southern Lakki plain, Nisyros (Greece), *Geophysical*  
713 *Research Letters*, 28(1), 69–72.
- 714 Brousse R., Rançon J.P., Le Garrec M.J., Tempier P., Suire J., Veyret-Mekdjian Y., D'Arcy D.,  
715 Périchaud J.J., 1990, Explanatory Notes to the 1:50,000-scale geological map of La Tour-  
716 d'Auvergne, BRGM Editions, Orléans, France.

- 717 Burton M.R., Sawyer G.M., Granieri D., 2013, Deep carbon emissions from volcanoes,  
718 *Reviews in Mineralogy and Geochemistry*, 75(1), 323-354.
- 719 Camarda M., Gurrieri S., Valenza M., 2006, CO<sub>2</sub> flux measurements in volcanic areas using  
720 the dynamic concentration method: Influence of soil permeability, *Journal of Geophysical*  
721 *Research*, 111(B05202) doi:10.1029/2005JB003898.
- 722 Camarda M., Gurrieri S., Valenza M., 2009, Effects of soil gas permeability and recirculation  
723 flux on soil CO<sub>2</sub> flux measurements performed using a closed dynamic accumulation  
724 chamber, *Chemical Geology* 265, 387–393.
- 725 Carapezza M.L., Barberi F., Ranaldi M., Ricci T., Tarchini L., Barrancos J., Fischer C., Granieri  
726 D., Lucchetti C., Melian G., Perez N., Tuccimei P., Vogel A., Weber K., 2012, Hazardous gas  
727 emissions from the flanks of the quiescent Colli Albani volcano (Rome, Italy), *Applied*  
728 *Geochemistry* 27, 1767-1782.
- 729 Chiodini G., Frondini F., Raco B., 1996, Diffuse emission of CO<sub>2</sub> from the Fossa Crater,  
730 Vulcano Island (Italy), *Bulletin of Volcanology*, 58(1), 41–50.
- 731 Chiodini G., Cioni R., Guidi M., Raco B., Marini L., 1998, Soil CO<sub>2</sub> flux measurements in  
732 volcanic and geothermal areas, *Applied Geochemistry*, 13(5), 543-552.
- 733 Chiodini G., Baldini A., Barberi F., Carapezza M.L., Cardellini C., Frondini F., Granieri D.,  
734 Ranaldi M., 2007, Carbon dioxide degassing at Latera caldera (Italy): Evidence of geothermal  
735 reservoir and evaluation of its potential energy, *Journal of Geophysical Research*,  
736 112(B12204), doi:10.1029/2006JB004896.
- 737 Chiodini G., Caliro S., Cardellini C., Granieri D., Avino R., Baldini A., Donnini M., Minopoli C.,  
738 2010, Long-term variations of the Campi Flegrei, Italy, volcanic system as revealed by the

- 739 monitoring of hydrothermal activity, *Journal of Geophysical Research*, 115(B03205),  
740 doi:10.1029/2008JB006258.
- 741 Czernochowski-Lauriol I., Pauwels H., Vigouroux P., Le Nindre Y.-M., 2003, The French  
742 carbogaseous province: an illustration of natural processes of CO<sub>2</sub> generation, migration,  
743 accumulation and leakage, In: Gale K., Kaya Y., Editors, Greenhouse gas control technologies,  
744 vol. 1. Amsterdam: Pergamon, p. 411–416.
- 745 Etiope G., Martinelli G., 2002, Migration of carrier and trace gases in the geosphere: an  
746 overview, *Physics of the Earth and Planetary Interiors* 129, 185–204.
- 747 Etiope G., Zwahlen C., Anselmetti F.S., Kipfer R., Schubert C.J., 2010, Origin and flux of a gas  
748 seep in the Northern Alps (Giswil, Switzerland), *Geofluids*, 10, 476-485.
- 749 Etiope G., 2015, Natural Gas Seepage – The Earth's Hydrocarbon Degassing, Springer Eds.,  
750 199 p., DOI 10.1007/978-3-319-14601-0.
- 751 Evans W.C., Sorey M.L., Kennedy B.M., Stonestrom D.A., Rogie J.D., Shuster D.L., 2001, High  
752 CO<sub>2</sub> emissions through porous media: transport mechanisms: and implications for flux  
753 measurement and fractionation, *Chemical Geology* 177, 15-29.
- 754 Favara R., Giammanco S., Inguaggiato S., Pecoraino G., 2001, Preliminary estimate of CO<sub>2</sub>  
755 output from Pantellaria Island volcano (Sicily, Italy): evidence of active mantle degassing,  
756 *Applied Geochemistry* 16, 883-894.
- 757 Fleischer R.L., Mogro-Campero A., 1978, Mapping of integrated radon emanation for  
758 detection of long-distance migration of gases within the Earth: Techniques and Principles,  
759 *Journal of Geophysical Research*, 83(B7), 3539-3549

- 760 France L., Demacon M., Gurenko A.A., Briot D., 2016, Oxygen isotopes reveal crustal  
761 contamination and a large, still partially molten magma chamber in Chaîne des Puys (French  
762 Massif Central), *Lithos* 260, 328-338.
- 763 Fridriksson T., Kristjansson B.R., Armannsson H., Margretardottir E., Olafsdottir S., Chiodini  
764 G., 2006, CO<sub>2</sub> emissions and heat flow through soil, fumaroles, and steam heated mud pools  
765 at the Reykjanes geothermal area, SW Iceland, *Applied Geochemistry*, 21, 1551-1569.
- 766 Frondini F., Chiodini G., Caliro S., Cardellini C., Granieri D., Ventura G., 2004, Diffuse CO<sub>2</sub>  
767 degassing at Vesuvio, Italy, *Bulletin of Volcanology*, 66, 642-651.
- 768 Gal F., Brach M., Braibant G., Jouin F., Michel K., 2011, CO<sub>2</sub> escapes in the Laacher See  
769 region, East Eifel, Germany: application of natural analogue onshore and offshore  
770 geochemical monitoring, *International Journal of Greenhouse Gas Control* 5, 1099-1118.
- 771 Gal F., Gadalia A., 2011, Soil gas measurements around the most recent volcanic system of  
772 metropolitan France (Lake Pavin, Massif Central), *Comptes Rendus Geosciences* 343, 43-54.
- 773 Gal F., Brach M., Braibant G., Bény C., Michel K., 2012, What can be learned from natural  
774 analogues studies in view of CO<sub>2</sub> leakage issues in Carbon Capture and Storage applications?  
775 Geochemical case study of Sainte-Marguerite area (French Massif Central), *International*  
776 *Journal of Greenhouse Gas Control* 10, 470-485.
- 777 Gal F., Proust E., Bentivegna G., Leconte S., De Lary de Latour L., Loschetter A., Pokryszka Z.,  
778 Collignan B., 2017, What may be the consequences of a CO<sub>2</sub> leakage? Insights from soil gas  
779 measurements in an urban area – Clermont-Ferrand, French Massif Central, *Energy Procedia*  
780 114, 3006-3019.

- 781 Halmer M.M., Schmincke H.U., Graf H.F., 2002, The annual volcanic gas input into the  
782 atmosphere, in particular into the stratosphere: a global data set for the past 100 years,  
783 *Journal of Volcanology and Geothermal Research* 115, 511-528.
- 784 Hermansson P.H., Akerblom G., Chyssler J., Linden A., 1991, Geogas—a carrier or a tracer?  
785 Statens Karnbransle Namnd (SKN) Report 51, National Board for Spent Nuclear Fuel,  
786 Stockholm, p. 66.
- 787 Hernández P.A., Pérez N.M., Salazar J.M., Nakai S.I., Notsu K., Wakita H., 1998, Diffuse  
788 emission of carbon dioxide, methane, and helium-3 from Teide Volcano, Tenerife, Canary  
789 Islands, *Geophysical Research Letters*, 25(17), 3311-3314.
- 790 Hernández-Perez P., Notsu K., Tsurumi M., Mori T., Ohno M., Shimoike Y., Salazar J., Pérez  
791 N., 2003, Carbon dioxide emissions from soils at Hakkoda, north Japan, *Journal of*  
792 *Geophysical Research*, 108(B4), 2210, doi:10.1029/2002JB001847.
- 793 Hinkle M., 1994, Environmental conditions affecting concentrations of He, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> in  
794 soft gases, *Applied Geochemistry*, 9, 53-63.
- 795 Holloway S., Pearce J.M., Hards V.L., Ohsumi T., Gale J., 2007, Natural emissions of CO<sub>2</sub> from  
796 the geosphere and their bearing on the geological storage of carbon dioxide, *Energy* 32,  
797 1194-1201.
- 798 Inguaggiato S., Jácome Paz M.P., Mazot A., Delgado Granados H., Inguaggiato C., Vita F.,  
799 2013, CO<sub>2</sub> output discharged from Stromboli Island (Italy), *Chemical Geology* 339, 52-60.
- 800 Jähne B., Heinz G., Dietrich W., 1987, Measurement of the diffusion coefficients of sparingly  
801 soluble gases in water, *Journal of Geophysical Research*, 92(C10), 10767-10776

- 802 Jézéquel D., Michard G., Viollier E., Agrinier P., Albéric P., Lopes F., Abril G., Bergonzini L.,  
803 2015, Carbon Cycle in a Meromictic Crater Lake: Lake Pavin, France, *In Lake Pavin - History,*  
804 *Geology, Biogeochemistry, and Sedimentology of a Deep Meromictic Maar Lake*, Sime-  
805 Ngando T., Boivin P., Chapron E., Jézéquel D., Meybeck M. Eds, Springer, 10.1007/978-3-319-  
806 39961-4.
- 807 Judd A., 2005, Gas Emissions from Mud Volcanoes. In: Martinelli G., Panahi B. (eds) *Mud*  
808 *Volcanoes, Geodynamics and Seismicity*. NATO Science Series (Series IV: Earth and  
809 *Environmental Series*), vol. 51. Springer, Dordrecht.
- 810 Kerrick D.M., 2001, Present and past non-anthropogenic CO<sub>2</sub> degassing from the solid earth,  
811 *Reviews of Geophysics*, 39(4), 565-585.
- 812 Krüger M., Jones D., Frerichs J., Oppermann B.I., West J., Coombs P., Green K., Barlow T.,  
813 Lister R., Shaw R., Strutt M., Möller I., 2011, Effects of elevated CO<sub>2</sub> concentrations on the  
814 vegetation and microbial populations at a terrestrial CO<sub>2</sub> vent at Laacher See, Germany,  
815 *International Journal of Greenhouse Gas Control*, 5, 1093-1098.
- 816 Kämpf H., Bräuer K., Schumann J., Hahne K., Strauch G., 2013, CO<sub>2</sub> discharge in an active,  
817 non-volcanic continental rift area (Czech Republic): Characterisation ( $\delta^{13}\text{C}$ ,  $^3\text{He}/^4\text{He}$ ) and  
818 quantification of diffuse and vent CO<sub>2</sub> emissions, *Chemical Geology*, 339, 71-83.
- 819 Lewicki J.L., Bergfeld D., Cardellini C., Chiodini G., Granieri D., Varley N., Werner C., 2005,  
820 Comparative soil CO<sub>2</sub> flux measurements and geostatistical estimation methods on Masaya  
821 volcano, Nicaragua, *Bulletin of Volcanology*, 68, 76-90.

- 822 Lewicki J.L., Birkholzer J., Tsang C.-F., 2007, Natural and industrial analogues for leakage of  
823 CO<sub>2</sub> from storage reservoirs: identification of features, events, and processes and lessons  
824 learned, *Environmental Geology*, 52, 457-467.
- 825 Liuzzo M., Di Muro A., Giudice G., Michon L., Ferrazzini V., Gurrieri S., 2015, New evidence of  
826 CO<sub>2</sub> soil degassing anomalies on Piton de la Fournaise volcano and the link with volcano  
827 tectonic structures, *Geochemistry Geophysics Geosystems*, 16, 4388-4404,  
828 doi:10.1002/2015GC006032.
- 829 Meybeck M., 2015, Pavin, the Birthplace of French Limnology (1770–2012), and Its Degassing  
830 Controversy (1986–2016), *In Lake Pavin - History, Geology, Biogeochemistry, and*  
831 *Sedimentology of a Deep Meromictic Maar Lake*, Sime-Ngando T., Boivin P., Chapron E.,  
832 Jézéquel D., Meybeck M. Eds, Springer, 10.1007/978-3-319-39961-4.
- 833 Mörner N.-A., Etiope G., 2002, Carbon degassing from the lithosphere, *Global and Planetary*  
834 *Change* 33, 185-203.
- 835 Notsu K., Mori T., Chanchah Do Vale S., Kagi H., Ito T., 2006, Monitoring quiescent volcanoes  
836 by diffuse CO<sub>2</sub> degassing: case study of Mt. Fuji, Japan, *Pure Applied Geophysics* 163, 825-  
837 835.
- 838 Oertel C., Matschullat J., Zurba K., Zimmermann F., Erasmi S., 2016, Greenhouse gas  
839 emissions from soils — A review, *Chemie der Erde* 76, 327-352.
- 840 Parkin T.B., Kaspar T.C., 2003, Temperature controls on diurnal carbon dioxide flux:  
841 implications for estimating soil carbon loss, *Soil Science Society of America Journal* 67, 1763-  
842 1772.

- 843 Parkin T.B., Venterea R.T., 2010, Sampling Protocols – Chapter 3 – Chamber-Based Trace Gas  
844 Flux Measurements, *In Sampling Protocols*. R.F. Follett editor, 3-1 to 3-39.
- 845 Pearce J., Czernichowski-Lauriol I., Lombardi S., Brune S., Nador A., Baker J., Pauwels H.,  
846 Hatziyannis G., Beaubien S., Faber E., 2004, A review of natural CO<sub>2</sub> accumulations in Europe  
847 as analogues for geological sequestration, *Geological Society, London, Special Publications*,  
848 233, 29-41.
- 849 Pedone M., Viveiros F., Aiuppa A., Giudice G., Grassa F., Gagliano A.L., Francofonte V.,  
850 Ferreira T., 2015, Total (fumarolic + diffuse soil) CO<sub>2</sub> output from Furnas volcano, *Earth*,  
851 *Planets and Space* 67:174.
- 852 Pokryszka Z., Adelise F., Farret R., Lafortune S., Michel E., Rupasinghe S., 2017, Valeurs de  
853 référence du flux de CO<sub>2</sub> et de CH<sub>4</sub> d'origine naturelle biogénique des sols, Rapport INERIS  
854 DRS-17-164646-05731A, 48 p.,  
855 [https://www.ineris.fr/sites/ineris.fr/files/contribution/Documents/INERIS\\_DRS-17-164646-](https://www.ineris.fr/sites/ineris.fr/files/contribution/Documents/INERIS_DRS-17-164646-05731_Referentiel-flux-CO2-CH4-sols_ZPo.pdf)  
856 [05731\\_Referentiel-flux-CO2-CH4-sols\\_ZPo.pdf](https://www.ineris.fr/sites/ineris.fr/files/contribution/Documents/INERIS_DRS-17-164646-05731_Referentiel-flux-CO2-CH4-sols_ZPo.pdf)
- 857 Rinaldi A.P., Vandemeulebrouck J., Todesco M., Viveiros F., 2012, Effects of atmospheric  
858 conditions on surface diffuse degassing, *Journal of Geophysical Research*, 117(B11201),  
859 doi:10.1029/2012JB009490.
- 860 Roberts J.J., Wood R.A., Haszeldine R.S., 2011, Assessing the health risks of natural CO<sub>2</sub> seeps  
861 in Italy, *PNAS*, 108(40), 16545-16548.
- 862 Rogie J.D., Kerrick D.M., Chiodini G., Frondini F., 2000, Flux measurements of non-volcanic  
863 emission from some vents in central Italy, *Journal of Geophysical Research*, 105(B4), 8435-  
864 8445.

- 865 Romanak K.D., Bennett P.C., Yang C., Hovorka S.D., 2012, Process-based approach to CO<sub>2</sub>  
866 leakage detection by vadose zone gas monitoring at geologic CO<sub>2</sub> storage sites, *Geophysical*  
867 *Research Letters* 39, L15405.
- 868 Sinclair A.J., 1974, Selection of thresholds in geochemical data using probability graphs,  
869 *Journal of Geochemical Exploration*, 3, 129-149.
- 870 Smith A.Y., Barretto P.M.C., Pournis S., 1976, Radon methods in uranium exploration, IAEA  
871 paper SM-208/52, in Exploration for uranium ore deposits - Proceedings of a symposium  
872 held in Vienna, 29 March - 2 April 1976, organized by IAEA and NEA (OECD), IAEA  
873 SI/PUB/434, ISBN 92-0-040076-0.
- 874 Sorey M.L., Evans W.C., Kennedy B.M., Farrar C.D., Hainsworth L.J., Hausback B., 1998,  
875 Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath Mammoth  
876 Mountain, California, *Journal of Geophysical Research* 103(B7), 15303-15323.
- 877 Toutain J.P., Baubron J.C., 1999, Gas geochemistry and seismotectonics: a review,  
878 *Tectonophysics* 304, 1-27.
- 879 Viveiros F., Ferreira T., Vieira J.C., Silva C., Gaspar J.L., 2008, Environmental influences on soil  
880 CO<sub>2</sub> degassing at Furnas and Fogo volcanoes (São Miguel Island, Azores archipelago), *Journal*  
881 *of Volcanology and Geothermal Research*, 177(4), 883-893.
- 882 Viveiros F., Ferreira T., Silva C., Gaspar J.L., 2009, Meteorological factors controlling soil  
883 gases and indoor CO<sub>2</sub> concentration: A permanent risk in degassing areas, *Science of the*  
884 *Total Environment* 407, 1362-1372.
- 885 Viveiros F., Cardellini C., Ferreira T., Caliro S., Chiodini G., Silva C., 2010, Soil CO<sub>2</sub> emissions at  
886 Furnas volcano, São Miguel Island, Azores archipelago: Volcano monitoring perspectives,

- 887 geomorphologic studies, and land use planning application, *Journal of Geophysical Research*,  
888 115 (B12208), doi:10.1029/2010JB007555.
- 889 Viveiros F., Vandemeulebrouck J., Rinaldi A.P., Ferreira T., Silva C., Cruz J.V., 2014, Periodic  
890 behavior of soil CO<sub>2</sub> emissions in diffuse degassing areas of the Azores archipelago:  
891 Application to seismovolcanic monitoring, *Journal of Geophysical Research Solid Earth*, 119,  
892 7578-7597, doi:10.1002/2014JB011118.
- 893 Weiss R.F., 1971, Solubility of helium and neon in water and seawater, *Journal of Chemical*  
894 *and Engineering Data*, 16, 235-241.
- 895 Weiss R.F., 1974, Carbon dioxide in water and seawater: the solubility of a non-ideal gas,  
896 *Marine Chemistry*, 2, 203-215.
- 897 Werner C., Brantley S., Boomer K., 2000, CO<sub>2</sub> emissions related to the Yellowstone volcanic  
898 system. 2. Statistical sampling, total degassing and transport mechanism, *Journal of*  
899 *Geophysical Research*, 105(B5), 10831-10846.
- 900 Werner C., Brantley S., 2003, CO<sub>2</sub> emissions from the Yellowstone volcanic system,  
901 *Geochemistry Geophysics Geosystems*, 4(7), 1061, doi:10.1029/2002GC000473.
- 902 Werner C., Evans W.C., Poland M., Tucker D.S., Doukas M.P., 2009, Long-term changes in  
903 quiescent degassing at Mount Baker Volcano, Washington, USA; Evidence for a stalled  
904 intrusion in 1975 and connection to a deep magma source, *Journal of Volcanology and*  
905 *Geothermal Research* 186, 379–386.
- 906 Werner C., Bergfeld D., Farrar C.D., Doukas M.P., Kelly P.J., Kern C., 2014, Decadal-scale  
907 variability of diffuse CO<sub>2</sub> emissions and seismicity revealed from long-term monitoring

908 (1995–2013) at Mammoth Mountain, California, USA, *Journal of Volcanology and*  
909 *Geothermal Research*, 289, 51–63.

910 **Figure captions**

911 *Figure 1: Location of the study area.*

912 *Top: Location of soil-gas sampling sites (red squares) performed around Lake Pavin (Gal and*  
913 *Gadalia, 2011).*

914 *Bottom: Detailed view of the Escarot site: yellow arrows indicate the precise position of the*  
915 *mofette as defined in the 2011 paper and the piezometer defined as a “wet mofette” by*  
916 *Bräuer et al. (2017). Sampling sites of soil-gas flux and soil-gas concentration in June 2017*  
917 *are indicated by blacked and concentric circles, respectively. Blue pictograms show areas*  
918 *where gas bubbles are observed in stagnant surface puddles.*

919 *Background satellite view from Google Earth.*

920 *Figure 2: Typology of the flux emissions (CO<sub>2</sub> flux and O<sub>2</sub> depletion).*

921 *Point A15 show regular CO<sub>2</sub> enrichment inside the chamber; points A8 and Z16 show short-*  
922 *term variations of the CO<sub>2</sub> enrichment; point E12 show quick sensor saturation; point Z32*  
923 *show decrease of the CO<sub>2</sub> concentration over time; points BZ8 and E12 show O<sub>2</sub> depletion.*  
924 *Location of the measurement points is indicated on the satellite view.*

925 *Figure 3: Top: Atmospheric meteorological conditions (air temperature, atmospheric*  
926 *pressure, wind speed and amount of precipitation) just before before and during the June*  
927 *2017 survey, on an hourly basis (data from Laqueuille weather station*  
928 *<http://www.meteociel.fr/climatologie/villes.php?code=204&mois=6&annee=2017>).*

929 *Bottom: Detailed view of the survey parameters; temperature, pressure and relative humidity*  
930 *data from the sensors mounted on the flux chamber are indicated by black, red and green*  
931 *dots, respectively.*

932 *Figure 4: A: Box plots for soil-gas concentrations data – studies from 2008 to 2012.*  
933 *B: Box plots for soil-gas concentrations data – 2017 study.*  
934 *C: Box plots for soil CO<sub>2</sub> flux. 1: Standard Temperature- and Pressure-corrected data. 2: STP*  
935 *data using steepest slopes in case of fluctuating gas emissions corresponding to gas flushes.*  
936 *3: STP data corrected to take into account the existence of these gas flushes) and box plot for*  
937 *O<sub>2</sub> depletion. 4. The Coefficient of Variation (CV = Standard Deviation divided by mean value)*  
938 *is indicated for each dataset (in blue).*

939 *Figure 5: A: O<sub>2</sub> vs. CO<sub>2</sub> binary plot; dilution lines correspond to the intrusion of CO<sub>2</sub> as a pure*  
940 *phase with end-members corresponding to the CO<sub>2</sub>-O<sub>2</sub> composition of the atmosphere, and*  
941 *to the CO<sub>2</sub>-O<sub>2</sub> composition of biologically produced CO<sub>2</sub> and consumed O<sub>2</sub> (at 5% and 10%*  
942 *CO<sub>2</sub>).*

943 *B: <sup>4</sup>He vs. CO<sub>2</sub> binary plot.*

944 *C: O<sub>2</sub> depletion vs. STP-normalized CO<sub>2</sub> flux binary plot (domain of biological flux from the*  
945 *synthesis of CO<sub>2</sub> fluxes in France; Pokryszka et al., 2017). Flux data including a gas-flush*  
946 *correction are indicated by yellow stars.*

947 *Figure 6: A: CO<sub>2</sub> concentration vs. CO<sub>2</sub> flux binary plot.*

948 *B: <sup>4</sup>He vs. CO<sub>2</sub> flux binary plot; blue triangles: data from June 26<sup>th</sup>; pink triangles: data from*  
949 *June 27<sup>th</sup>; green domain: data from Pokryszka et al. (2017); other domains: see text for*  
950 *explanation.*

951 *Figure 7: Influence of precipitation events on flux acquisition – see text for explanation. The*  
952 *X-axis shows the duration of the measurement (typically 3 minutes) and the Y-axis shows the*  
953 *increase of CO<sub>2</sub> concentration inside the chamber.*

954 *Figure 8: Relation between STP-corrected CO<sub>2</sub> flux and CO<sub>2</sub> flux corrected from gas flushes*  
955 *(blue squares), and CO<sub>2</sub> flux corrected from gas flushes and from the effect of precipitation*  
956 *events (red squares); green domain: data from Pokryszka et al. (2017).*

957 *Figure 9: Probability plots for CO<sub>2</sub> and helium concentrations, and CO<sub>2</sub> flux. CO<sub>2</sub>-flux data are*  
958 *considered as measured in the field (normalized to STP conditions) and corrected for*  
959 *precipitation influence (see text for the correction procedure). The 2008-2012 dataset refers*  
960 *to the entire dataset, i.e. Gal and Galalia (2011) plus some unpublished data from 2012.*

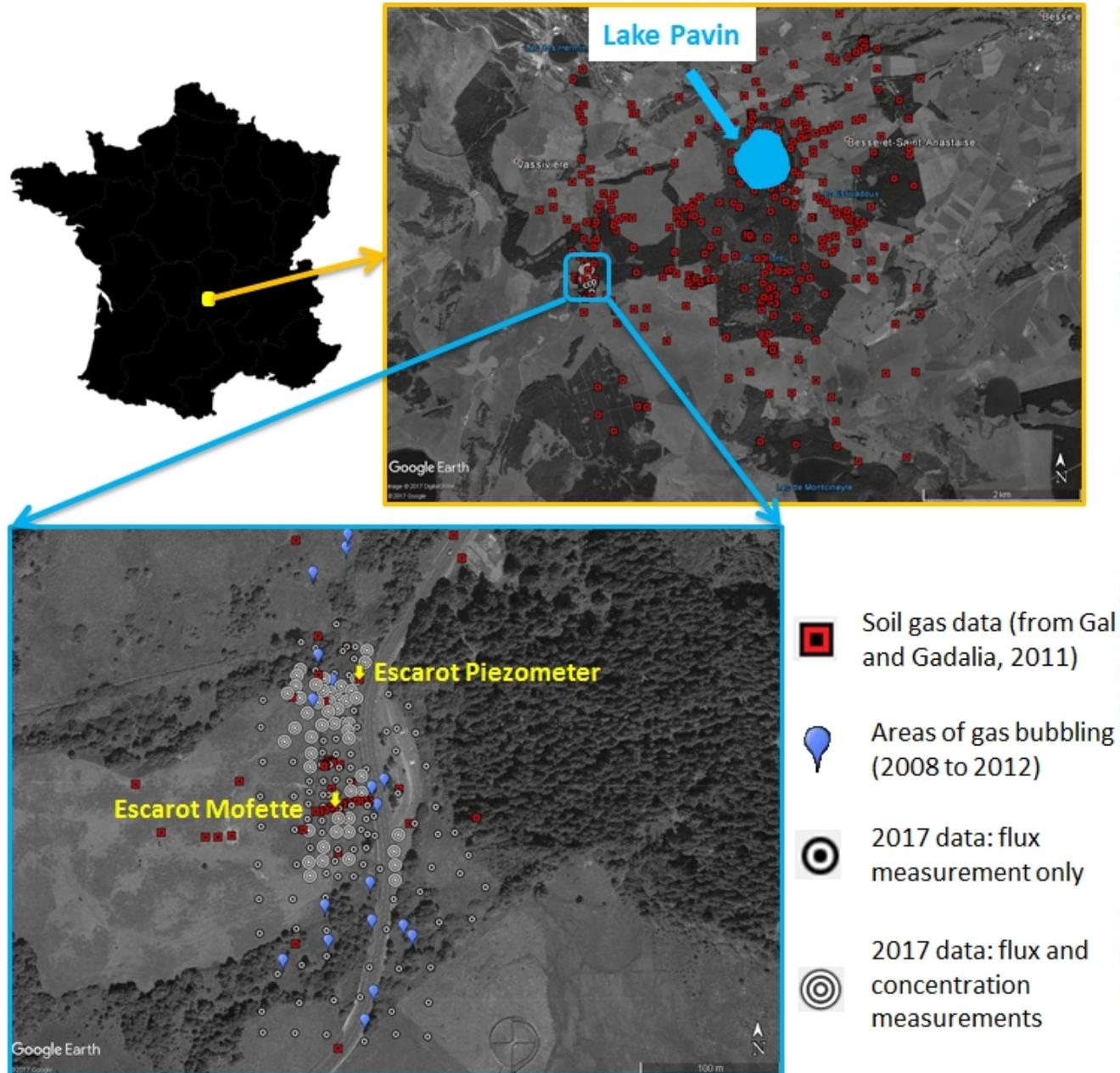
961 *Figure 10: A: Various interpolated maps for CO<sub>2</sub> flux: from left to right: using STP normalized*  
962 *data; using STP-normalized data and the gas-flush correction; using additional correction to*  
963 *account for precipitation effect. Dashed line shows the NNW-SSE direction.*

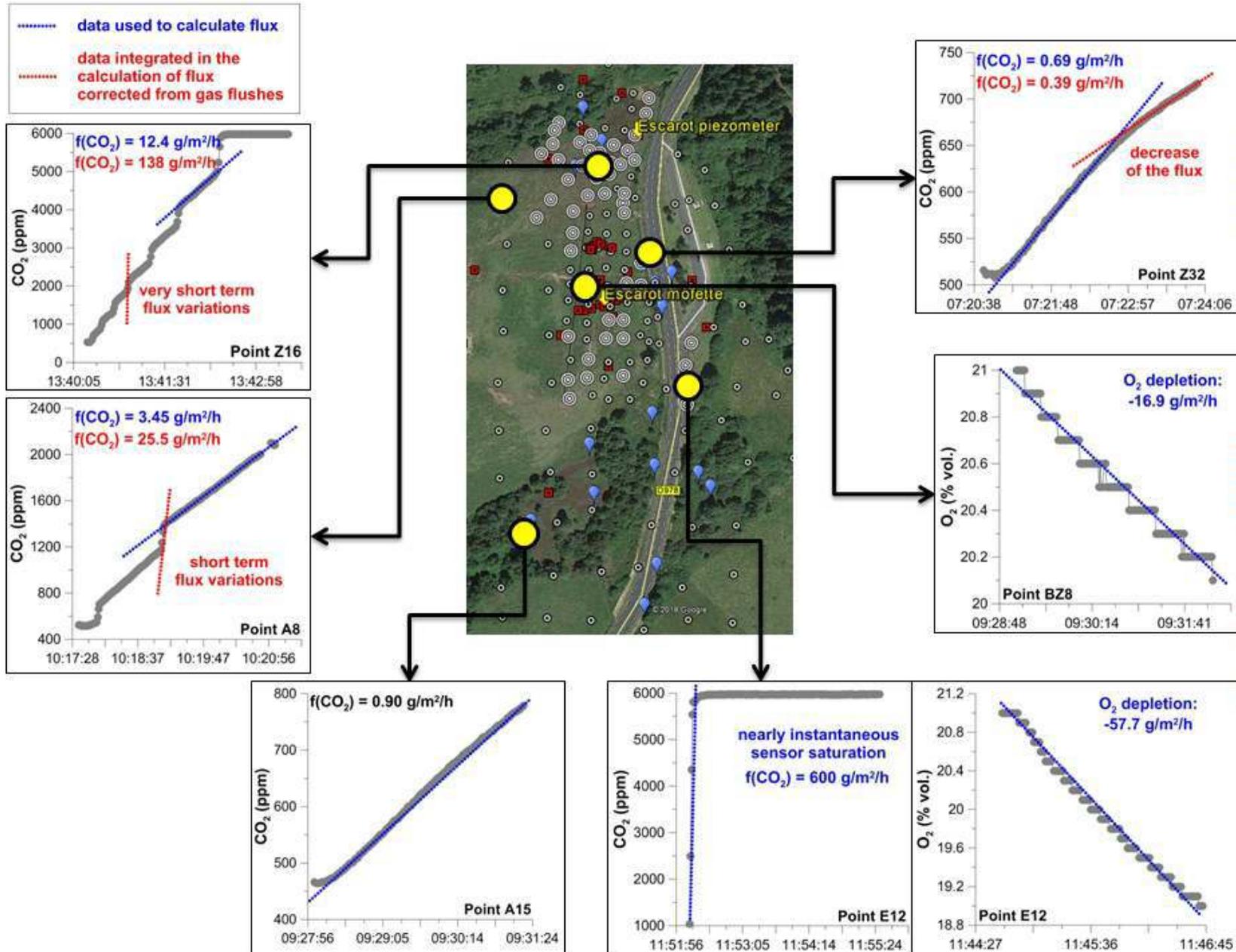
964 *B: Interpolated map for O<sub>2</sub> depletion – scale similar to that of CO<sub>2</sub> flux. On the right, part of*  
965 *the 1:50,000-scale geological map showing the NNW-SSE fault (dashed line).*

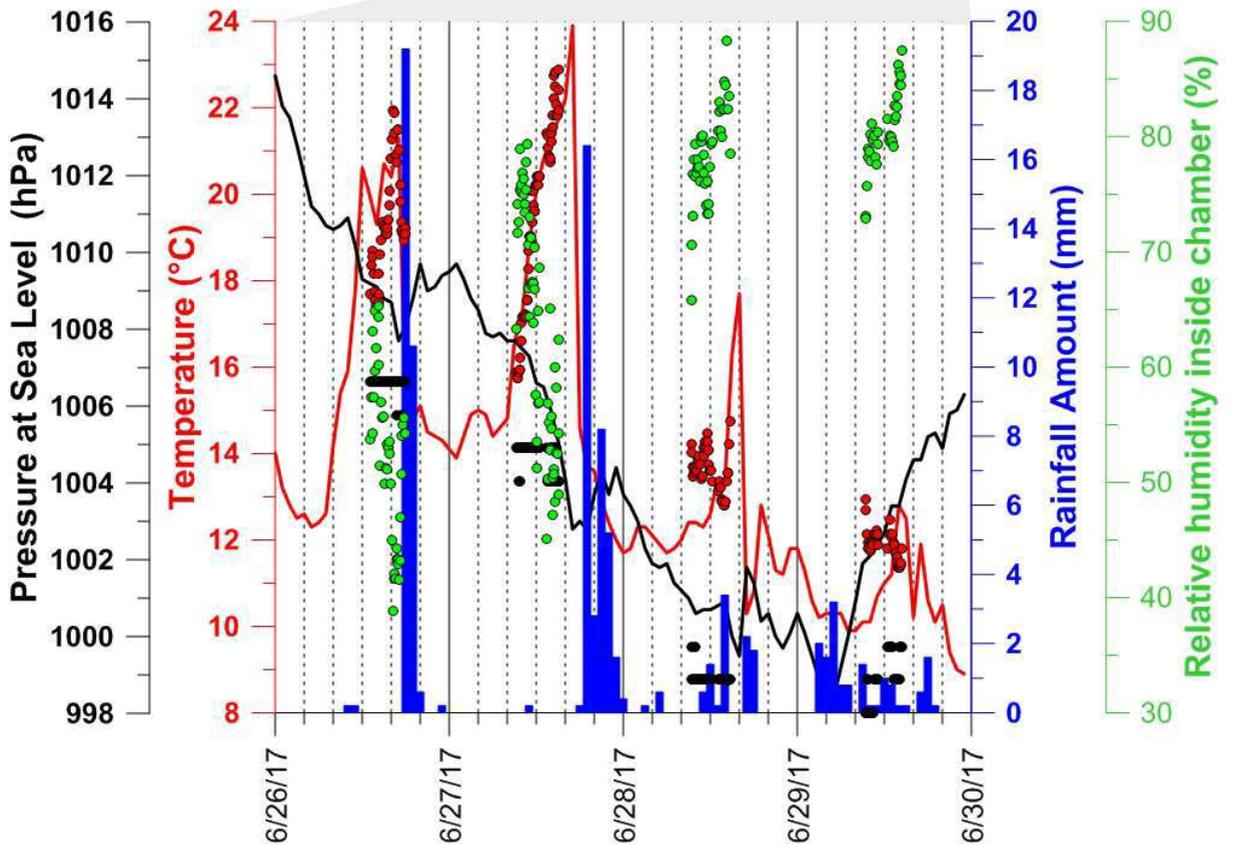
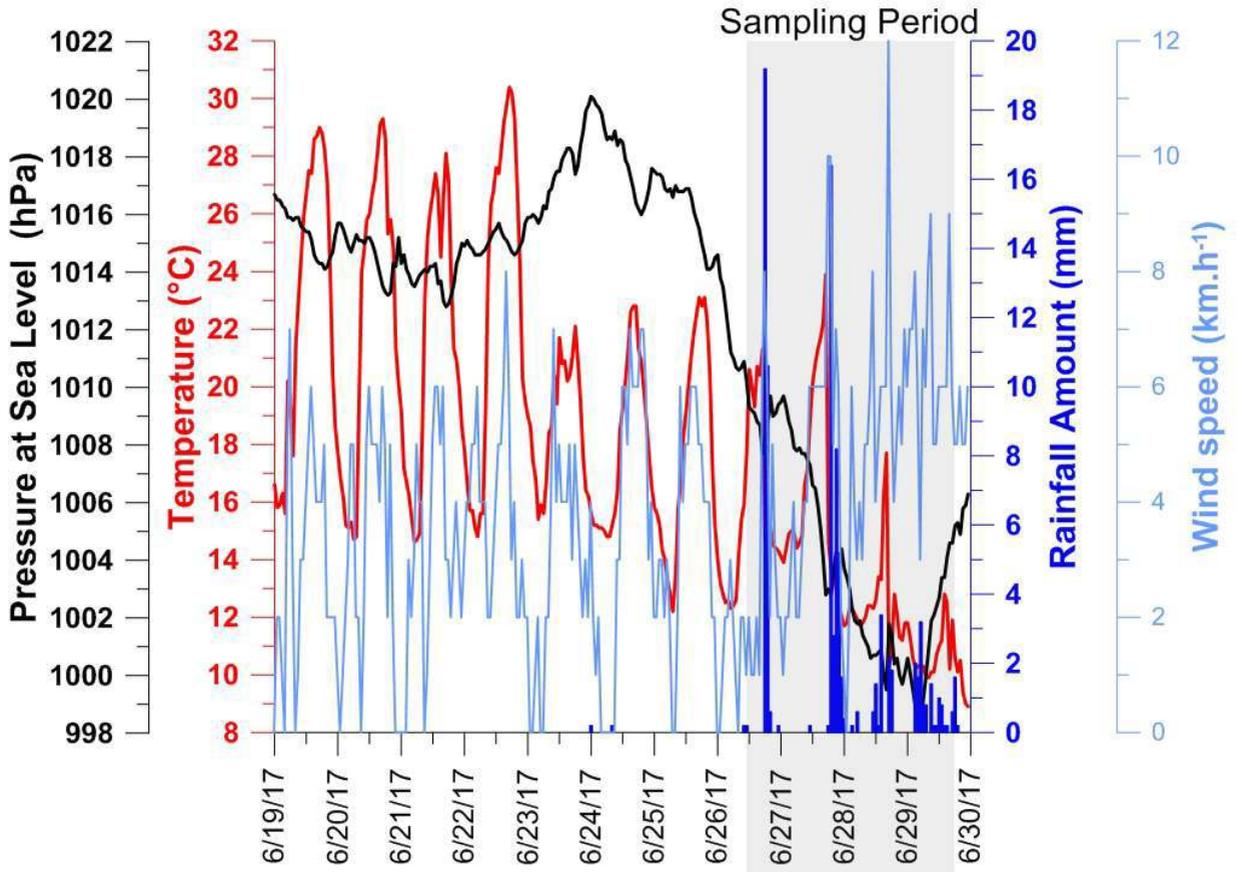
966 *C: From left to right: interpolated maps for CO<sub>2</sub>, O<sub>2</sub> and <sup>4</sup>He concentrations in soil gas (dashed*  
967 *rectangles show the area used for flux interpolations). All maps were constructed with*  
968 *variogram results.*

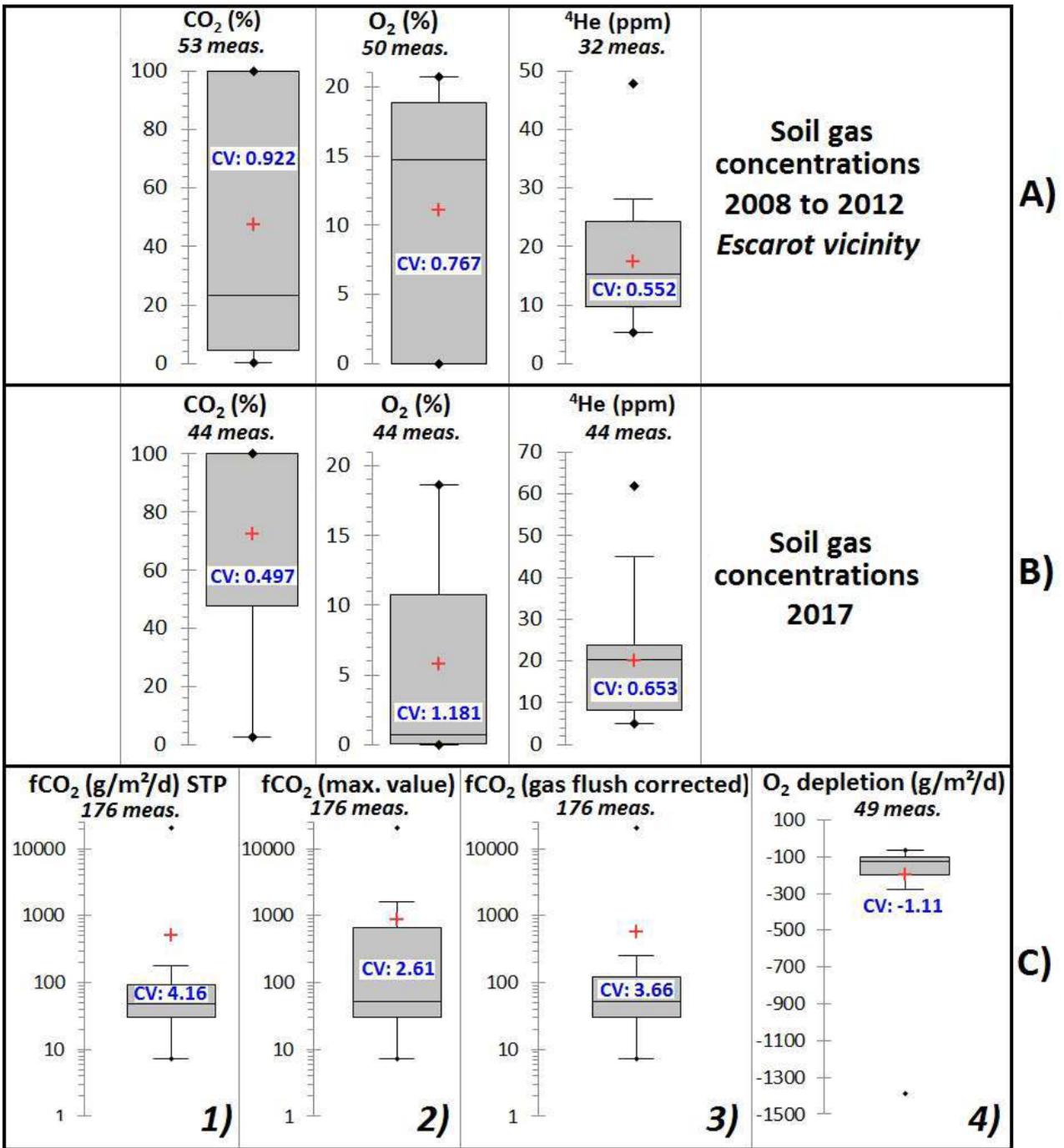
969 **Table caption**

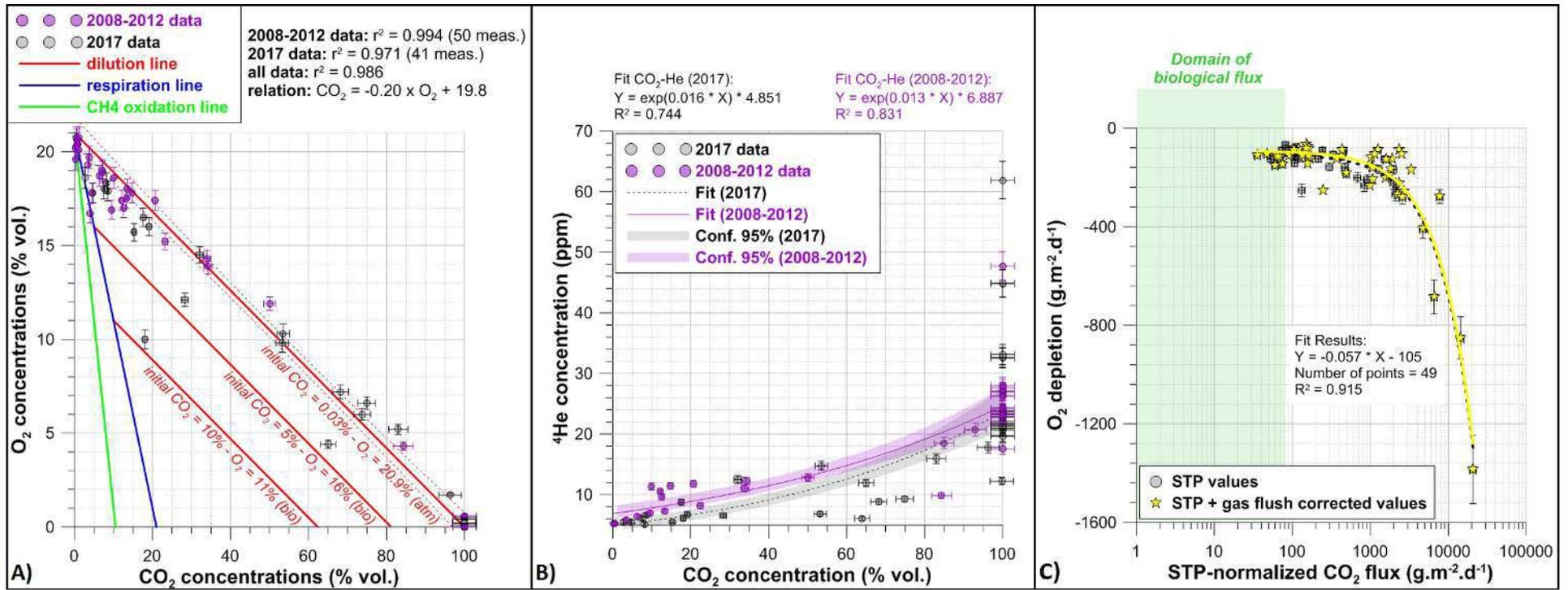
970 *Table 1: evaluation of CO<sub>2</sub> emissions in the atmosphere; see text for details.*

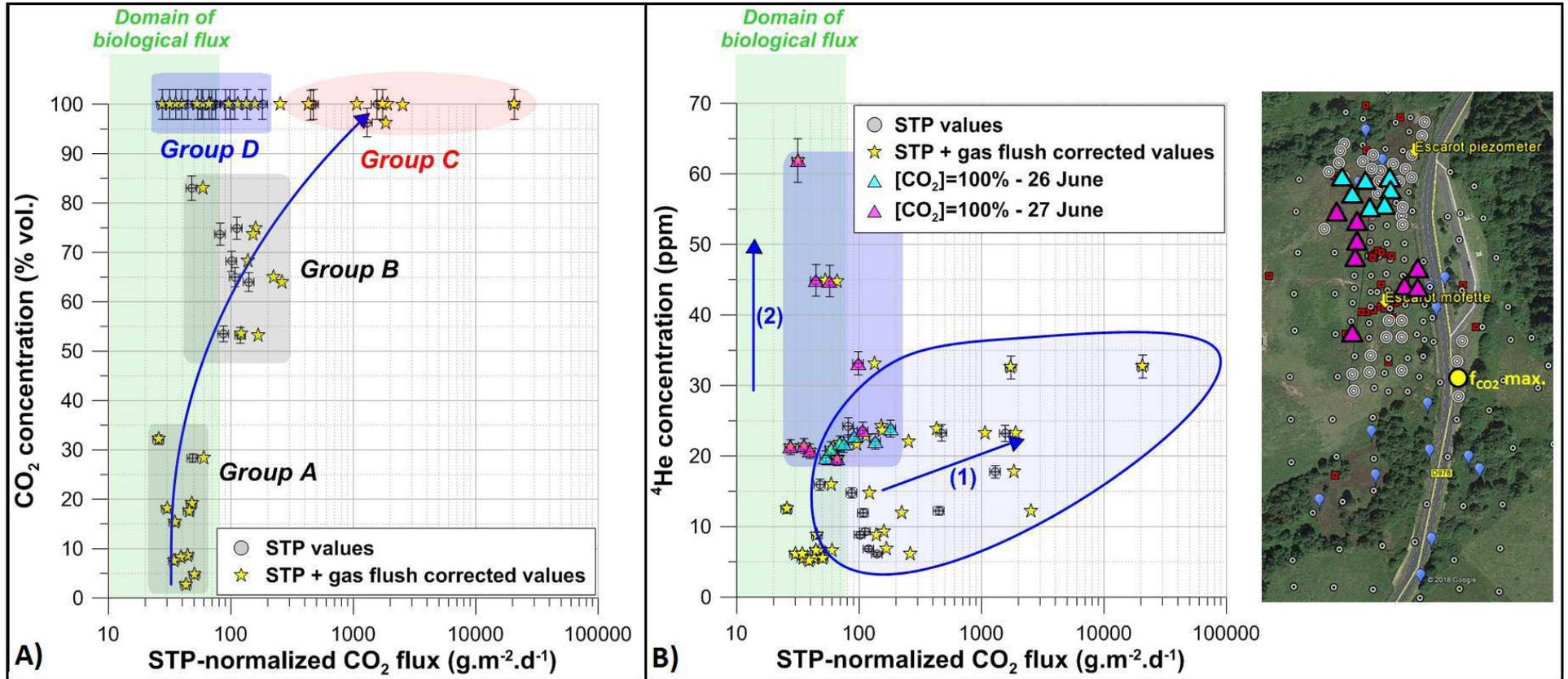


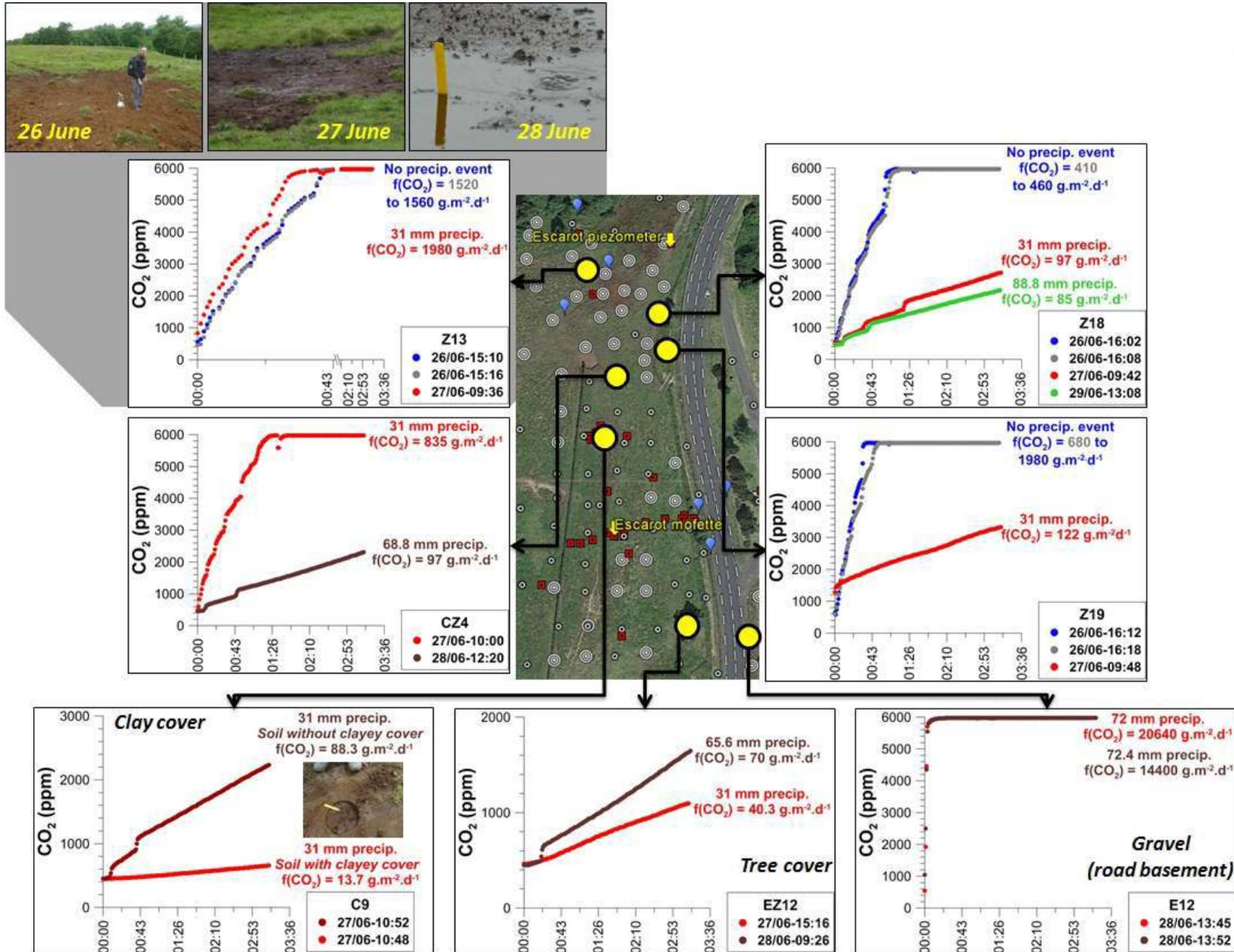


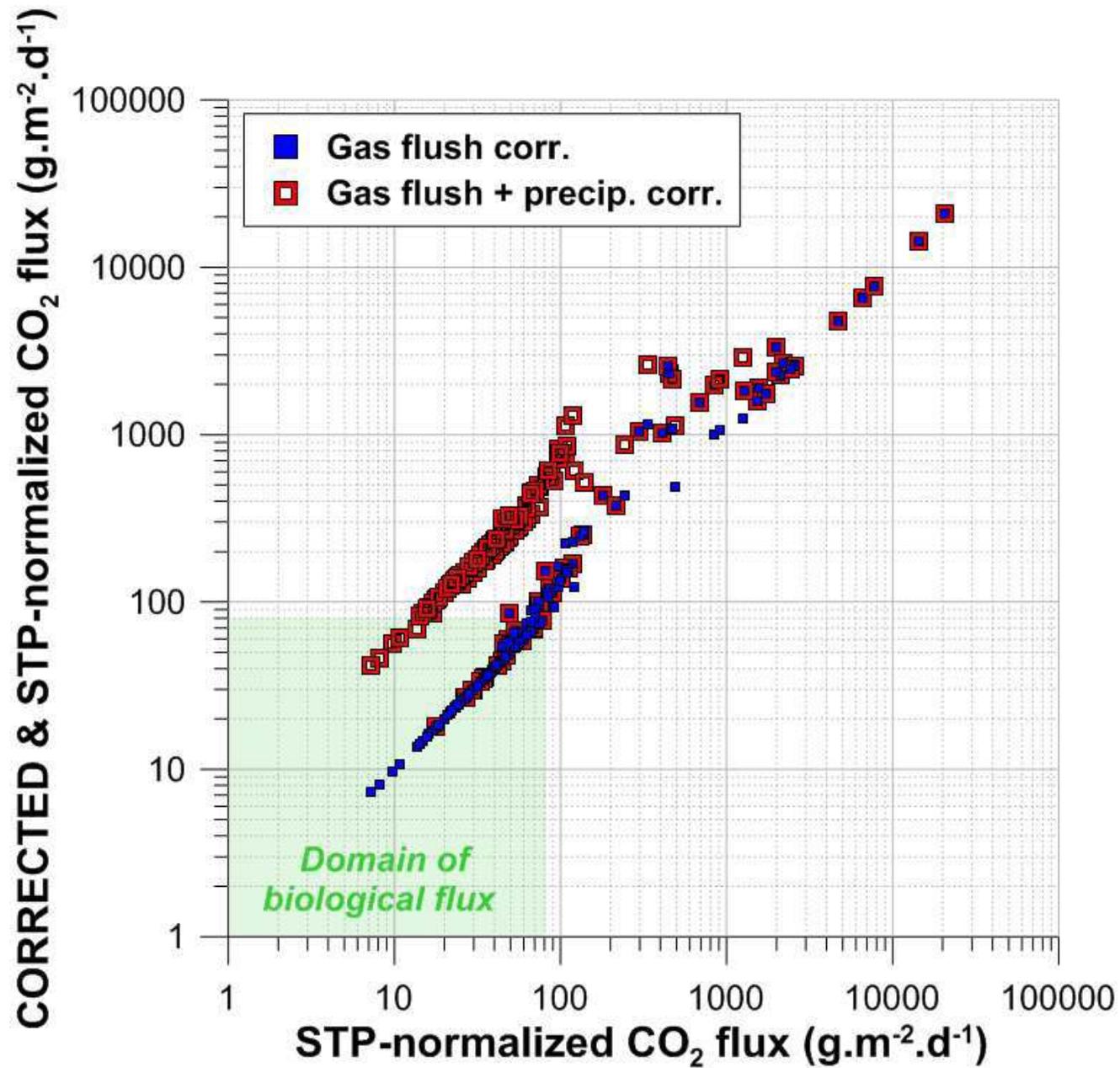


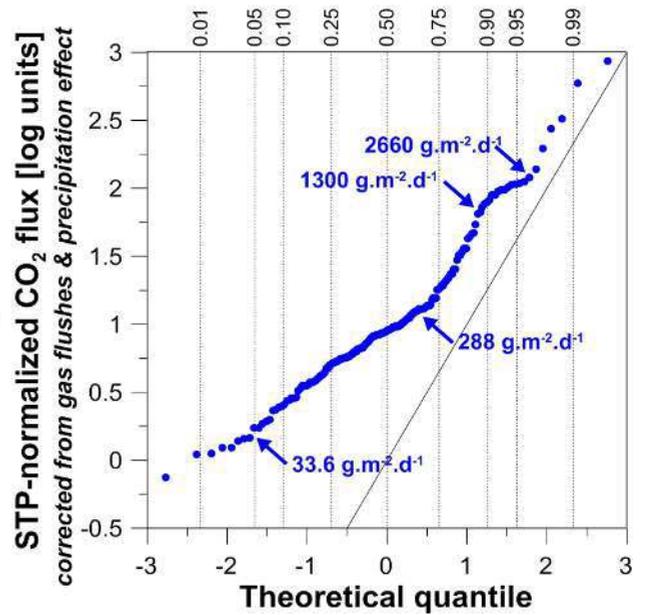
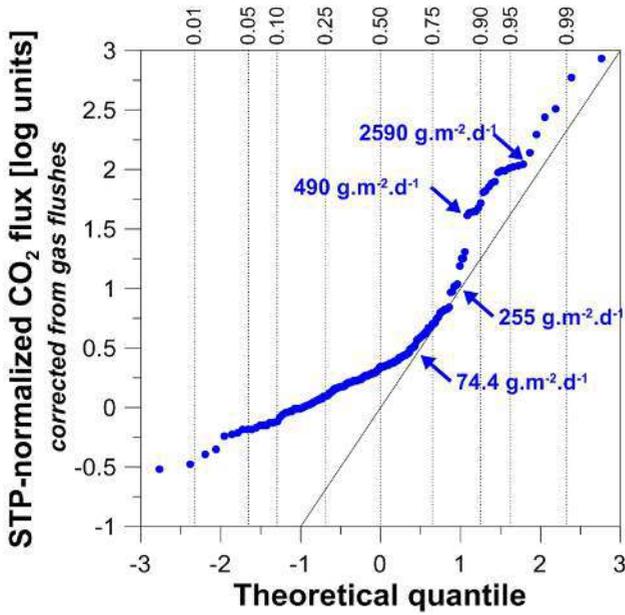
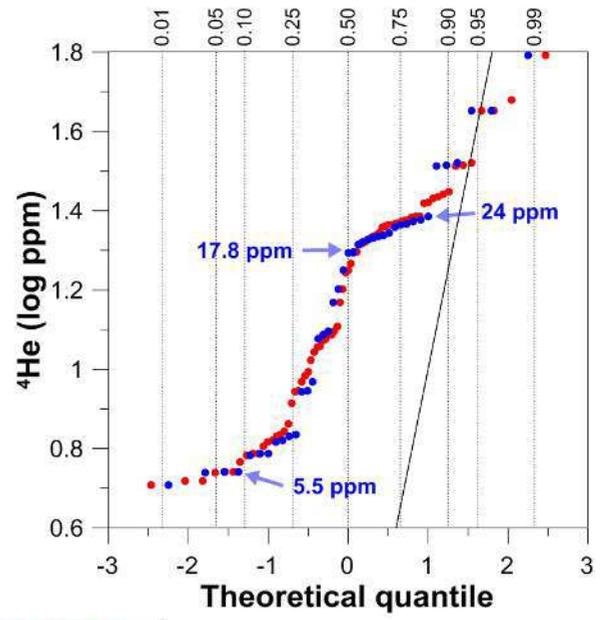
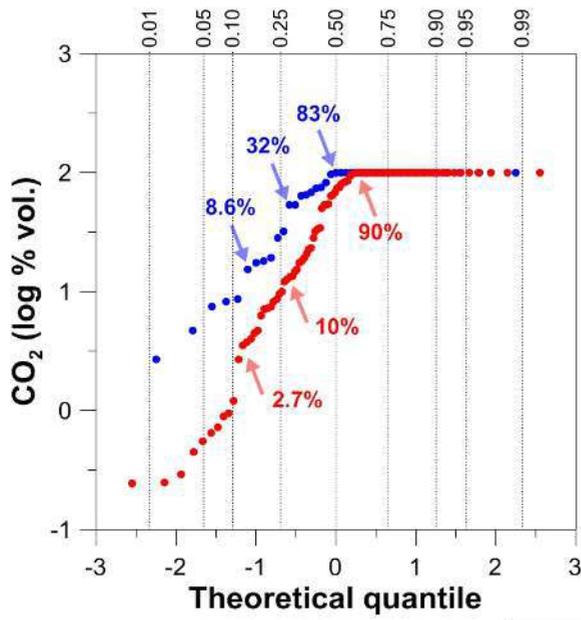


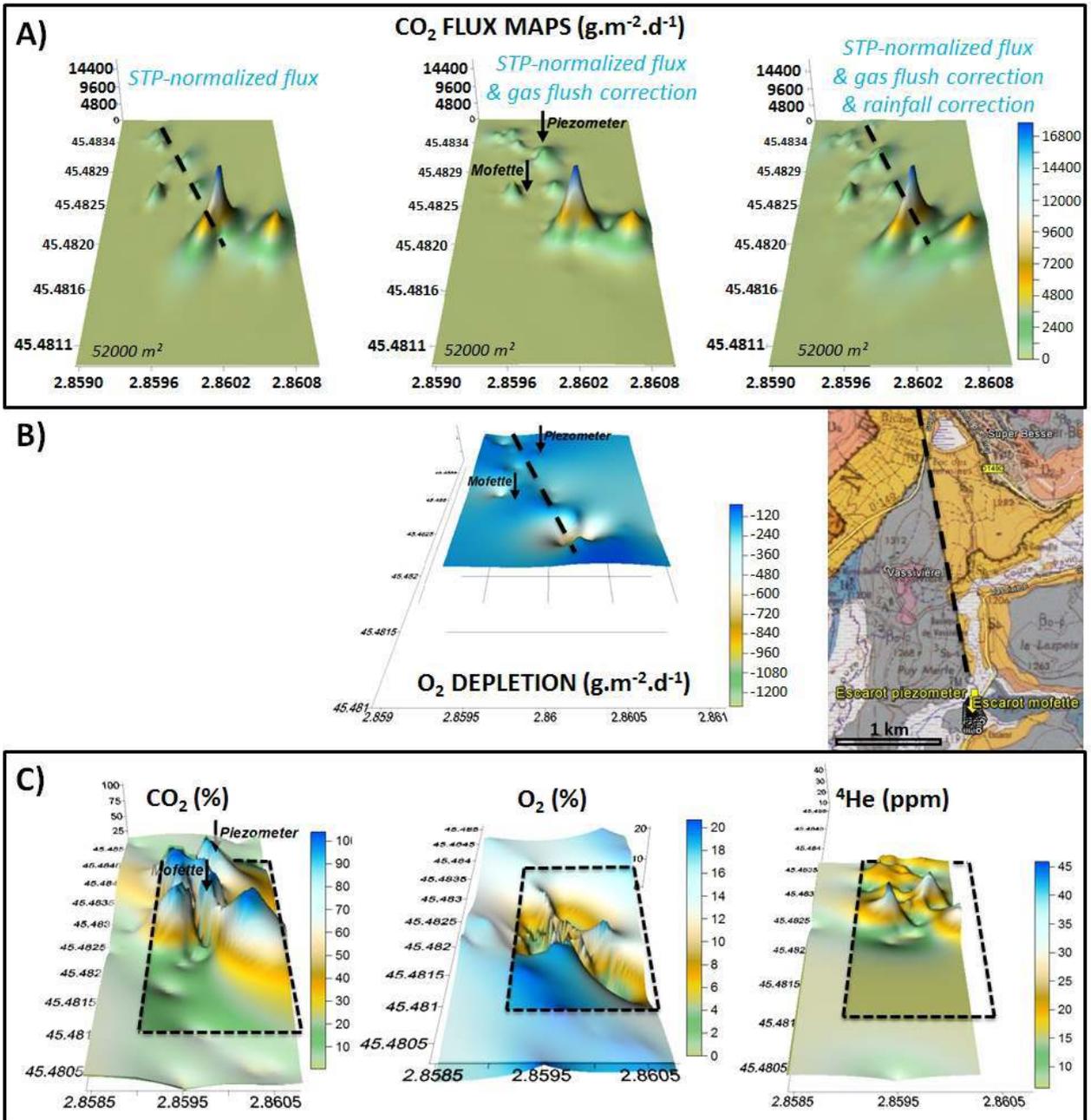












## Other emissions to the atmosphere

The rise of deep-seated CO<sub>2</sub> to the surface and its final emission into the atmosphere is not only accompanied by the degassing of other gases, such as helium, but also by the release of chemical elements such as trace metals. This aspect of degassing is less studied than the emission of gases itself, but, e.g. Mehlhorn *et al.* (2014) described the consequences of trace-element release/remobilization associated with mofettes, and Bagnato *et al.* (2014) discussed mercury releases associated with volcanic centres. Other work was done for mineral exploration purposes (Pauwels *et al.*, 1999; Castillo *et al.*, 2015; Noble *et al.*, 2017). Here we present some data showing that the Escarot mofette is also prone to such emission of elements. These data were not collected using the approach referring to the use of passive samplers and the adsorption of aerosols; they are the result of a one-day sampling session in February 2009 when a snow cover was present (*Figure A*). We used this snow cover as a natural passive sampler to test if some gases—and thus some chemical elements—can percolate and accumulate in the snow.

On this February day, three locations were investigated. First, the snow cover was removed and the soil-gas atmosphere at 1-m depth was analysed. This allowed defining a location characteristic of the mofette (referred to as Pt200; 100% CO<sub>2</sub> concentration in the soil gas), a location set some metres away, in a less active environment (Pt2000; 22.5% CO<sub>2</sub>) and finally a remote location (Pt2001; 0.4% CO<sub>2</sub>). Once the soil gas was characterized, we installed PVC pipes at 2 to 3 different levels in the snow cover, to collect snow for subsequent laboratory analyses and to measure the CO<sub>2</sub> concentration once the pipe was removed.

The most interesting results came from Point 200 (*Figure A-A*). The gas phase in the snow cover was influenced by CO<sub>2</sub> release from the mofette: 5 cm above ground level, the

concentration was as high as 10.7%. The concentration then decreaseds to 2.5%, 30 cm above the ground level and to 0.1%, 60 cm above the ground level (or 10 cm below the snow/atmosphere interface). The other two points did not show any enrichment in CO<sub>2</sub> in the snow thus confirming that only areas with high CO<sub>2</sub> fluxes can produce a gas flux that is strong enough to percolate upward into the snow cover.

The concentrations in dissolved elements were also informative (*Figure AB and -C*). Points 2000 and 2001 have similar element concentrations and show little variability with emplacement in the snow cover. Na-Cl contents appear are homogeneous at site scale with a slight tendency of higher contents close to the snow/atmosphere boundary. This may be a consequence of salt spreading on roads, remobilization as dust when the salt has dried and is dispersed by wind. This also highlights that there is no input of Na or Cl from the gas vent. However, enrichment in Ca and K exists for Pt200 5 cm above the soil (enrichment factor: 4 to 5). The concentrations decrease progressively as the distance with soil increases. Similar statements can be made for trace elements such as Pb, Zn, Sr, Cd, Mn, Ni (enrichment factors of 3 at least) and also for Al or As (not shown in *Figure A1*). Some species are not detected at Pt2000 or Pt2001 and are only occur close to the soil surface at Pt200<sub>2</sub>, such as Fe and Cr and Li (not shown in *Figure A*). But these data are too scarce to pretend at a general rule on the release of elements associated to gas seeps, even if they highlight a common behaviour between these two endmembers near the surface.

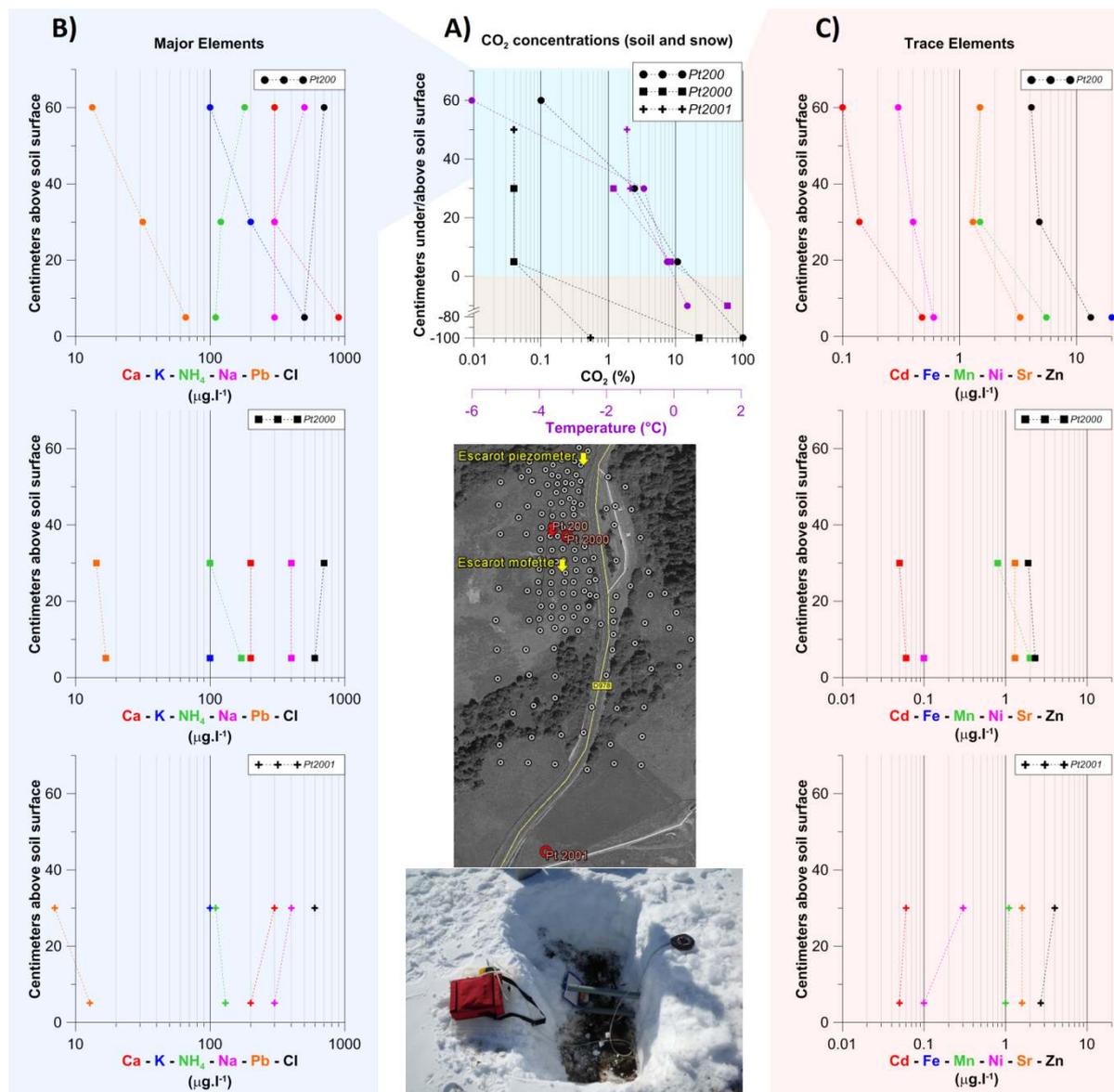


Figure A1: A: CO<sub>2</sub> concentrations in soil (1 m depth) and in the snow cover at 5, 30 and 50 or 60 cm above the ground level as measured on 29 February 2009; temperatures are also indicated – location of the points is plotted on the satellite picture; an overview of the procedure is given in the bottom picture.

B: Some major-element (except Pb) concentrations measured in the snow 5, 30 and 50 or 60 cm above the soil surface.

C: Some trace-element concentrations measured in the snow 5, 30 and 50 or 60 cm above the soil surface.

References:

Bagnato E., Barra M., Cardellini C., Chiodini G., Parello F., Sprovieri M., 2014, First combined flux chamber survey of mercury and CO<sub>2</sub> emissions from soil diffuse degassing at Solfatara of Pozzuoli crater, Campi Flegrei (Italy): Mapping and quantification of gas release, *Journal of Volcanology and Geothermal Research* 289, 26-40.

Castillo P.I.C., Townley B.K., Emery X., Puig A.F., Deckart K., 2015, Soil gas geochemical exploration in covered terrains of northern Chile: data processing techniques and interpretation of contrast anomalies, *Geochemistry: Exploration, Environment, Analysis*, 15, 222-233, doi:10.1144/geochem2014-283.

Mehlhorn J., Beulig F., Küsel K., Planer-Friedrich B., 2014, Carbon dioxide triggered metal(loid) mobilisation in a mofette, *Chemical Geology* 382, 54-66.

Noble R.R.P., Seneshen D.M., Lintern M.J., Anand R.R., Pagès A., Pinchand G.T., 2017, Soil-gas and weak partial soil extractions for nickel exploration through transported cover in Western Australia, *Geochemistry: Exploration, Environment, Analysis*, <https://doi.org/10.1144/geochem2017-026>.

Pauwels H., Baubron J.-C., Freyssinet P., Chesneau M., 1999, Sorption of metallic compounds on activated carbon: application to exploration for concealed deposits in southern Spain, *Journal of Geochemical Exploration* 66, 115-133.