



**HAL**  
open science

## What can be learned from natural analogue studies in view of CO<sub>2</sub> leakage issues in Carbon Capture and Storage applications? Geochemical case study of Sainte-Marguerite area (French Massif Central)

Frédéric Gal, Michel Brach, Gilles Braibant, Claire Bény, Karine Michel

### ► To cite this version:

Frédéric Gal, Michel Brach, Gilles Braibant, Claire Bény, Karine Michel. What can be learned from natural analogue studies in view of CO<sub>2</sub> leakage issues in Carbon Capture and Storage applications? Geochemical case study of Sainte-Marguerite area (French Massif Central). *International Journal of Greenhouse Gas Control*, 2012, 10, pp.470-485. 10.1016/j.ijggc.2012.07.015 . hal-00723404

**HAL Id: hal-00723404**

**<https://brgm.hal.science/hal-00723404>**

Submitted on 9 Aug 2012

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **What can be learned from natural analogues studies in view of CO<sub>2</sub> leakage issues in**  
2 **Carbon Capture and Storage applications? Geochemical case study of Sainte-**  
3 **Marguerite area (French Massif Central).**

4

5 GAL Frédéric, BRACH Michel, BRAIBANT Gilles, MICHEL Karine, BENY Claire

6

7 BRGM (Bureau de Recherches Géologiques et Minières)

8 Metrology, Monitoring and Analyses Division

9 3 Avenue C. Guillemin

10 BP36009

11 45060 Orléans cedex 1, France

12

13 Phone : + 33 (0)2 38 64 38 86

14 Fax: + 33 (0)2 38 64 37 11

15

16 E-mail : [f.gal@brgm.fr](mailto:f.gal@brgm.fr)

17

18 **Abstract**

19 Natural analogue studies have received much interest over past years through the CO<sub>2</sub>  
20 capture and storage applications. In this paper we focus on one natural analogue in leakage  
21 situation in order to describe the nature of the gas leakage, its interaction with surrounding  
22 rocks and aquifers and its behaviour over time. Soil gas and water monitoring techniques are  
23 used to gather point and continuous records. Leakage occurs along discrete sections relying  
24 on the nature of surface formations and the permeability of discontinuities. Main gas vents are  
25 perennial, relative proportions of different gas phases (CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He) being dependent  
26 from the interaction with surface deposits and the distance to main tectonic pathways.

27 Mineral waters were also monitored as they represent integrative bodies that exist above  
28 nearly all CCS sites. Constraints on chemical processes occurring at depth are brought by  
29 characterisation of the dissolved constituents and by related isotopic systematics. Such  
30 determination of mixing processes and their influence is important, as leakage from CCS site  
31 may be evidenced through the mixing of the water from the storage complex and overlying  
32 aquifers. Longer term monitoring was conducted for physico-chemical parameters  
33 highlighting noticeable variations for pH, dissolved oxygen, redox potential and dissolved  
34 CO<sub>2</sub>.

35

36 **Keywords**

37 Natural analogue

38 Carbon Capture and Storage

39 Soil gas monitoring

40 Water monitoring

41

## 42 **1. Introduction**

43 Natural analogues studies have received much interest over past years through the prism of  
44 CO<sub>2</sub> capture and storage (CCS) applications. Several references on this topic may be found in  
45 very recent papers such as *e.g.* Schütze *et al.* (2012). Natural analogues can either be in steady  
46 state conditions, *i.e.* in a non-leaking state, or at the opposite they can experience more or less  
47 developed leakages. In this paper we choose to focus on this second situation in order to  
48 evaluate how valuable information may be learnt from natural CO<sub>2</sub> leakages and extrapolated  
49 to CCS sites. In this particular case of leaking analogues, features devoted to the study of  
50 storage integrity are by definition unrealistic. Nevertheless, such analogues represent a good  
51 opportunity to illustrate what must be avoided for CCS sites (Bachu, 2003).

52 Even if vertical gas flows are often much greater than those expected in case of undesired  
53 CO<sub>2</sub> leakage from CCS site, natural analogues provide the opportunity to study the nature of a  
54 gas leakage, its interaction with surrounding rocks and aquifers, its behaviour over time or its  
55 potential impacts on surface environments (Lewicki *et al.*, 2007). Consequently, natural  
56 analogues monitoring is an appropriate way to study natural seepages and is from the authors'  
57 point of view complementary with induced leak experiments such as the ZERT (Spangler,  
58 2010) or the CO<sub>2</sub>FieldLab ones (<http://www.sintef.no/Projectweb/co2fieldlab/>).

59 The Sainte-Marguerite site allows the study of both CO<sub>2</sub> leakage in shallow aquifers and gas  
60 escapes in near surface environments. Apart from pressure and temperature consideration,  
61 leakage in aquifers is the most critical parameter to assess for ensuring of CCS sites integrity.  
62 One must be confident with near surface monitoring technologies prior to use them in deeper  
63 environments. Second, monitoring of CO<sub>2</sub> escapes as a gas phase may consist in the ultimate  
64 warning prior to leakage in the atmosphere. Health and risk assessment and public acceptance  
65 directly rely on those two aspects.

66 Another interesting parameter to evaluate is the behaviour of natural analogues over long time  
67 periods. CO<sub>2</sub> injection is a very recent process compared to timescale of geological processes.  
68 Consequently, apart from failures linked to defective constraint of a CCS site (leakage due to  
69 abandoned wells, existence of fractures or leakage through the caprock; Lemieux, 2011),  
70 leakage may occur at low rate over years and may not be highlighted by monitoring  
71 technologies at depth, especially geochemical ones that rely on discrete measurements. A  
72 better understanding of how the gas migrates from depth and how it imprints surface  
73 environments is a challenging question that may be addressed by studying naturally leaking  
74 sites. Defining the origin of the gas phase is an important issue in case of leakage at a CCS  
75 site, helping to decipher whether the gas originates from the reservoir itself or from other  
76 sources that do not involve CCS processes (*e.g.* Gilfillan *et al.*, 2011).

77  
78 The Sainte-Marguerite area belongs to the French Massif Central and more precisely to the  
79 southern part of the Limagne d'Allier basin (Figure 1). This tertiary basin is mainly filled by  
80 limestones with frequent sandy-clayey intercalations that are contemporary of the Oligocene  
81 to Miocene West European rifting. Alluvial and colluvial deposits from the Allier River partly  
82 overlie these tertiary strata and from place to place volcanic series crosscut the sedimentary  
83 formations. Mineral waters emerging in the Limagne d'Allier basin are strongly influenced by  
84 their deep circulation in the crystalline basement and the occurrence of deep CO<sub>2</sub> sources  
85 (Fouillac, 1983). The main tectonic structures, inherited from the Hercynian orogeny, are  
86 respectively N10-N30 and N110-N130 (Merle and Michon, 2001). The Sainte-Marguerite  
87 area is also characterised by the presence of travertine deposits formed from water degassing  
88 at springs (Casanova *et al.*, 1999; Fouillac, 1983; Rihs *et al.*, 2000).

89 While studies on mineral waters – mostly of sodium bicarbonate type with CO<sub>2</sub> present as a  
90 gas phase – from the Allier River valley are numerous (*e.g.* Négrel *et al.*, 1997a and

91 references therein), initial investigations of soil gas composition in the Sainte-Marguerite area  
92 were performed during the 90's to locate new boreholes for perpetuating the commercial  
93 exploitation of this water (Appora-Gnekindy, 1992; Baubron *et al.*, 1992). Earlier  
94 measurements were made in the 70's on the west bank of the Allier River at the Saladis spring  
95 (Batard *et al.*, 1978).

96 The objective of this study is therefore, in light of the work done in the 90's, to compare the  
97 similarities and differences of gas emanations separated by 20 years. Point measurements and  
98 longer records will be used to examine the relationships existing between the near surface  
99 compartment and deeper seated processes.

100

101 Figure 1

102

## 103 **2. Methods**

104 Two types of investigative methods were used: soil gas characterisation and description of  
105 water flows. Soil gas measurements were made using procedures and equipment identical to  
106 those described by the authors elsewhere (*e.g.* Battani et al., 2010; Gal and Gadalia, 2011).

107 The monitoring methodology was based on the following:

- 108 - CO<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> soil gas concentrations were directly quantified in the field using  
109 landfill gas analyser (LFG20 gas analyser, ADC Gas Analysis Limited, UK). Gas  
110 content was measured at 1 m depth in order to minimize the effect of atmospheric  
111 gases. CO<sub>2</sub> and CH<sub>4</sub> contents were determined by non-dispersive infrared absorption  
112 and O<sub>2</sub> contents by electrochemistry. No CH<sub>4</sub> was found during the successive surveys  
113 indicating concentrations lesser than 0.01% volume in the gas phase. As the CO<sub>2</sub>  
114 concentrations ranged from less than 1% up to 100%, precision of the measurements

115 varied between  $\pm 0.5\%$  of the reading for  $\text{CO}_2 < 10\%$  to  $\pm 5\%$  of the reading for  $\text{CO}_2 >$   
116  $50\%$ .

117 -  $^4\text{He}$  and  $^{222}\text{Rn}$  concentrations were also systematically determined using samples  
118 collected in Tedlar bags for  $^4\text{He}$  and vacuumed scintillating flasks for  $^{222}\text{Rn}$ ,  
119 respectively. Concentrations were obtained using mass spectrometry for  $^4\text{He}$  (Adixen  
120 ASM102S leak detector, France) and scintillation counting for  $^{222}\text{Rn}$  (Calen, Algade,  
121 France).

122 - Some additional grab samples were collected for laboratory determination of the  $\delta^{13}\text{C}$   
123 of the  $\text{CO}_2$ . The isotopic ratio was determined using a Delta S Thermo/Finnigan mass  
124 spectrometer and expressed as ‰ VPDB (Vienna Pee Dee Belemnite). A Varian 3400  
125 gas chromatography was used for the determination of  $\text{N}_2$ , Ar,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{C}_n\text{H}_{2n+2}$  ( $n$   
126 = 1 to 6).

127 - Continuous data acquisition was also performed on  $^{222}\text{Rn}$  content using Barasol probes  
128 (absorption spectrometry via a silicon detector; Algade) for long-term acquisitions  
129 (from October 2008 to March 2010). Barasol probes were protected by a PVC tube,  
130 covered by a Goretex membrane and buried at 1 m depth in the ground.

131

132 The joint determination of these gaseous species allow to compare information from tracers  
133 that may be enriched through geothermal reservoir processes ( $^4\text{He}$ ), from poorly mobile  
134 elements that may help highlight areas with significant gas fluxes ( $^{222}\text{Rn}$ ) and from a widely  
135 existing gas ( $\text{CO}_2$ ) that may be tracer of soil/atmosphere exchanges or of deep seated  
136 endogenic processes. Weather conditions were also taken into account for the interpretation of  
137 the soil gas data and will be discussed together with the data.

138

139 Secondly, as the Sainte-Marguerite area is known for its mineral water resources, chemical  
140 characterisation of some springs (physico-chemical parameters and dissolved ions content)  
141 was also performed as well as the monitoring of the Brissac Geyser during several hours using  
142 a multi-parameter Idronaut probe (*Idro316Plus*). Dissolved ion contents were determined at  
143 laboratory using ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy)  
144 and chromatographic methods. Isotope ratios were measured by gas phase mass spectrometry  
145 ( $\delta^{18}\text{O}$  and  $\delta\text{D}$  are expressed in ‰ VSMOW – Vienna Standard Mean Oceanic Water). The  
146 Idronaut probe was used to monitor the short-time evolution of temperature, pH, specific  
147 conductance, dissolved oxygen, redox potential and dissolved  $\text{CO}_2$  content of the water.

148

### 149 **3. Gas and water measurements**

#### 150 3.1 Soil gas data

151 A dataset of nearly 1000 data points for each gas specie ( $\text{CO}_2$ ,  $^{222}\text{Rn}$  and  $^4\text{He}$ ) is available,  
152 half of them from the 90's measurements and the rest from more recent measurements (Table  
153 1).

154

155 Table 1

156

157  $\text{CO}_2$  concentrations range from values close to those of the atmosphere up to 100% vol. The  
158 frequency distributions are different between the two measurement periods in relation to the  
159 spatial arrangement of the measurements that is dictated by the tectonic and geological  
160 structure of the study area. As a consequence, the mean  $\text{CO}_2$  concentration is significantly  
161 greater for the 2006-2010 dataset than for the 1992 dataset.

162 Radon-222 ( $^{222}\text{Rn}$ ) concentrations also fall within similar ranges during the two periods,  
163 minimum values being close to  $150 \text{ Bq.m}^{-3}$  and greater ones around  $2 \times 10^6 \text{ Bq.m}^{-3}$ . The mean



164 values were again higher for the 2006-2010 period as a consequence of data acquisition  
165 mainly focused on the Western part of the area. Nevertheless the variation of mean  
166 concentrations is only a factor of two whereas it was a factor of four for CO<sub>2</sub> concentrations.  
167 Helium-4 (<sup>4</sup>He) concentrations are on average quite close to the atmospheric content but this  
168 value hides important differences. Both in 1992 and 2006-2010 some measurements showed  
169 very strong depletions when compared to the atmospheric content while others had strong  
170 enrichments ( $\geq 10$  ppm).

171

172 Most of the CO<sub>2</sub> measurements made between 2006 and 2010 were also supplemented by  
173 measurements of the O<sub>2</sub> concentrations in soils. A very homogeneous inverse behaviour exists  
174 between those species (Figure 2). Almost all data exhibit an O<sub>2</sub> decrease that is not  
175 proportional with the increase of the CO<sub>2</sub> content on a per mole basis. Depletion of O<sub>2</sub> is  
176 much faster with a factor close to 5. This suggests that CO<sub>2</sub> is supplied in abundance by a  
177 powerful process probably related to a deep gas source (crustal and/or mantle origin) as will  
178 be discussed later.

179

180 Figure 2

181

182 This strong O<sub>2</sub> depletion is also confirmed by the gas chromatography measurements reported  
183 in Figure 3. Correlations with other gas species follow linear regression with  $r^2$  between 0.991  
184 and 0.998, and also suggest a different behaviour between the CO<sub>2</sub> end-member and the N<sub>2</sub>-  
185 O<sub>2</sub>-Ar triptych, with CO<sub>2</sub> becoming predominant as the other three gases diminish and vice-  
186 versa. This was particularly true for a 30 m deep borehole where atmospheric constituents  
187 were only detected at trace levels (0.13% N<sub>2</sub>; 0.023% O<sub>2</sub>; 0.002% Ar). Using the relationship  
188 presented in Figure 3, it is then possible to recalculate an average composition for the

189 atmospheric end-member. Ar and N<sub>2</sub> contents were respectively at 0.932% and 79.6%, levels  
190 that are very close to those usually reported for the atmosphere (respectively 0.934 and  
191 78.08%; <http://encyclopedia.airliquide.com/>). Unlike O<sub>2</sub>, which is subject to a more active  
192 kinetic of replacement, N<sub>2</sub> and Ar are diluted in the soil gas by equimolar replacement with  
193 CO<sub>2</sub>.

194

195 Figure 3

196

197 Finally, the δ<sup>13</sup>C isotope ratio of the CO<sub>2</sub> gas was also evaluated on these samples and ranged  
198 between -3 to -5.1‰ VPDB for CO<sub>2</sub> in the 14 – 100% vol. range.

199

200

### 201 3.2 Water measurements

202 The main physico-chemical properties of mineral springs sampled during the study are listed  
203 in Table 2. A rain event collected in October 2008 is also reported for comparison. The  
204 emergence temperatures range between 16 and 30°C and pH between 6.2 and 7.2, therefore  
205 comparable to those reported by Négrel *et al.* (1997b) for the carbogaseous waters known  
206 throughout the French Massif Central. Specific conductances vary between 2.5 and 8.4  
207 mS.cm<sup>-1</sup>, Chapelle springs (used for bottling) having total mineralization approximately half  
208 of other sampled waters. The mineralization is dominated by HCO<sub>3</sub> (1.3 to 4 g.L<sup>-1</sup>), Na (0.3 to  
209 1.5 g.L<sup>-1</sup>) and Cl (0.2 to 1.5 g.L<sup>-1</sup>). If this Na-Cl-HCO<sub>3</sub> facies predominates, the Ca and Mg  
210 amounts, less variable (respectively 120 to 310 mg.L<sup>-1</sup> and 100 to 140 mg.L<sup>-1</sup>), allow the  
211 Chapelle springs – due to their lower dissolved elements concentrations – to be linked with  
212 the Ca-Mg pole, suggesting a secondary enrichment associated with the chemical hardness of  
213 bicarbonate-rich waters (Michard *et al.*, 1981). Similarly, the Chapelle springs have an

214 oxidizing character contrary to Tennis and Geysir Brissac waters that are characterized by a  
215 marked reducing character. Characteristics of isotope ratios reported in Table 2 will be  
216 discussed in section 5.

217

218 Table 2

219

220

## 221 **4. Interpretation of soil gas data**

### 222 4.1 Point data

223 One of the first steps to considered for highlighting a potential leakage at a CCS site is to  
224 characterise the CO<sub>2</sub> phase. Concentration measurements are of great interest but they may  
225 not be sufficient *e.g.* in case of small leakage rate. Additional information may be gathered  
226 using isotope systematics, mobile systems nowadays allowing on-site measurements (*e.g.*  
227 Picarro or Aerodyne lasers).  $\delta^{13}\text{C}$  isotope ratio measurements will not give direct indication of  
228 the process that may be involved in the production of the CO<sub>2</sub> phase but will allow 1) to  
229 discriminate between several origins and 2) to discard some unrealistic origins.

230 In the case of Sainte-Marguerite, CO<sub>2</sub> concentrations in soils are supposed to evolve primarily  
231 under the influence of deep seated processes rather than surface processes. Indeed, the range  
232 of  $\delta^{13}\text{C}_{\text{CO}_2}$  isotope ratios in soil gas (-3 to -5.1‰) is related to deep crustal and/or mantle  
233 degassing (-4 to -8‰; Gerlach and Taylor, 1990). Similarly,  $\delta^{13}\text{C}_{\text{CO}_2}$  are close to ratios  
234 measured on the gaseous phase of low helium concentrated, CO<sub>2</sub>-rich waters from the Massif  
235 Central (-6.4‰; Dégranges *et al.*, 1978). The more depleted ratio (-5.1‰) was measured in  
236 the 30 m borehole, where the gas phase was 100% CO<sub>2</sub> with no <sup>4</sup>He (< 0.05 ppm), whereas  
237 soil gas measurements (1 m depth) were slightly enriched in carbon-13 (*i.e.* greater than -  
238 4.8‰). This slight isotopic enrichment of upper soil horizons may be the result of two

239 complementary phenomena, first the percolation of CO<sub>2</sub> through surface aquifers ( $\delta^{13}\text{C}$  of  
240 dissolved carbon from local springs close to 10.2‰; Mercier, 1987) and second the  
241 interaction with travertine deposits ( $\delta^{13}\text{C}$  between 5.4 and 7.7‰; Casanova *et al.*, 1999).

242

243 In the case of leakage originated from a CCS site, such characterisation using the only  $\delta^{13}\text{C}$   
244 isotope ratio will be much more difficult as overlaps between several gas origins and frequent  
245 re-equilibration will certainly occur. A way to better constrain gas emanation is to measure  
246 other gas species with different chemical properties.

247 In the present study we mainly refer to  $^{222}\text{Rn}$  and  $^4\text{He}$ . As  $^{222}\text{Rn}$  and  $^4\text{He}$  are only present as  
248 trace levels in the free atmosphere (respectively around 50 Bq.m<sup>-3</sup> or less and 5.24 ppm), an  
249 enrichment would favour the existence of phenomena occurring either in the soil or in the  
250 upper regolith ( $^{222}\text{Rn}$ ) or deeper in the ground ( $^4\text{He}$ ; Battani *et al.*, 2010; Gilfillan *et al.*, 2011).  
251 Relationships between CO<sub>2</sub>,  $^{222}\text{Rn}$  and  $^4\text{He}$  are presented in Figure 4.

252

253 Figure 4

254

255 For  $^{222}\text{Rn}/\text{CO}_2$  and  $^4\text{He}/\text{CO}_2$  couples, graphical relationships (Figure 4A) confirm the different  
256 origin of these two gases and highlight that the genesis of  $^4\text{He}$  from radioactive decay of  
257 uranium in the near surface has little influence on the  $^4\text{He}$  concentrations. This should also  
258 result in an increase of the  $^4\text{He}$  concentration when  $^{222}\text{Rn}$  activities are high. This is not the  
259 case, since there is rather a gradual depletion when the  $^{222}\text{Rn}$  activities exceed 10<sup>6</sup> Bq.m<sup>-3</sup>  
260 (Figure 4A). Moreover, these high  $^{222}\text{Rn}$  concentrations are measured at precise locations  
261 which correspond to surface discharges of springs (old factory and Tennis; Figure 1) that form  
262 tens of centimetres to several meters thick travertine beds. These very high  $^{222}\text{Rn}$  activities are  
263 presumably related to these travertines, consequently richer in uranium than the alluvial

264 formations and the local waters (Casanova *et al.*, 1999). In this particular case, the CO<sub>2</sub> source  
265 is not strong enough to dilute the <sup>222</sup>Rn as may occur farther from travertine deposits. As a  
266 consequence, perennial <sup>222</sup>Rn high concentrations exist locally.

267 The behaviour of <sup>222</sup>Rn and CO<sub>2</sub> is also complex for <sup>222</sup>Rn concentrations lesser than 300,000  
268 Bq.m<sup>-3</sup> (Figure 4B). Two distinct trends seem to exist, one with fast <sup>222</sup>Rn enrichment with  
269 low CO<sub>2</sub> concentrations (red squares), and the other with weaker <sup>222</sup>Rn enrichment when CO<sub>2</sub>  
270 concentrations rise (blue lozenges). These two behaviours correspond to various spatial  
271 locations (Figure 5). Most of the “high <sup>222</sup>Rn – low CO<sub>2</sub>” samples plot on the eastern part of  
272 the site on sedimentary deposits (mean altitude 350 to 365 m), whereas the majority of the  
273 “low <sup>222</sup>Rn – high CO<sub>2</sub>” group is restricted to a lower terrace of the Allier river (westward  
274 from longitude 669,100 in Figure 5 – mean altitude 335 to 345 m; see also Battani *et al.*, 2010  
275 for geological cross-section). Near the Allier River, the thickness of geological formations  
276 overlying permeable paths is lesser than eastward. The CO<sub>2</sub> gas interacts to a lesser extent  
277 with surface formations, leading to moderate <sup>222</sup>Rn enrichment. On the contrary, on the  
278 eastern part of the site, CO<sub>2</sub> has to go through thicker formations (alluvial and Oligocene  
279 formations), leading to smaller CO<sub>2</sub> amounts and also to <sup>222</sup>Rn enrichment due to the  
280 percolation of the CO<sub>2</sub> into these formations. An intermediate behaviour occurs above  
281 travertines deposits (Figures 4 and 5) where the <sup>222</sup>Rn content is also dependent from the  
282 uranium content of these formations. An additional process can also act in a complementary  
283 fashion. Deep CO<sub>2</sub> may be less diluted on the western part of the site than on the eastern part,  
284 indicating a more pronounced upward flow that allows the dilution of radon signal (Baubron,  
285 1992; Gal *et al.*, 2011).

286 No relationship can be highlighted for the <sup>4</sup>He/CO<sub>2</sub> couple except from a very weak tendency  
287 of having slightly lower <sup>4</sup>He concentrations when CO<sub>2</sub> concentration is greater than 50%  
288 (Figure 4A). If considering the 30 m depth borehole as the most representative of the deep

289 end-member, then uprising gas flow is  $^4\text{He}$  depleted. A strong  $\text{CO}_2$  flux can act as a flushing  
290 agent on  $^4\text{He}$ . For lesser  $\text{CO}_2$  amounts, flushing effect may be less important and  $^4\text{He}$   
291 concentrations are higher or even enriched depending on the amounts of  $^4\text{He}$  upward  
292 migrating.

293

294 Figure 5

295

296 The great variability of soil gas concentrations on a small area is not only dependent from  
297 deep processes but also from the heterogeneity of surface formations and pathways. Such a  
298 problematic is critical for CCS sites especially in areas where potential leakage pathways are  
299 not well characterised. This will raise the question on how detect surface leakage if *e.g.* a  
300 leakage occurred in deep groundwaters. Nevertheless, a positive point is the persistence of  
301 leakage structures over years.

302 As a result, the Sainte-Marguerite area presents a patchy repartition of anomalies at surface,  
303 as evidenced by the equal concentration lines reported on Figure 6. Data are interpolated  
304 using natural neighbour algorithm. This interpolation method is more rugged than *e.g.*  
305 kriging, but it has the advantage in not extrapolating the contours beyond the convex hull of  
306 the dataset. The whole dataset is presented top of Figure 6. Separate contributions from the  
307 data acquired during the 90's and during the 2000's are respectively presented middle and  
308 bottom parts of Figure 6. A good match is highlighted between these 15-year interval datasets  
309 especially on the Western part of the study site where strong  $\text{CO}_2$  enrichments remain  
310 perennial. The match cannot be achieved for the Southern part as a new bottling facility has  
311 been built in between time therefore no measurement is yet possible. The North-South to N10  
312 anomalous zone is well in agreement with structural directions reported in the Limagne  
313 d'Allier basin (Merle and Michon, 2001). This direction is also suggested by variogram

314 computations (data not shown) which suggest, under a spherical model, a significant nugget  
315 effect (40% of the variability) and a reduced leg (20 m). Consequently, there seems to be at  
316 site scale a structure directly related the Hercynian tectonic and at a smaller scale a less  
317 obvious structure that is difficult to model even with a large amount of data.  
318 For CCS site management, this suggests that once fed by seepage or microseepage, a leakage  
319 pathway will remain active over a long time period. Its characterisation will then be possible  
320 but remediation actions will be very difficult to undertake.

321

322 Figure 6

323

324 The complex CO<sub>2</sub> distribution in soils is not restricted to this gas phase. A well characterised  
325 time coherence for <sup>222</sup>Rn concentrations (90's and 2000's datasets) also exists and reveals an  
326 anomalous area close to the flow axis of the Allier river (Figures 2 and 6). A N170 direction is  
327 suggested by variogram calculations, with a leg identical to that defined for CO<sub>2</sub> but with  
328 increased nugget effect (50% of the variability). This may be linked to the location of the area  
329 of maximum <sup>222</sup>Rn concentrations, close to the high CO<sub>2</sub> area but with no coinciding peaks,  
330 and due to the difference of origin for these two gases, radon being preferentially produced in  
331 shallower environments than CO<sub>2</sub> in the present case.

332

333 The evolution of <sup>4</sup>He concentrations in the area where <sup>222</sup>Rn and CO<sub>2</sub> anomalies are located is  
334 very interesting to detail (Figure 6). This area is characterized by a complex intricacy of  
335 positive and negative anomalies in helium *i.e.* tracing enrichment or depletion with respect to  
336 the atmospheric content. This complexity in <sup>4</sup>He emanations is remarkably stable over time.  
337 Low <sup>4</sup>He concentrations are preferentially measured along a N10 axis, locally reinforced by a

338 complementary N160 direction. The adjustment on a spherical model of the variogram  
339 suggests a maximum correlation distance of 40 m between two points without a nugget effect.  
340

341 In order to better assess the behaviour of CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He, a linearization of the data was  
342 made using the scheme proposed by Michel – Le Pierrès *et al.* (2010). The resulting  
343 interpolation map is presented in Figure 7. By assumption, CO<sub>2</sub> and <sup>4</sup>He are considered as  
344 deep end-members and <sup>222</sup>Rn as a near surface produced gas. This is consistent with gas  
345 origins suggested by Jeandel *et al.* (2010) that found a nearly half/half mantle/crust origin for  
346 helium and a predominant crustal origin for CO<sub>2</sub>. This strengthens previous results indicating  
347 that CO<sub>2</sub> and <sup>4</sup>He amounts are not directly proportionally linked. The linearization process is  
348 then intended to lower the influence of <sup>222</sup>Rn and to over-estimate the one of <sup>4</sup>He by assigning  
349 a value between 0 and 1 to each of the gas specie. The 0.05 to 100% CO<sub>2</sub> range is restricted in  
350 the 0 – 1 interval and so on for <sup>222</sup>Rn (140 to 248,000 Bq.m<sup>-3</sup>) and <sup>4</sup>He (0.05 to 9.83 ppm).  
351 Using this procedure, <sup>4</sup>He concentrations account for *c.a.* 75% of the total variability, CO<sub>2</sub> for  
352 22% and <sup>222</sup>Rn for the rest (*c.a.* 3%). Despite this bias introduced in the dataset (Figure 7), the  
353 surface geometry of the anomalies is still primarily guided by the distribution of CO<sub>2</sub>  
354 concentrations, the influence of <sup>4</sup>He been of second order. Consequently, it is the deep CO<sub>2</sub>  
355 source that governs the spatial distribution of anomalies in soil gas through the N10-N30 and  
356 N110-N130 structures (Merle and Michon, 2001). Other gaseous species evolve either  
357 through the heterogeneous composition of the regolith or through the existence of complex  
358 phenomena including convective transport, stripping or mixing. This strong imprint of  
359 geological structures on the occurrence of anomalies also appears in the comparison of data  
360 acquired 15 years apart, since changes between these two periods remain small. This  
361 statement is strengthened by comparison with CO<sub>2</sub> flux data available in the area (Battani *et*  
362 *al.*, 2010). The most anomalous CO<sub>2</sub> areas correspond to those marked by fluxes reaching or



363 exceeding  $500 \text{ cm}^3 \cdot \text{min}^{-1} \cdot \text{m}^{-2}$ , while the radon anomalies are superimposed on areas where the  
364 fluxes are smaller (lesser than  $100 \text{ cm}^3 \cdot \text{min}^{-1} \cdot \text{m}^{-2}$ ).

365

366 Figure 7

367

#### 368 4.2 Time evolution of soil gas concentrations

369 Evaluation of short-term variability of soil gas concentrations was evaluated using point  
370 measurements ( $\text{CO}_2$ ,  $^{222}\text{Rn}$  and  $^4\text{He}$ ) and continuous measurements (on the  $\text{CO}_2$  phase using  
371 Fourier Transform Infrared gas spectrometry). Repeated point measurements over 3 days  
372 (points 1 to 4 in Figure 1) indicated that the points located northward of the site experienced  
373 low variability of their gas concentrations ( $\pm 60\%$  for  $\text{CO}_2$ ). At the opposite points located in  
374 the southern part of the site had much greater variations rising up to a factor of 80 for  $\text{CO}_2$  and  
375 200 for  $^{222}\text{Rn}$  (point 4). Continuous measurements in upper soil horizons in the vicinity of the  
376 Brissac Geyser had an intermediate variation factor of 8 over few hours, with periodicity  
377 influenced by the geyser own kinetic (mean period of 21 minutes).

378 Assessing the variability of gas emanations at short time scale is important for the  
379 comprehension of phenomena occurring at a natural analogue, but such a time scale is not  
380 fully matching requirements of CCS site monitoring. Longer chronicles shall be available in  
381 order to highlight any deviation from environmental background noise. The Sainte-Marguerite  
382 site has then been instrumented for longer-term measurements. They were performed only on  
383 the  $^{222}\text{Rn}$  phase for practical reasons. Even if deviations that may be recorded will not be  
384 linked to deviations from an environmental background noise in the present case, one must be  
385 confident in the capacity of monitoring devices to properly register unexpected events.

386 Points 2 and 4 (Figure 1) were instrumented with Barasol probes from October 2008 to  
387 January 2009 for hourly monitoring and afterwards only the point 4 remained. Soil  
388 temperature and barometric pressure were simultaneously recorded at 1 m depth in the soil.  
389 Meteorological data were got from an airport weather station located 14 km NNW from  
390 Sainte-Marguerite, at similar altitude. Two distinct time responses exist (Figure 8):

- 391 - Pressures measured at 1 m depth in soils perfectly replicate the variations of  
392 atmospheric pressure and provide accurate description of local evolutions (Figure 8a);
- 393 - Temperatures measured in the soil are different from those measured in the  
394 atmosphere (Figure 8b). Soil temperatures exhibit a smoother daily variability and are  
395 higher than atmospheric temperatures. There is a time-lag between the maxima of  
396 temperature in the atmosphere and in the soil, the former occurring 5 to 6 hours before  
397 the later.

398 In December 2008 and January 2009, there is however a difference between temperatures  
399 measured by the two probes (Figure 8b). The probe located in the southern part of the study  
400 area (point 4 in Figure 1) recorded higher temperatures (from 5 to 10°C) than those measured  
401 a few hundred meters northward (point 2 in Figure 1). Point 4 being located in a depression  
402 close to mineral springs (25 to 29°C at the orifice), this warming may be related to their  
403 influence into higher groundwater level during winter times.

404

405 Figure 8

406

407 Radon activities measured by the 2 probes during the October 2008 - January 2009 period  
408 showed trends with site-specific evolution but the variability of the measurement remained in  
409 a similar range (Figure 8c). There is a good agreement between average  $^{222}\text{Rn}$  concentrations  
410 computed from Barasol records (Table 3) and that from point measurements performed at site

411 scale (Table 1). Marked activity peaks nevertheless occurred. At the end of January 2009  
412 (Figure 8c), phenomenal concentrations were reached (up to  $80 \times 10^6 \text{ Bq.m}^{-3}$ ). Such  
413 concentrations remain under saturation threshold of the probe ( $10^9 \text{ Bq.m}^{-3}$ ) but are far greater  
414 than maximum values found during spot sampling ( $2.5 \times 10^6 \text{ Bq.m}^{-3}$ ). During this January 2009  
415 event, a perfect synchronism was found between the 2 probes with a very quick increase  
416 followed by very small  $^{222}\text{Rn}$  amounts few hours later. This event is therefore not related to  
417 malfunctioning of the equipment. The measurements suggest a gas burst sweeping the area of  
418 Sainte-Marguerite, leading to a huge increase in  $^{222}\text{Rn}$  and a subsequent strong depletion.  
419 Concentrations remained low until radioactive decay produced again a sufficient amount of  
420  $^{222}\text{Rn}$ . Another peak of activity was also detected in September 2009 (Figure 8c). However, as  
421 only one sensor was deployed and as it experienced some operational problems, we prefer not  
422 trying to interpret this latter signal.

423

424 Table 3

425

426 Apart from these specific periods, the  $^{222}\text{Rn}$  concentrations change cyclically (Figure 8).  
427 Cycle analysis returned variable results depending on the analysed time period and even on  
428 the location of the probe (Table 3). There was no clear influence of external forcing such as  
429 daily or diurnal variations over long time periods or the existence of pulsation of longer  
430 duration. It is therefore not possible to highlight regular gas emanations as may be possible  
431 regionally such as in the vicinity of Lake Pavin (Gal and Gadalia, 2011).

432 Nevertheless, during periods characterised by less noisy  $^{222}\text{Rn}$  signals (March 2009; Figure  
433 9a, b and c), a daily cyclicity (24 hours period) clearly appeared even if trends of greater  
434 wavelength may also contribute to the shape of the recorded signal (Figure 9d). Principal  
435 Component Analysis were calculated by combining the factors accounting for maximum

436 variability (Figures 9e and f). The only apparent trend was an inverse correlation between  
437  $^{222}\text{Rn}$  concentration and soil temperature. Given the interdependence between soil and  
438 atmospheric temperature, this trend can be extended to this second parameter. Thermal  
439 forcing seemed to be more efficient than pressure gradients to influence the short-term  
440 temporal evolution of  $^{222}\text{Rn}$  concentrations, apart from sudden phenomena such as “gas  
441 bursts”.

442

443 Figure 9

444

445 As previously described, the occurrence of large  $^{222}\text{Rn}$  concentration peaks was very  
446 intriguing. The origin of such short pulses may typically be attributed to external causes such  
447 as earthquakes. Radon is frequently used as an indicator of crustal movement (precursor),  
448 although each earthquake does not raise an  $^{222}\text{Rn}$  anomaly and each anomaly is not  
449 necessarily followed by an earthquake (*e.g.* Al-Hilal *et al.*, 1998). According to dislocation  
450 model (Fleischer, 1981; Fleischer and Mogro-Campero, 1985), variations of  $^{222}\text{Rn}$   
451 concentrations issued from stress changes can be detected even at great distances from  
452 epicentres, involving a wide set of mechanisms (Kharatian *et al.*, 2002). Continuous  
453 measurements of  $^{222}\text{Rn}$  in soil gas sometimes allow the identification of spike-like anomalies  
454 just before the earthquake, the post-seismic stage being characterised by a rapid return to  
455 natural background values (Chyi *et al.*, 2002). Although highly variable, increases in  $^{222}\text{Rn}$   
456 concentrations at 1 m depth in soils (Wattananikorn *et al.*, 1998) often occur between 4 and  
457 15 days before earthquakes of magnitude 2 to 6 with distances from the epicentre to the  
458 measuring station comprised between 15 to 250 km (Das *et al.*, 2006; Ghosh *et al.*, 2007;  
459 Ramola *et al.*, 2008).

460 Referring to these constraints, we searched the available databases (<http://www-dase.cea.fr/>)  
461 for events reported in an area covering 4 degrees in longitude and 3 degrees in latitude,  
462 centered on Sainte-Marguerite. Twelve earthquakes were recorded between January 28 (12  
463 hours after the  $^{222}\text{Rn}$  peak) and February 13 (17 days after the  $^{222}\text{Rn}$  peak) within this area, at  
464 distances between 40 and 70 km from Sainte-Marguerite. All were characterised by very low  
465 magnitudes less than 2.5. Although some of the cited literature reports a sensitivity of  $^{222}\text{Rn}$   
466 measurements for low seismic magnitudes, no clear relationship exists in the present case  
467 between  $^{222}\text{Rn}$  peaks and tectonic activity.

468 Such excursions of  $^{222}\text{Rn}$  signal were earlier reported on the Weyburn site, which is not  
469 known to be tectonically active (Riding and Rochelle, 2009). Phenomena observed at  
470 Weyburn were short (3 hours) and activities varied by factors of 7 to 15. At Sainte-Marguerite  
471 variations were consequently higher (100 to 1000 times) and the sensitivity of  $^{222}\text{Rn}$   
472 concentrations to pressure changes was less obvious than stated at Weyburn. This renders  
473 improbable an origin related to transient phenomena affecting the pressure.

474 Even if not really successful during the monitoring period, long-term measurements of soil  
475 gas emanations are of strong interest in view of CCS applications. Data main not only be  
476 gathered on the  $^{222}\text{Rn}$  phase but mostly on  $\text{CO}_2$  and/or  $\text{O}_2$  phases. This is crucial for assessing  
477 if variations are linked to natural processes, either originated from surface processes or deeper  
478 ones, or caused by CCS operations. Continuous monitoring is not designed to cover great  
479 areas, one limiting factor being costs, but is complementary with point techniques and may be  
480 deployed in most prominent locations highlighted by point monitoring.

481

482 **5. Chemistry of mineral waters**

483 The Sainte-Marguerite site offers the opportunity to monitor gas escapes into more or less  
484 mineralised water bodies. We will first describe water chemical compositions and then  
485 discuss what is important in view of long term water monitoring.

486

#### 487 5.1 Point sampling

488 Mineralisation of these waters form two groups, one rich in dissolved constituents and  
489 belonging to the Na-Cl-HCO<sub>3</sub> end-member, the other (Chapelle springs) more influenced by  
490 the Ca and Mg species. This distinction remains when referring to  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotope ratios  
491 (Table 2). Chapelle springs are always under the local meteoric water line (Fouillac *et al.*,  
492 1991), *i.e.* enriched in heavy isotopes contrary to other springs which fall on this meteoric  
493 water line. This may be related to evaporation (Négrel *et al.*, 1997b and references therein), to  
494 mixing in various proportions between deep and surface end-members (*e.g.* Michard *et al.*,  
495 1981) or to mixing between different deep end-members (Négrel *et al.*, 1997b; Rihs *et al.*,  
496 2000). These differences in isotope ratios denote spatial disparities within walking distance  
497 but do not imply the existence of compartmented geological structures. Theoretical  
498 calculations of the <sup>13</sup>C isotope signature of gas in equilibrium with the waters provide ratios  
499 between -2.8 and -5.1‰ (Table 2) that exactly match the range measured in soil gas. Water  
500 mixing must then occur under open system conditions allowing different end-members to  
501 interact one with each other, *pro parte* explaining temporal variations reported in the area  
502 (Négrel *et al.*, 1997b).

503 Strontium isotope ratio of water (<sup>87</sup>Sr/<sup>86</sup>Sr) is known to derive from that of minerals with  
504 which the water interacts and to be lower than that of the whole rock, in response to different  
505 dissolution rates between the mineral species (*e.g.* Michard *et al.*, 1978). <sup>87</sup>Sr/<sup>86</sup>Sr ratios  
506 (Table 2) suggest that Tennis and Geyser Brissac waters fall in the range of ratios known  
507 across the Limagne d'Allier (0.71338; Stettler, 1977) and therefore reflect the signature of a

508 deep end-member. Lower ratios of Chapelle springs suggest either an interaction with  
509 lithologies different from those present in the supply circuit of Tennis and Geysers Brissac  
510 springs (e.g. plagioclase from the Coudes granite at 0.71028; Rihs *et al.*, 2000) or a mixing  
511 with near surface groundwaters (ratio close to 0.71102; Négrel *et al.*, 1997b). In the first case  
512 (mixture of 2 groundwaters, one coming from plagioclase weathering), a contribution of the  
513 deep end-member (represented by Geysers Brissac or Tennis springs) close to 32% can be  
514 calculated using a binary mixing law, whereas in the second case (dilution by surface water),  
515 the proportion of the deep end-member may be close to 57%.

516

517 Using this deep end-member – or at least the end-member less affected by mixtures –  
518 equilibrium temperatures with basement rocks may be evaluated referring to cationic  
519 geothermometers. As geothermometers induce the existence of equilibrium between waters  
520 and rocks, we neither refer to Ca and Mg geothermometers, strongly affected by mixing  
521 processes (Michard *et al.*, 1981), nor to silica -rich species, oversaturated with water at the  
522 spring orifice. Na/K (Michard, 1979, 1990, Truesdell, 1975) and Na/Li (Fouillac and  
523 Michard, 1981; Michard, 1990) geothermometers are preferred as saturation indices of  
524 mineral species containing Na indicate under saturation with water. Deep reservoir  
525 temperature is estimated between 180 and 210°C (Na/K) and 195 and 205°C (Na/Li). This  
526 estimate is in agreement with that of Fouillac and Michard (1981) and Fouillac (1983).

527

528 Isotope characterisation of waters is often restricted to the monitoring of  $^{18}\text{O}$ ,  $^2\text{H}$  or  $^{13}\text{C}$   
529 species in view of CCS problematic. Such characterisation is important but water monitoring  
530 of deep aquifers, such as the storage complex itself of overlying aquifers, may include other  
531 species. O, H, C species may suffer from several processes such as water/rock interaction of  
532 mixing between different water bodies. Monitoring other isotopes, such as Sr, Nd, B, Li, Ca

533 or U may also allow getting information on deep seated processes, better define water/rock  
534 interaction or describe redox processes. A better comprehension of deep phenomena may  
535 allow improved constraint on CO<sub>2</sub> migration in deep horizons if leakage from the storage  
536 reservoir may occur.

537

## 538 5.2 Continuous monitoring of Geyser Brissac

539 Here we describe short-term evolution of some key physico-chemical parameters of the  
540 Geyser Brissac mineral water. Requirements of CCS monitoring will obviously not imply  
541 high frequency measurements but one must be confident on the short time scale before  
542 assessing variations of longer period.

543 Results of this monitoring are presented in Figure 10 and Table 4. Two days were  
544 characterised by sunny conditions whereas rainfall events of variable magnitude occurred  
545 during day 4 and especially day 3. The evolution of dissolved CO<sub>2</sub> is reported on Figure 10  
546 even if quantification is not accurate using pH-based sensors (Gal *et al.*, 2011), in order to  
547 bring qualitative information.

548

549 Figure 10

550 Table 4

551

552 A cyclical pattern is clearly apparent for all the parameters, directly related to Geyser Brissac  
553 dynamics (Figure 10). Two parameters mainly influence the water temperature: 1) intrinsic  
554 processes, the eruption of the geyser progressively warming the water and 2) atmospheric  
555 forcing, higher water temperatures being recorded around 16:00 in the evening. This is due to  
556 to the location of the Geyser Brissac, emplaced in a 1 m deep, 5 m diameter bowl filled with  
557 mineral water. Measurements were performed at the bottom of this bowl, closest to the drain



558 where the geyser overflows. The presence of non-flowing waters induced the occurrence of  
559 thermal forcing on this water mass: time is needed for the water directly flowing from the  
560 geyser when it erupts to warm up the bowl. Similarly, amplitude of the temperature peaks  
561 becomes smaller through the day and the water mass becomes hotter as solar heats the water  
562 mass. Dilution effects due to rainfall may happen and significantly affect the water  
563 temperature and the specific conductance (day 3, Table 4).

564 Apart from external causes, time evolution of the records is dependent from the geyser  
565 activity. Temperature peaks, which correspond to the maximum of the activity of the geyser,  
566 lasted 4 to 5 minutes. They are synchronous to increase of the dissolved CO<sub>2</sub>, slight decrease  
567 of the pH value (-0.05 pH unit) and decreases of the dissolved O<sub>2</sub> concentration and of the  
568 redox potential. Such evolutions are self-consistent and reflect the progressive replacement of  
569 O<sub>2</sub> by CO<sub>2</sub> in the bowl as the eruption takes place. Specific conductance is also affected, CO<sub>2</sub>  
570 inflows leading to harmonic variations of the record. Nevertheless, diurnal heating affects the  
571 dissolved CO<sub>2</sub> measurements, one of the drawbacks of this sensor elsewhere reported (Gal *et*  
572 *al.*, 2011).

573

574 Spectral density analysis is best constrained using dissolved O<sub>2</sub>, pH and redox potential redox.  
575 Main period is around 22±1 minutes in good agreement with infrared measurements  
576 performed in soils (see section 4.2). As measurements were not conducted over several days,  
577 it is not possible to identify periodicity of greater wavelength such as that determined from  
578 Barasol probe acquisitions.

579 Long-term monitoring of water bodies is one of the key procedures in order to ensure of the  
580 safety of CO<sub>2</sub> storage. Monitoring performed at Sainte-Marguerite natural analogue shows  
581 that this method is sensitive to strong CO<sub>2</sub> leakage well over thresholds expected in deeper  
582 environments. Nevertheless devices have the capacity to record variations of lower

583 magnitude. The main issue nowadays existing relies on the stability of the sensors over time.  
584 Long-term deployment at depth generally involves CTD probes, *i.e.* probes that measure only  
585 temperature, specific conductance and depth. This only involves solid state sensors. Idronaut  
586 probe has chemical sensors for all other parameters and such sensors are subject to drift.  
587 Dissolved oxygen may be better constrained using optical sensors. Until now, no long-term  
588 pH or redox monitoring has been reported without frequent recalibration of the devices. This  
589 question is of crucial importance, as pH is one of the most sensitive parameter to monitor  
590 changes linked to CO<sub>2</sub> dissolution.

591

## 592 **6. Concluding remarks**

593 This case study of Sainte-Marguerite natural analogue allows investigating both soil gas and  
594 water compartments.

595 Point soil gas measurements have suggested the presence of perennial pathways that favour  
596 gas escape from depth to the surface by comparing data acquired 15 years apart. Leakage does  
597 not occur along all the fault length as may be derived from geological maps but rather along  
598 discrete sections. At Sainte-Marguerite there is no visual impact on the vegetation as could  
599 exist in other similar environments (Krüger *et al.*, 2011; Schütze *et al.*, 2012). Permeability of  
600 faults does not exist as a whole mechanism but rather as narrow structures separated by less  
601 permeable sections filled by secondary mineralization. In terms of CCS monitoring strategy,  
602 this suggests that potential pathways that may be deduced from geological or geophysical  
603 works may not be the most prone to become pathways. It would be better to search for  
604 structures that are still open to fluid draining *i.e.* secondary fractures that are more likely to  
605 have intrinsic permeability than main discontinuities.

606 The CO<sub>2</sub> gas was found to be the main carrier gas leading to the existence of gas anomalies in  
607 near surface environments. Carbon isotope ratios are mainly imprinted from deep seated

608 processes with little interaction in near surface environments either resulting from percolation  
609 into surface waters or into travertines horizons. Helium concentrations measured in CO<sub>2</sub>-rich  
610 areas also highlighted this strong imprint of crustal contribution (Jeandel *et al.*, 2010). The  
611 interaction of fluids with travertine deposits also influenced the <sup>222</sup>Rn concentrations of the  
612 gas phase. Consequently, gas emanations were found to be mainly oriented along known  
613 regional directions of the tectonics with some complications induced by local surface geology.  
614 When alluvial deposits were the less developed the gas emanations were stronger. Thicker  
615 alluvial deposits were found to be less representative of the deep end-member due to more  
616 pronounced interaction with these formations. Gas migration from depth is a highly complex  
617 phenomenon that must be better constrained in order to build confidence in safety rules and  
618 remediation strategies of CCS projects. Even at the upper level, near surface features have a  
619 strong influence on degassing pattern as pointed out by coupled geochemical/geophysical  
620 investigations (Schütze *et al.*, 2012).

621 Soil gas surveys performed under “point acquisition” schematic are relevant for the thorough  
622 description of surface leakage over a restricted spatial array. They are not fully appropriate for  
623 the monitoring of large areas and may be time consuming for repeated data acquisitions. They  
624 do not allow to take into account for the variability linked to external causes such as climatic  
625 variability and its imprint on surface environments. They are nonetheless crucial to best settle  
626 monitoring equipment for long-term surveillance. Investigation done at Sainte-Marguerite  
627 was mostly oriented on the <sup>222</sup>Rn specie. It allowed highlighting excursion from background  
628 noise under “gas burst” event. Such events were characterised by influence radius of at least  
629 200 m. Scaling effects in case of leakage from CCS storage may not allow to get such  
630 amounts of gases percolating up to the surface.

631 Therefore, there is also a need to monitor integrative bodies such as aquifers. In nearly all  
632 cases, CCS sites are more or less deep and overlying aquifers exist. Monitoring aquifers in the

633 case of natural leaking analogues is from one side little frustrating as the initial composition  
634 of the waters is not known – water properties prior leakage from a CCS site are known a  
635 priori – but on the other hand these waters represent an opportunity to study deep degassing  
636 through the interaction with water and rocks – that will be the case for CCS sites. The  
637 harmonic pulsation of Geyser Brissac is an extreme case relying on the accumulation of gas  
638 until the degassing due to overpressure.

639 Point monitoring of waters is by definition subject to heterogeneity of spatial coverage, ways  
640 to collect samples being restricted to available outlets or wells. Constraints on chemical  
641 processes occurring at depth may be brought by specific characterisation of the dissolved  
642 constituents and by related isotopic systematics. Particularly, the determination of mixing  
643 processes and their influence is important, as leakage from CCS site may be evidenced  
644 through the mixing of the water from the storage complex and overlying aquifers. Such  
645 methodology is not restricted to dissolved constituents and can also be extended to associate  
646 gases such as  $^4\text{He}$  (Gilfillan *et al.*, 2011).

647 As for soil gases, monitoring at regular frequency of water bodies is complementary with  
648 point methods. Time scale of recording depends on the kinetic of the processes. At Sainte-  
649 Marguerite such monitoring was performed at high frequency in order to take into account  
650 variations over short time scales, cyclicity of the geyser being around 22 minutes. Most  
651 prominent variations were stated for pH, dissolved oxygen, redox potential and dissolved  $\text{CO}_2$   
652 content. From soil gas measurements it was also stated that geyser “breathing” influences the  
653 soil gas evolution over short periods at a radius close to 20-30 m.

654

655 Several conclusions arise when moving from analogue scale to industrial scale. Basically  
656 studies devoted to CCS projects separate into baseline data acquisitions, then monitoring  
657 actions during the injection and final monitoring operations after well closure and

658 abandonment. Baseline studies are essential as they represent the only data that will allow  
659 definition of anomalies during injection and post-injection. Establishing baseline values is a  
660 site-specific procedure but often their definition is based on a restricted dataset of  
661 measurement over limited time in order to match scientific issues on one side and industrial  
662 approach on the other side.

663 Natural analogue monitoring suggests that data acquisition should not be restricted in narrow  
664 perimeters above the storage complex itself but should encompass all the areas that may  
665 potentially be affected by leakage. One of the main concerns is the capability of the  
666 monitoring system to detect potential leaks. Anomalies are often restricted on narrow areas at  
667 surface and deploying monitoring devices on such small grids (20 to 200 m of array) is  
668 absolutely unrealistic if only considering costs. At surface, apart from such a net, it is  
669 therefore hypothetical to ensure a safely monitoring over great distances simply using  
670 punctual and point methods. Installation of equipment just above a potential leaking pathway  
671 that may not have been recognized by geological studies would be too lucky to be reproduced  
672 regularly over several deep CO<sub>2</sub> storages. Surveying methodologies are nowadays adapted to  
673 integrate gas emanations characteristics from hectometer to kilometer scales. Methods such as  
674 eddy covariance, open path laser, airborne hyper-spectral monitoring etc... are promising  
675 ones but until now they are not as robust as required for storages monitoring as they are often  
676 dependent from modeling of the atmosphere compartment that is strongly turbulent over short  
677 time periods and may therefore induce undesirable effects and false warnings (*e.g.* Klusman,  
678 2011).

679 Ways to overcome this limitation may be of several types. Monitoring at depth through  
680 boreholes, using geochemical and/or geophysical methods, appears to be the best way to get  
681 early detection and warning of unexpected events by focusing on the water phase and on  
682 dissolved gas contents. Monitoring should be performed under continuously deployed devices

683 or at least consisting in repeated measurements. Nevertheless, from a geochemical point of  
684 view, lot of the available monitoring equipment that may be deployed at depth has nowadays  
685 not reached the desirable level of reliability over long time periods.

686 Many efforts have been done in recent years to adapt technologies to CCS monitoring and to  
687 gain confidence in results, but long-term recording of parameters remains a challenging  
688 question.

689

690

### 691 **Acknowledgments**

692 This research was conducted through the fundings of French Research Agency projects  
693 Geocarbone Monitoring (2006-2008) and Sentinelle (2008-2011). Anne Bonhomme (Les  
694 Mousquetaires Group) is warmly thanked to allow the access to the Sainte-Marguerite site and  
695 subsequently fruitful data acquisition. BRGM people that performed laboratory analyses are  
696 gratefully acknowledged.

697 Two anonymous reviewers and the associate editor are also warmly thanked for their help in  
698 improving the manuscript.

699

### 700 **References**

701 Al-Hilal M., Sbeinati M. R., Darawcheh R. (1998) Radon variations and microearthquakes in  
702 Western Syria. Applied Radiation and Isotopes, 49, 117-123.

703

704 Appora-Gnekindy I. (1992) Etude spatiale et temporelle des émanations gazeuses de quelques  
705 zones thermominérales du Massif Central Français, rapport de stage BRGM, 92 p.

706

707 Bachu S. (2003) Screening and ranking of sedimentary basins for sequestration of CO<sub>2</sub> in  
708 geologic media, *Environmental Geology* 44(3), 277-289.  
709

710 Batard F., Billet C., Risler J.J. (1978) Prospection de CO<sub>2</sub> d'origine profonde dans le Massif  
711 Central, rapport BRGM 78-SGN-466-MCE, 16 p.  
712

713 Battani A., Deville E., Faure J.-L., Noirez S., Tocqué E., Jeandel E., Benoît Y., Schmitz J.,  
714 Parlouar D., Gal F., Le Pierrès K., Brach M., Braibant G., Bény C., Pokryszka Z., Charmoille  
715 A., Bentivegna G., Pironon J., de Donato P., Garnier C., Cailteau C., Barrès O., Radilla G.,  
716 Bauer A. (2010) Geochemical study of the natural CO<sub>2</sub> emissions in the French Massif  
717 Central: How to predict origin, processes and evolution of CO<sub>2</sub> leakage, *OGST*, vol. 65, No 4,  
718 615-633.  
719

720 Baubron J.C., Mercier F., Rouzaire D. (1992) Eaux minérales de Sainte Marguerite (Puy de  
721 Dôme) – Prospection géochimique in situ des gaz des sols, Rapport BRGM R-36492-AUV-  
722 4S-92, 35 p.  
723

724 Casanova J., Bodéan F., Négrel P., Azaroual M. (1999) Microbial control on the  
725 precipitation of modern ferrihydrite and carbonate deposits from the Cézallier hydrothermal  
726 springs (Massif Central, France), *Sedimentary Geology* 126, 125–145.  
727

728 Chyi L. L., Chou C. Y., Yang F. T. et al. (2002) Automated radon monitoring of seismicity in  
729 a fault zone. *Geofísica Internacional*, 41, 507-511.  
730

731 Das N. K., Bhandari R. K., Ghose D. et al. (2006) Explosive helium burst in thermal spring  
732 emanations. *Applied Radiation and Isotopes*, 64, 144-148.

733

734 Dégranges P., Bosch B., Derec F. (1978) Hélium et sources thermominérales en France,  
735 rapport BRGM 78-SGN-684-MCE, 22 p.

736

737 Fleischer R. L. (1981) Dislocation model for radon response to distant earthquakes.  
738 *Geophysical Research Letters*, 8, 477-480.

739

740 Fleischer R. L., Mogro-Campero A. (1985) Association of subsurface radon changes in  
741 Alaska and the northeastern United States with earthquakes. *Geochimica et Cosmochimica*  
742 *Acta*, 49, 1061-1071.

743

744 Fouillac, C., Michard, G. (1981) Sodium/lithium ratio in water applied to geothermometry of  
745 geothermal reservoirs. *Geothermics* 10, 55–70.

746

747 Fouillac C. (1983) Chemical geothermometry in CO<sub>2</sub>-rich thermal waters. Example of the  
748 French Massif Central, *Geothermics*, Vol. 12, No. 2/3, 149 – 160.

749

750 Fouillac C., Fouillac A.M., Chery L. (1991) Isotopic studies of deep and surface waters in the  
751 French Massif Central, *Proceedings of isotope techniques in water resources development*,  
752 Vienne, 11-15/03/1991, 646-648.

753

754 Gal F., Gadalia A. (2011) Mesure des gaz des sols autour du système volcanique le plus  
755 récent de France métropolitaine (lac Pavin, Massif Central). *Soil gas measurements around*



756 the most recent volcanic system of metropolitan France (lake Pavin, Massif Central), C. R.  
757 Geosciences 343, 43-54.

758

759 Gal F., Brach M., Braibant G., Jouin F., Michel K. (2011) CO<sub>2</sub> escapes in the Laacher See  
760 region, East Eifel, Germany: application of natural analogue onshore and offshore  
761 geochemical monitoring, International Journal of Greenhouse Gas Control, 5, 1099-1118.

762

763 Gerlach T. M., Taylor B. E. (1990) Carbon isotope constraints on degassing of carbon dioxide  
764 from Kilauea Volcano, GCA, 54, 2051-2058.

765

766 Ghosh D., Deb A., Sengupta R. et al. (2007) Pronounced soil-radon anomaly - Precursor of  
767 recent earthquakes in India. Radiation Measurements, 42, 466-471.

768

769 Gilfillan S.M.V., Wilkinson M., Haszeldine R.S., Shipton Z.K., Nelson S.T., Poreda R.J.  
770 (2011) He and Ne as tracers of natural CO<sub>2</sub> migration up a fault from a deep reservoir,  
771 International Journal of Greenhouse Gas Control, 5, 1507-1516.

772

773 Jeandel E., Battani A., Sarda P. (2010) Lessons learned from natural and industrial analogues  
774 for storage of carbon dioxide, International Journal of Greenhouse Gas Control, 4, 890-899.

775

776 Kharatian K., Travi Y., Igoumnov V. (2002) Activité du gaz radon dans l'air du sol et  
777 sismicité locale : exemple du bassin de l'Arax (Arménie). Comptes Rendus de Geosciences,  
778 334, 179-185.

779

780 Klusman R.W. (2011) Comparison of surface and near-surface geochemical methods for  
781 detection of gas microseepage from carbon dioxide sequestration, *International Journal of*  
782 *Greenhouse Gas Control*, 5, 1369-1392.

783

784 Krüger M., Jones D., Frerichs J., Oppermann B.I., West J., Coombs P., Green K., Barlow T.,  
785 Lister R., Shaw R., Strutt M., Möller I. (2011) Effects of elevated CO<sub>2</sub> concentrations on the  
786 vegetation and microbial populations at a terrestrial CO<sub>2</sub> vent at Laacher See, Germany,  
787 *International Journal of Greenhouse Gas Control* 5, 1093-1098.

788 Lemieux J.-M. (2011) Review: The potential impact of underground geological storage of  
789 carbon dioxide in deep saline aquifers on shallow groundwater resources, *Hydrogeology*  
790 *Journal*, 19, 757-778.

791

792 Lewicki J.L., Birkholzer J., Tsang C.-F. (2007) Natural and industrial analogues for leakage  
793 of CO<sub>2</sub> from storage reservoirs: identification of features, events, and processes and lessons  
794 learned, *Environ Geol*, 52, 457-467.

795

796 Mercier F., avec la collaboration de Ausseur Y. (1987) Fichier des eaux minérales du Puy de  
797 Dôme, rapport BRGM 87-SGN-780-AUV, 222 p.

798

799 Merle O., Michon L. (2001) The formation of the West European Rift: A new model as  
800 exemplified by the Massif central area, *Bull. Soc. Géol. France*, 172, 2, 81-89.

801

802 Michard G., Evrard M., Fouillac C., Lambert B. (1978) Acquisition des ions alcalino-terreux  
803 par les eaux carbogazeuses, *Earth Planet. Sci. Lett.* 41, 170-174.

804

805 Michard G. (1979) Géothermomètres chimiques. Bull. Du BRGM (2ème série) Section III 2,  
806 183–189.

807

808 Michard G., Fouillac C., Grimaud D., Denis J. (1981) Une méthode globale d'estimation des  
809 températures des réservoirs alimentant les sources thermales. Exemple du Massif Central  
810 Français, *Geochimica et Cosmochimica Acta*, 45, 1199-1207.

811

812 Michard G. (1990) Behaviour of major elements and some trace elements (Li, Rb, Cs, Sr, Fe,  
813 Mn, W, F) in deep hot waters from granitic areas. *Chem. Geol.* 89, 117–134.

814

815 Michel-Le Pierrès K., Gal F., Brach M., Guignat S. (2010) Radon, Helium and CO<sub>2</sub>  
816 measurements in soils overlying a former exploited oilfield, Pechelbronn district, Bas-Rhin,  
817 France, *J. Env. Rad.* 101, 835-846.

818

819 Négrel P., Fouillac C., Brach M. (1997a) Occurrence of mineral water springs in the the Allier  
820 River (Massif Central, France): stream channel of chemical and Sr isotope constraints, *Journal*  
821 *of Hydrology* 203, 143-153.

822

823 Négrel P., Fouillac C., Brach M. (1997b) Variations spatio-temporelles de la composition  
824 chimique et des rapports <sup>87</sup>Sr/<sup>86</sup>Sr des eaux minérales de la Limagne d'Allier, *C. R. Acad. Sci.*  
825 *Paris*, 325, 119-124.

826

827 Ramola R. C., Prasad Y., Prasad G. et al. (2008) Soil-gas radon as seismotectonic indicator in  
828 Garhwal Himalaya. *Applied Radiation and Isotopes*, 66, 1523-1530.

829

830 Riding J.B., Rochelle C.A. (2009) Subsurface characterisation and geological monitoring of  
831 the CO<sub>2</sub> injection operation at Weyburn, Saskatchewan, Canada, Geological Society, London,  
832 Special Publications, 313, 227-256.

833

834 Rihs S., Condomines M., Poidevin J.L. (2000) Long-term behaviour of continental  
835 hydrothermal systems: U-series study of hydrothermal carbonates from the French Massif  
836 Central (Allier Valley), *Geochimica et Cosmochimica Acta*, Vol. 64, No. 18, 3189–3199.

837

838 Schütze C., Sauer U., Beyer K., Lamert H., Bräuer K., Strauch G., Flechsig Ch., Kämpf H.,  
839 Dietrich P. (2012) Natural analogues: a potential approach for developing reliable monitoring  
840 methods to understand subsurface CO<sub>2</sub> migration processes, *Environ. Earth Sci.*, DOI  
841 10.1007/s12665-012-1701-4.

842

843 Spangler L.H. (2010) Foreword to the Special Issue on Zero Emission Research and  
844 Technology Center testing field site, Bozeman, Montana, USA, *Environ. Earth Sci.* 60, 225.

845

846 Stettler A. (1977) <sup>87</sup>Rb-<sup>87</sup>Sr systematic of a geothermal water-rock association in the Massif  
847 Central, France. *Earth and Planet. Sci, Lett.*, 34, 432-438.

848

849 Truesdell A.H. (1975) Geochemical techniques in exploration, summary of section III, In:  
850 Proceedings Second United Nation Symposium on the development and use of geothermal  
851 resources, vol. 1, pp. Iiii–Ixiii.

852

853 Wattanakorn K., Kanaree M., Wiboolsake S. (1998) Soil gas radon as an earthquake  
854 precursor: some considerations on data improvement. *Radiation Measurements*, 29, 593-598.

855

856 **Figure captions:**

857

858 Figure 1: location of the study area: dots locate points where soil gas data are available: black  
859 dots refer to 2006-2010 data acquisitions, red contoured dots are from the 90's dataset. Red  
860 dots represent the main mineral waters that are labelled in the inset. Yellow dots (labelled 1 to  
861 4) represent points where continuous monitoring was performed. Grey lines represent main  
862 roads.

863

864 Figure 2: O<sub>2</sub> – CO<sub>2</sub> relationship for the 2006-2010 soil gas measurements; the equimolar  
865 replacement line (1 mole CO<sub>2</sub> ⇌ 1 mole O<sub>2</sub>) is represented. Model line corresponds to the  
866 regression line between the 2 species; the 95% confidence interval of the regression is also  
867 indicated.

868

869 Figure 3: relationships between Ar, N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> concentrations (% vol.) on samples  
870 analysed using laboratory gas chromatography (samples from year 2007).

871

872 Figure 4: A: Relationships between CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He in soil gas (2006-2010 dataset); B:  
873 detail of the CO<sub>2</sub> - <sup>222</sup>Rn relationship for low <sup>222</sup>Rn concentrations (lesser than 300,000 Bq.m<sup>-3</sup>).  
874 <sup>3</sup>).

875

876 Figure 5: Relationships between CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He in soil gas.

877

878 Figure 6: spatial distribution of soil gas species (from left to right: CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He) along  
879 with time (from top to bottom). Interpolation is done using natural neighbour contouring.

880

881 Figure 7: CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He concentrations (2006 to 2010 measurements) recalculated in the  
882 0 – 1 interval to lower the influence of <sup>222</sup>Rn and strengthen the one of <sup>4</sup>He (arbitrary units).  
883 See text for explanation.

884

885 Figure 8: a: temporal evolution of pressure for Barasol probes (labelled as F10X) for points 2  
886 and 4 (Figure 1) and comparison with atmospheric data (Clermont-Ferrand Aulnat airport;  
887 <http://french.wunderground.com/>); b: evolution of soil temperatures and atmospheric  
888 temperature (same chart as for 8a); c: <sup>222</sup>Rn concentrations over time; blanked areas (F109  
889 probe) correspond to power supply deficiency or to electronical malfunctioning of the <sup>222</sup>Rn  
890 detector.

891

892 Figure 9: F109 Barasol probe (point 4 in Figure 1); period from the 26 February 2009 to the  
893 07 April 2009; a: temporal evolution of soil temperature and <sup>222</sup>Rn concentrations; b: temporal  
894 evolution of atmospheric pressure and <sup>222</sup>Rn concentrations; c: temporal evolution of  
895 atmospheric temperature and <sup>222</sup>Rn concentrations; d: spectral densities of <sup>222</sup>Rn  
896 concentrations; e and f: Principal Component Analysis using these 4 parameters.

897

898 Figure 10: a: temporal evolution of water temperature of Geyser Brissac during deployment;  
899 b: temporal evolution of temperature (°C), pH, specific conductance at 25°C (mS.cm<sup>-1</sup>),  
900 dissolved oxygen content (mg.L<sup>-1</sup>), redox potential (Eh, mV) and dissolved CO<sub>2</sub> (expressed as  
901 a mV value) during the second day of deployment.

902

903 **List of tables:**

904

905 Table 1: statistical parameters for the CO<sub>2</sub>, <sup>222</sup>Rn and <sup>4</sup>He concentrations during the 90's and  
906 2000's surveys (Sainte-Marguerite area; see Figure 1 for location).

907

908 Table 2: physico-chemical parameters of mineral waters from the Sainte-Marguerite area (see  
909 location in Figure 1). Major ion contents are reported; blanks indicate a non-detection of the  
910 specie or a non-measurement (isotope ratios). δ<sup>18</sup>O and δD isotope ratios are reported as well  
911 as the δD difference to the local meteoric water line (δD = 8 δ<sup>18</sup>O + 13.1; Fouillac *et al.*,  
912 1991). Equilibrium partial CO<sub>2</sub> pressure is computed using Diagrammes software  
913 (<http://www.lha.univ-avignon.fr/>).

914

915 Table 3: descriptive statistics for <sup>222</sup>Rn concentrations acquired using Barasol probes.

916

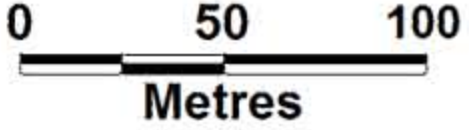
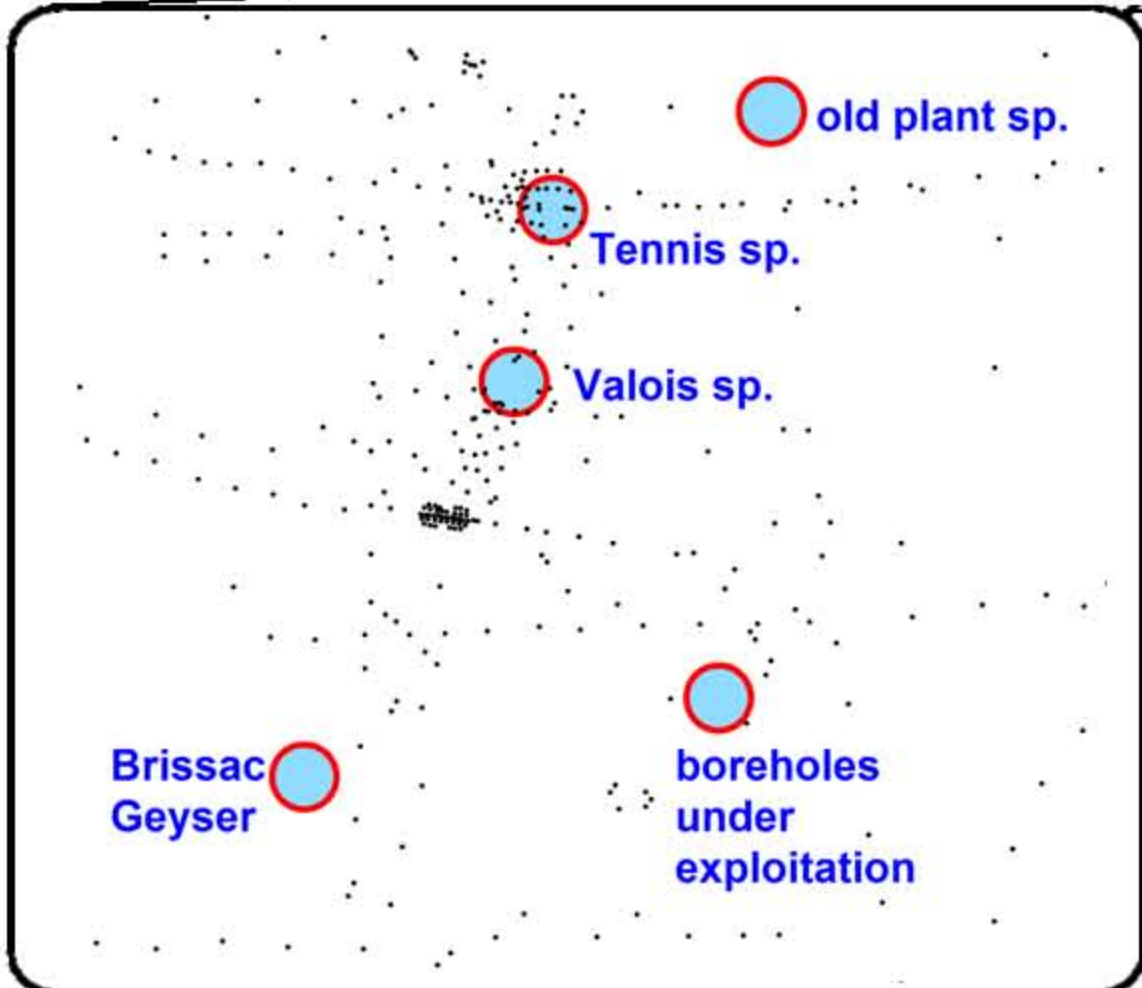
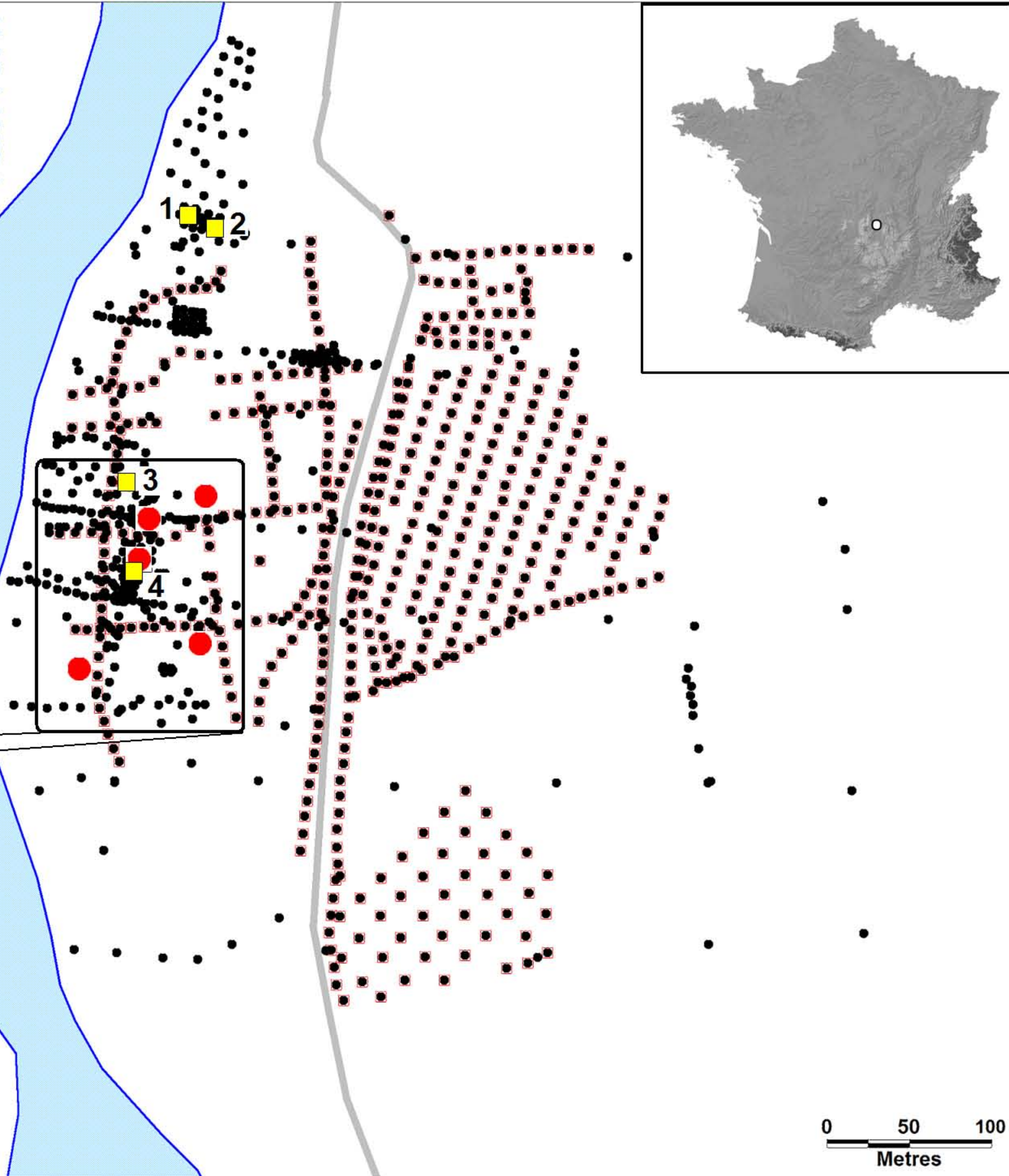
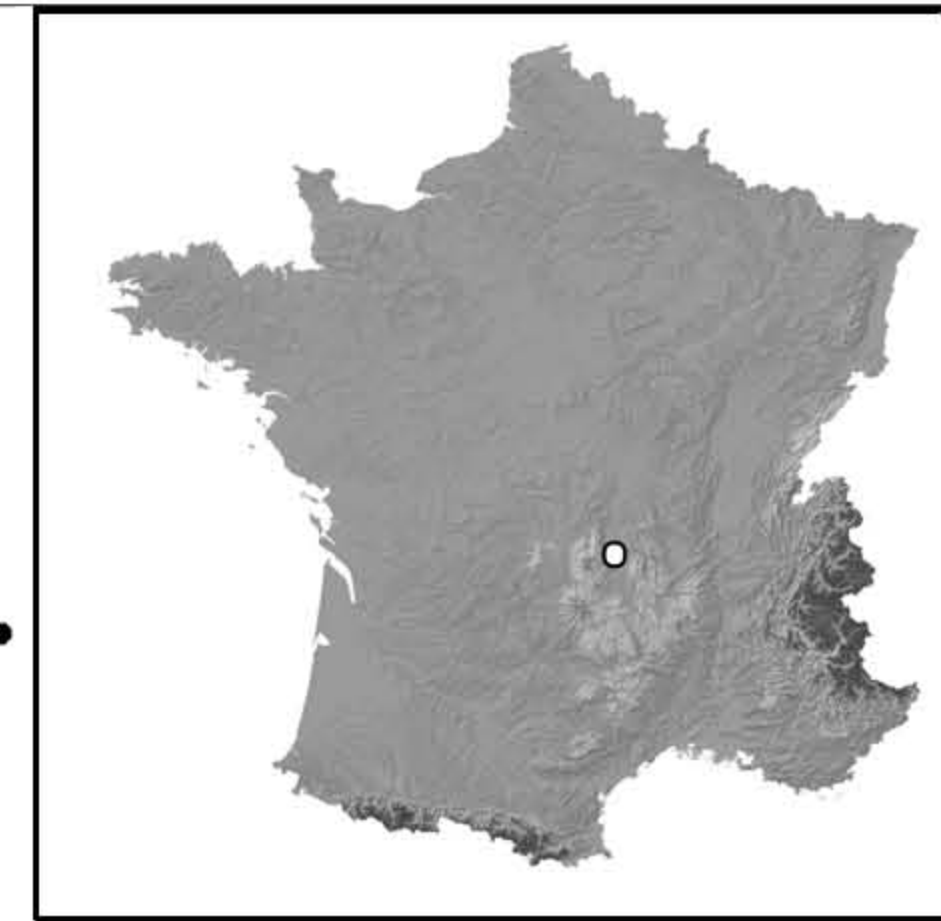
917 Table 4: top: evolution of temperature (°C), pH, specific conductance at 25°C (EC, mS.cm<sup>-1</sup>),  
918 dissolved oxygen content (mg.L<sup>-1</sup>), redox potential (Eh, mV) and dissolved CO<sub>2</sub> (expressed as  
919 a mV value) along the 4 days of monitoring of the Geyser Brissac (monitoring duration  
920 indicated into brackets); bottom: correlation matrix for each daily dataset. Geyser Brissac was  
921 sampled on day 3 (Table 2).





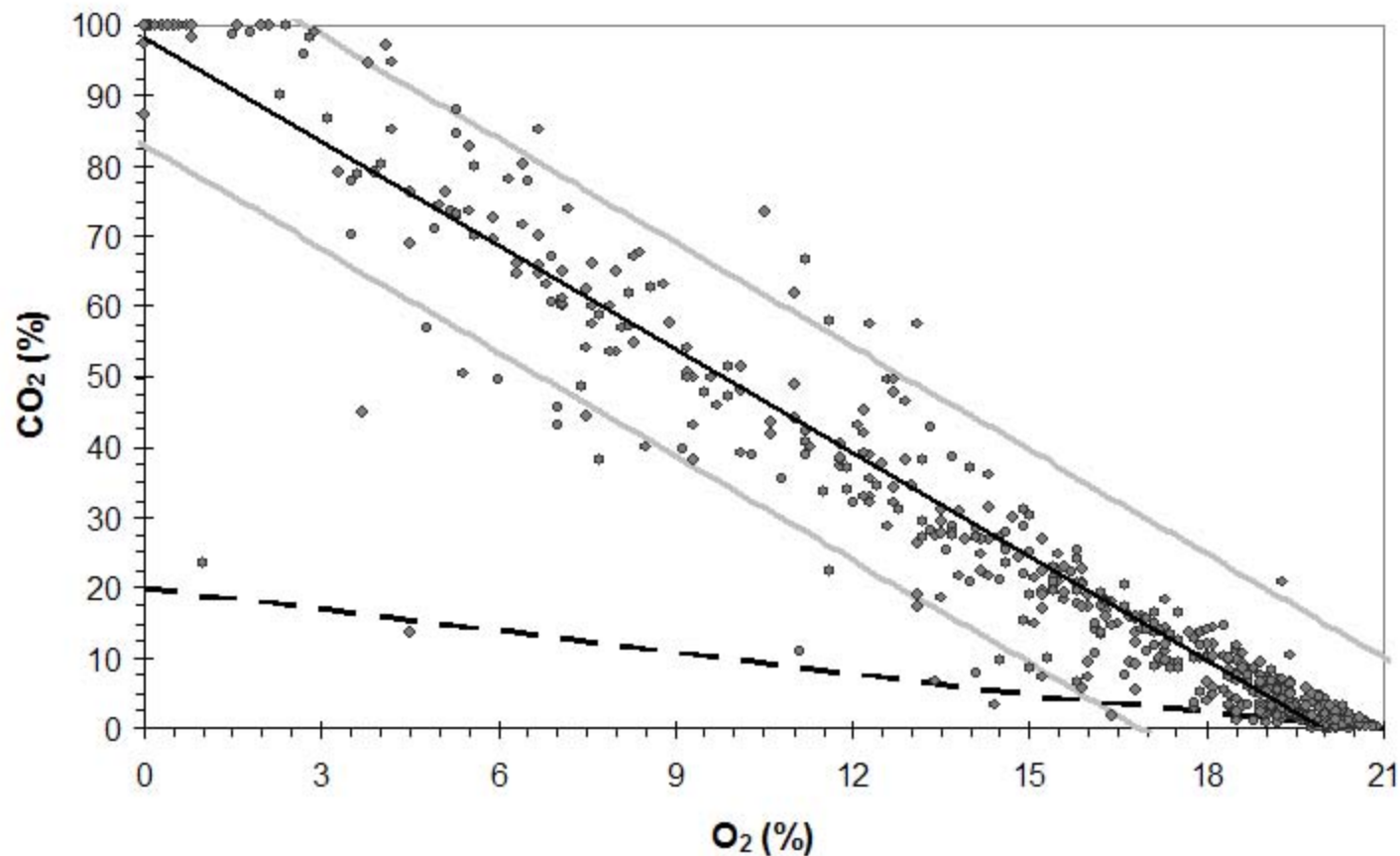
Saladis  
springs

Allier River





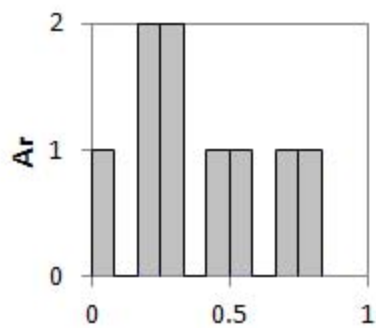
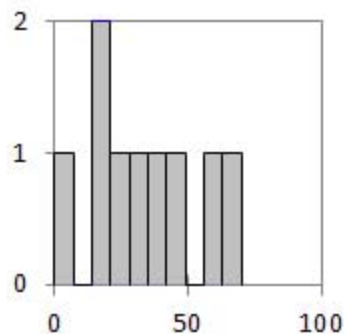
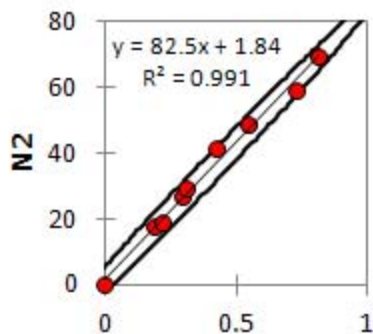
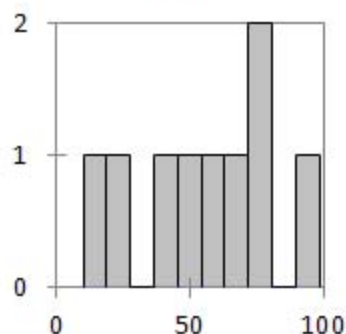
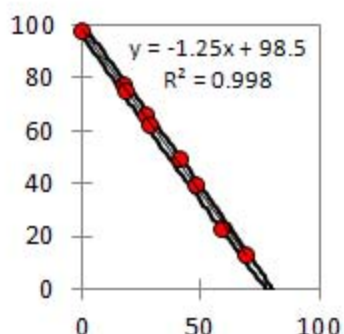
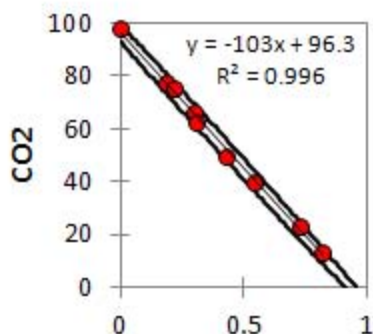
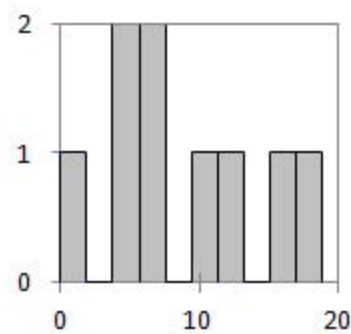
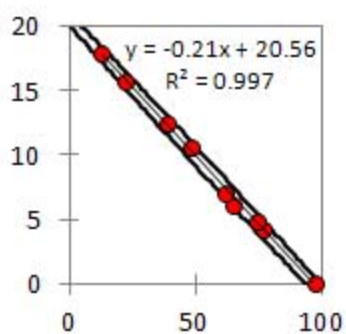
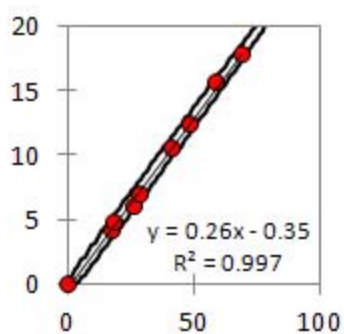
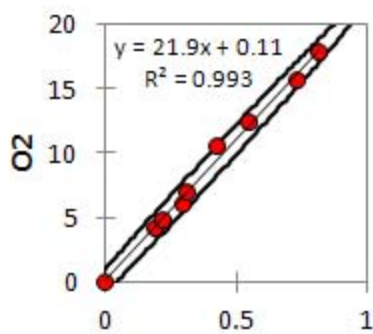
$$\text{CO}_2 (\%) = 98.2 - 4.92 \times \text{O}_2 (\%) \quad (R^2=0.943; n = 566)$$

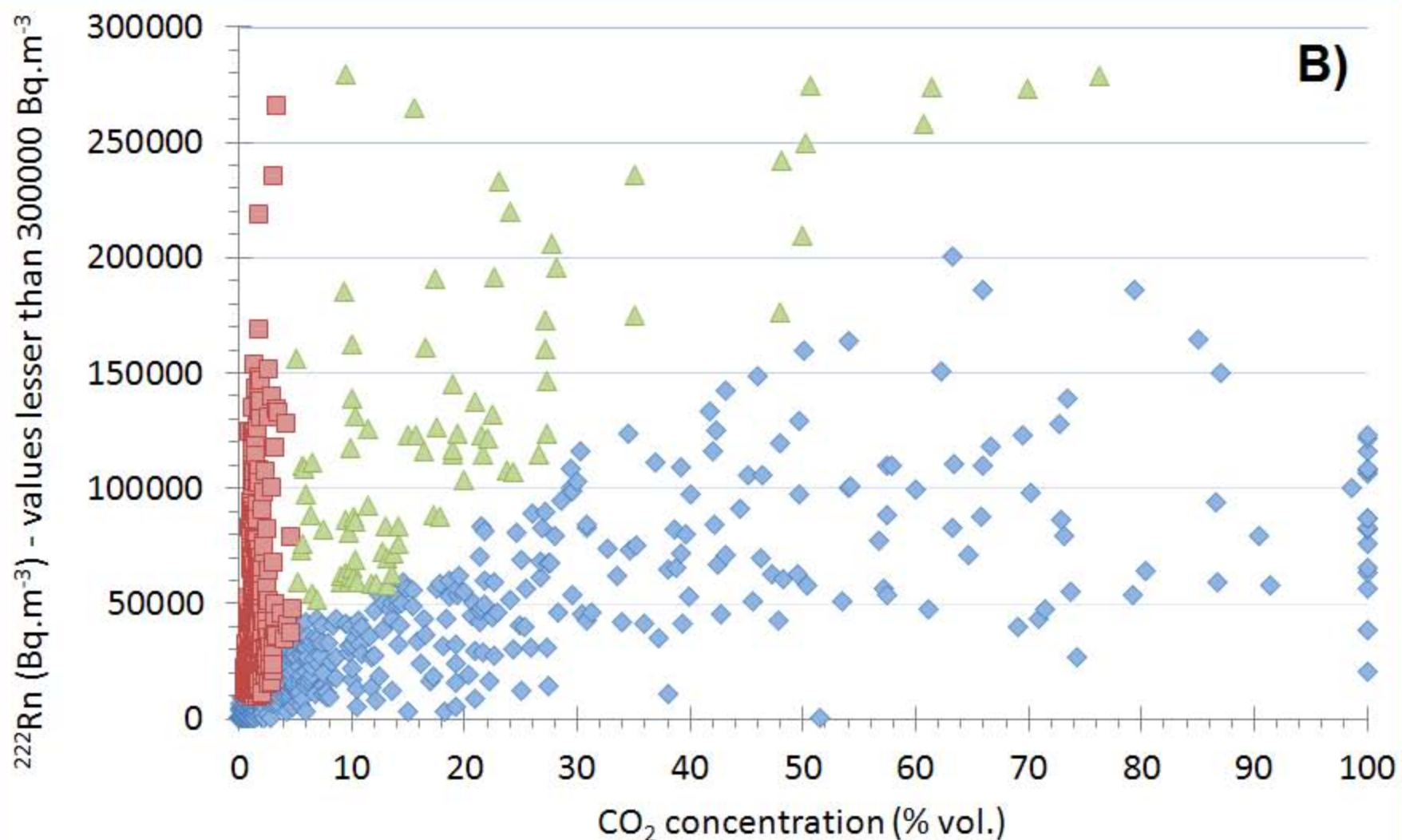
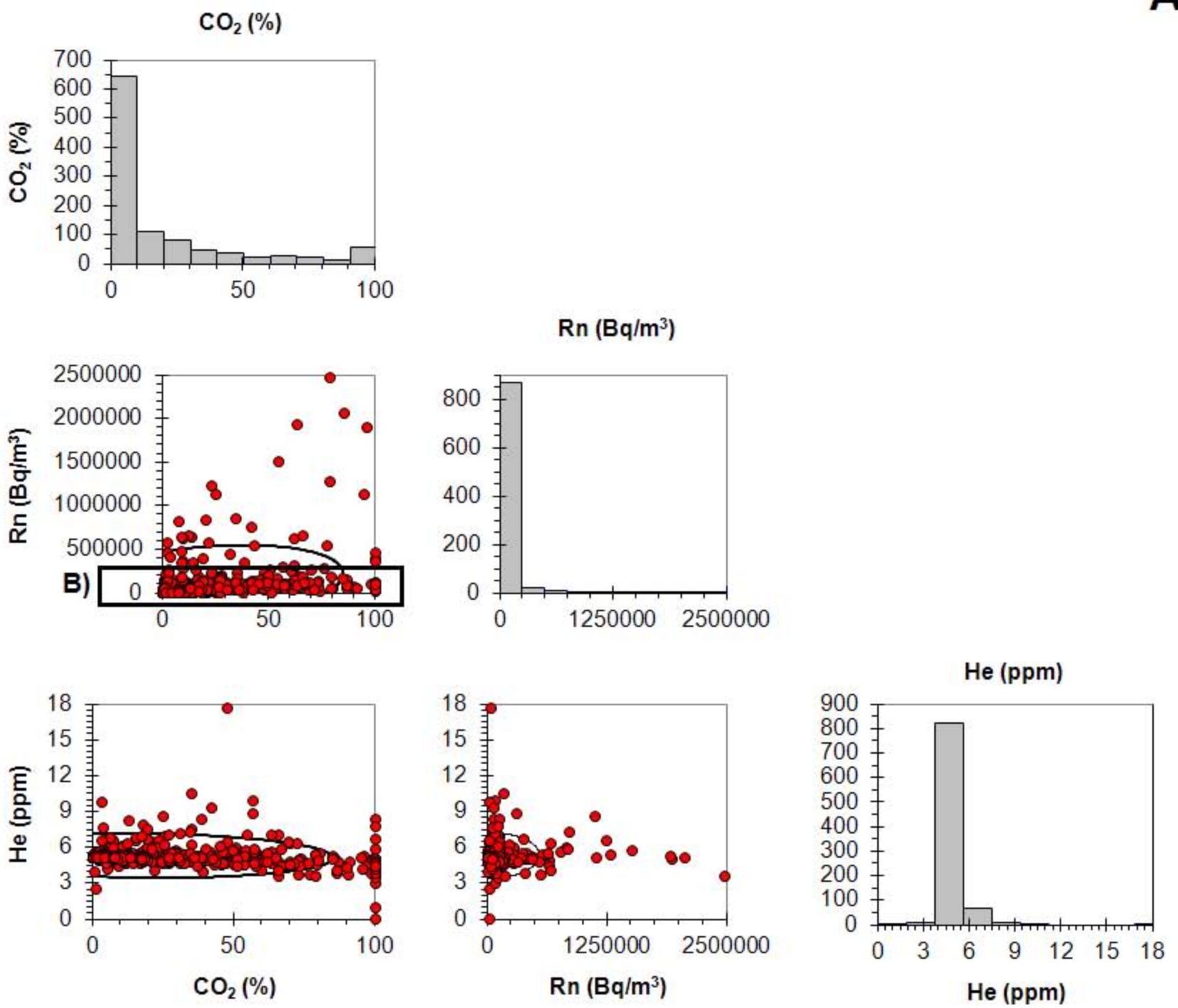


— Model

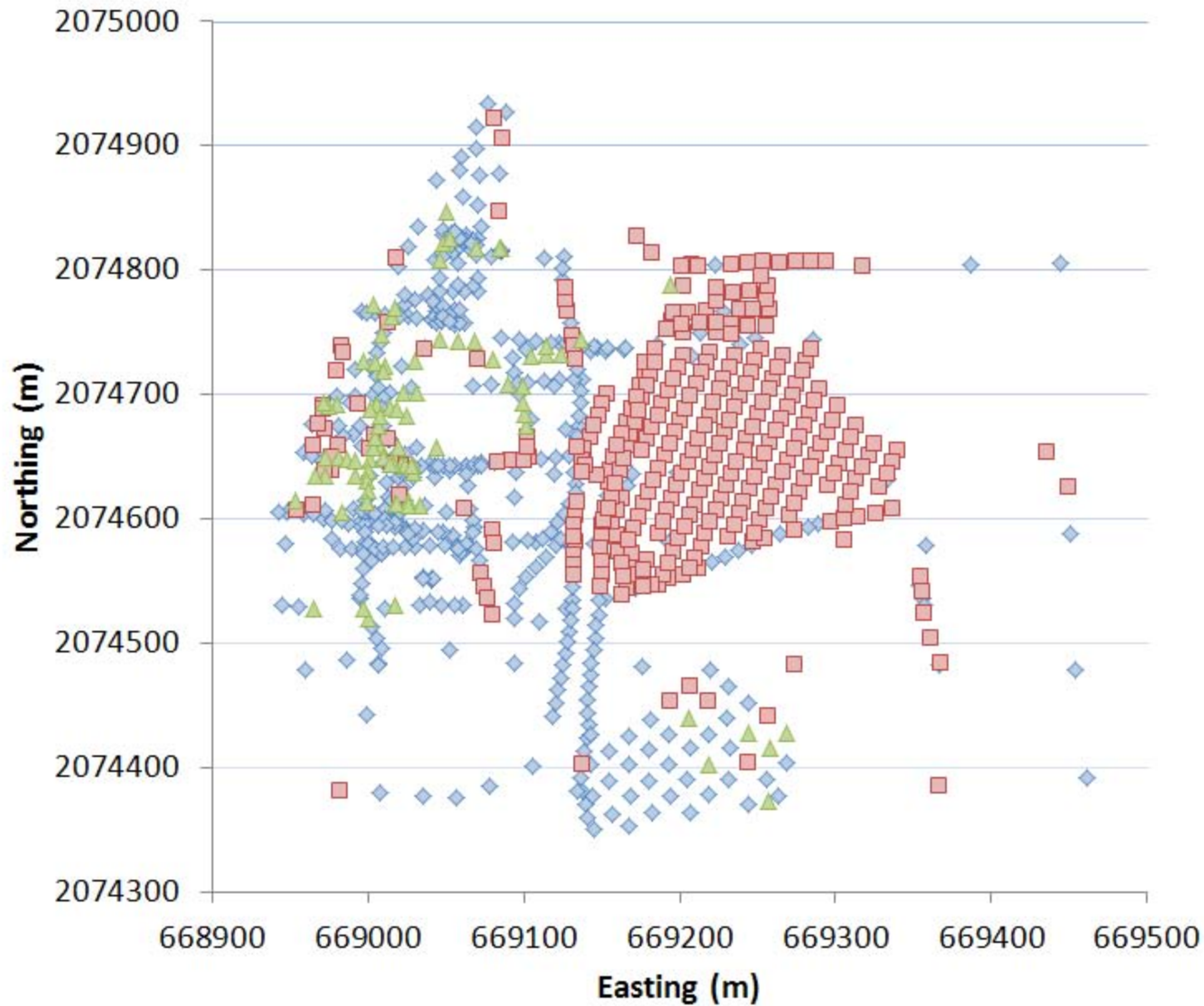
— Conf. int. (Obs. 95%)

- - 1:1 replacement

**Ar****N2****CO2****O2****Ar****N2****CO2****O2**

**A)**◆ slow  $^{222}\text{Rn}$  enrichment vs.  $\text{CO}_2$  enrichment■ fast  $^{222}\text{Rn}$  enrichment vs.  $\text{CO}_2$  enrichment

▲ intermediate tendency

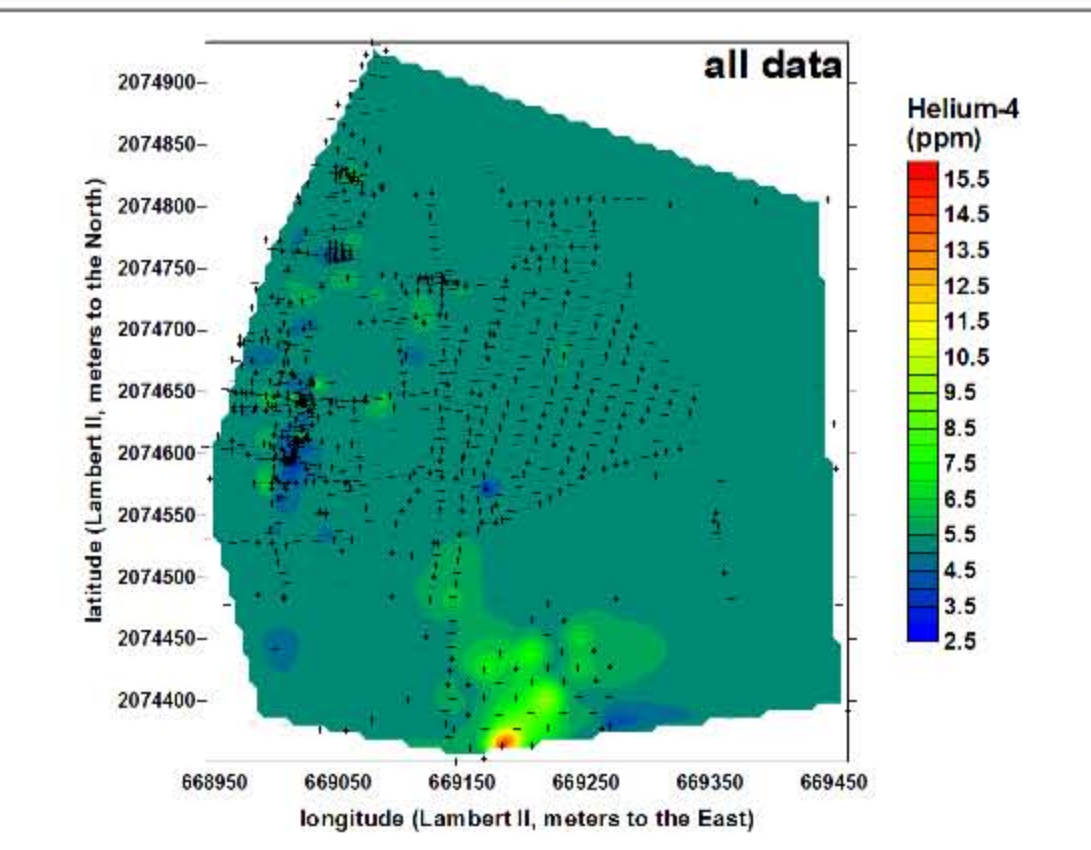
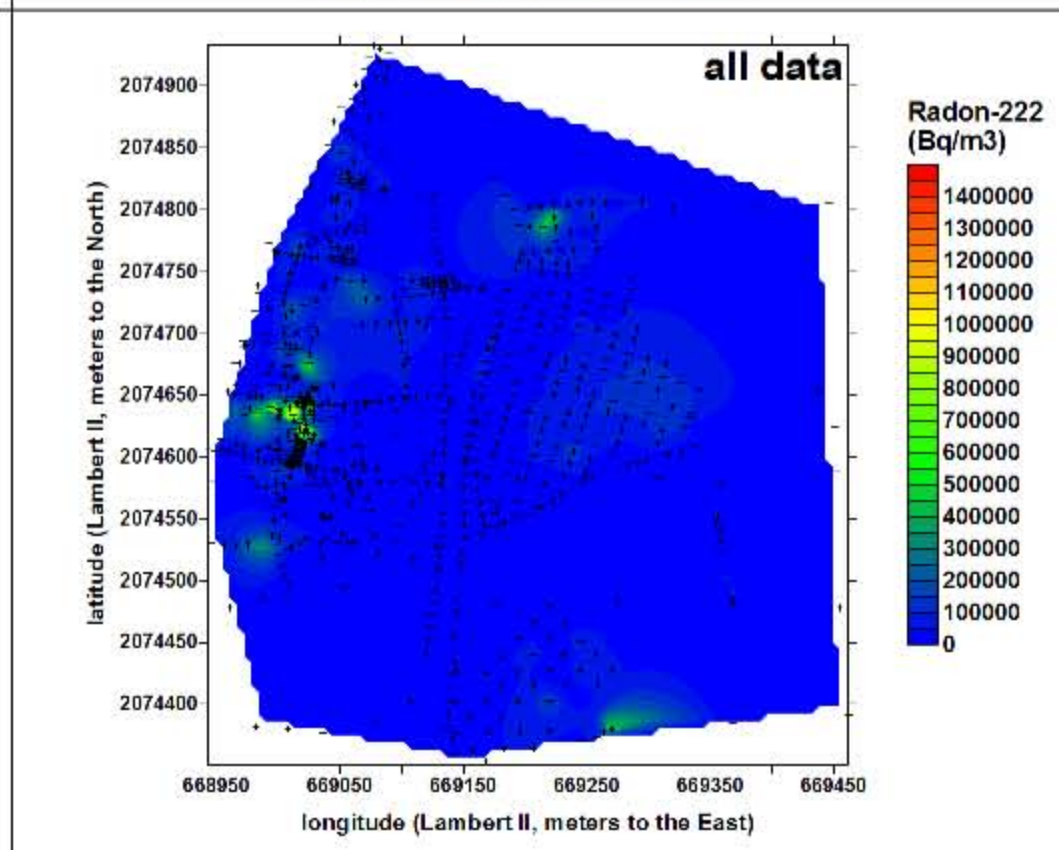
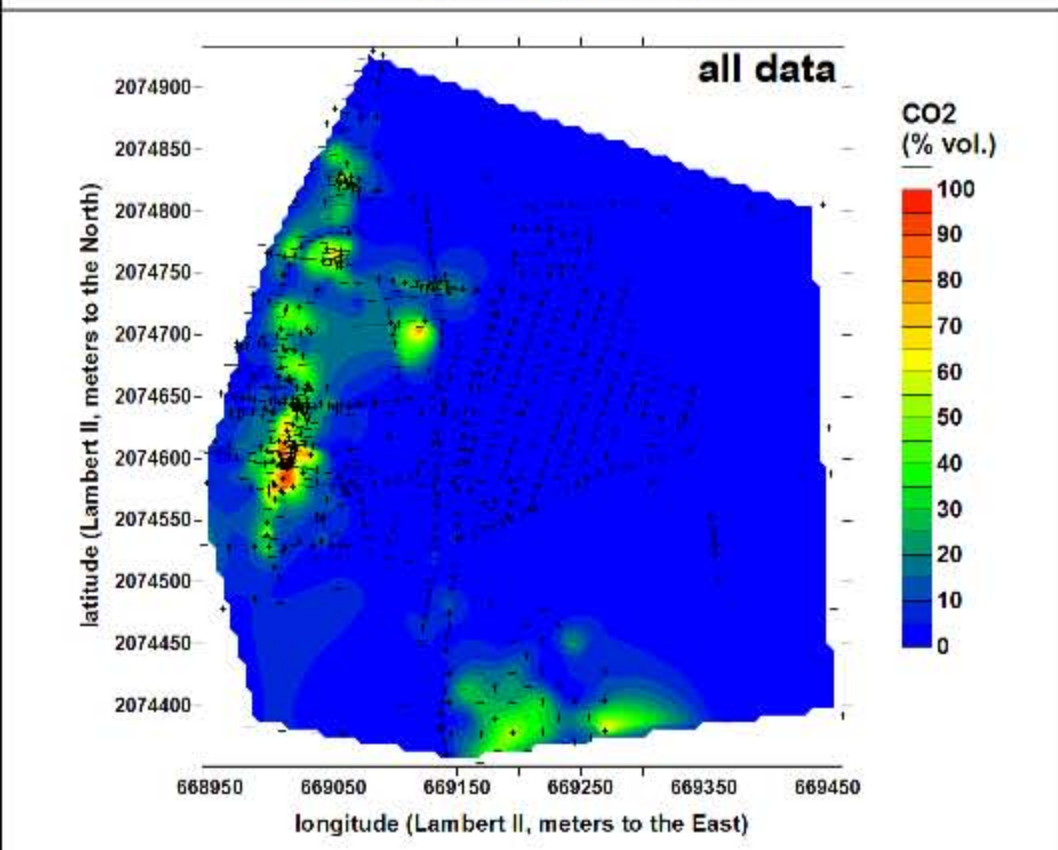
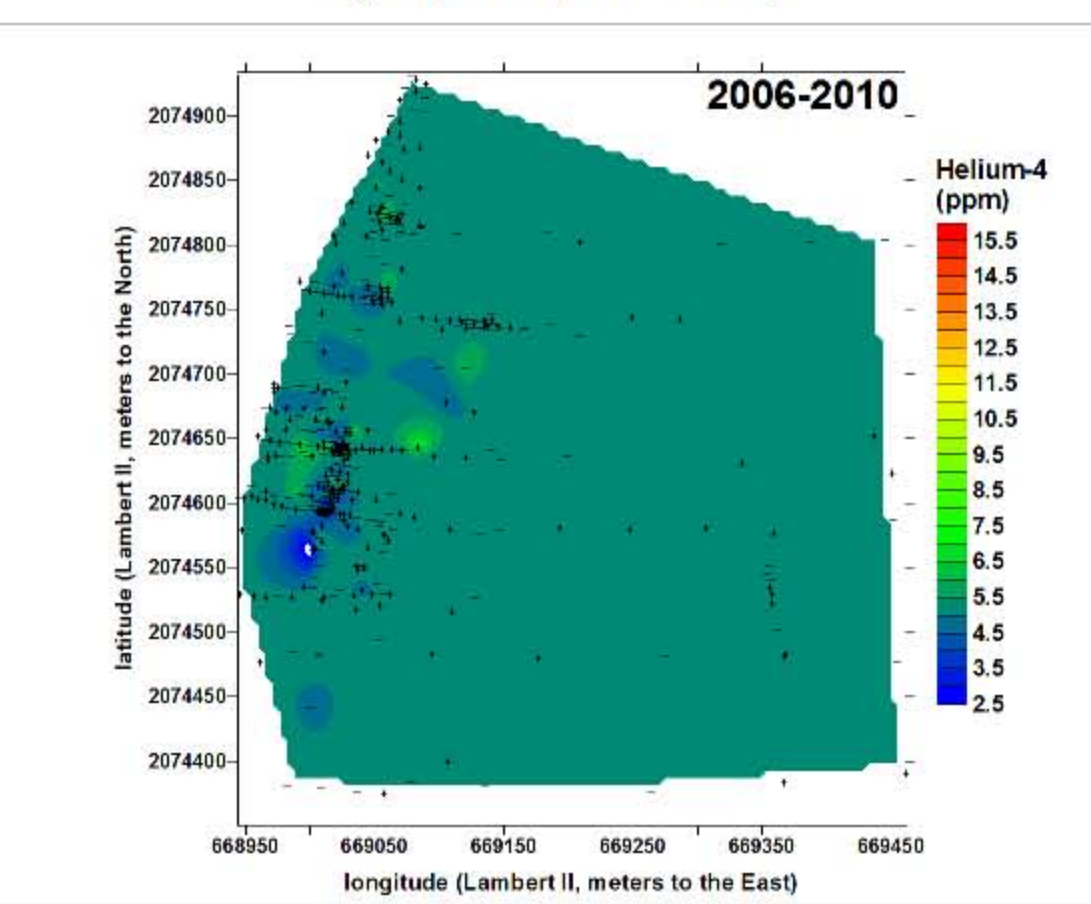
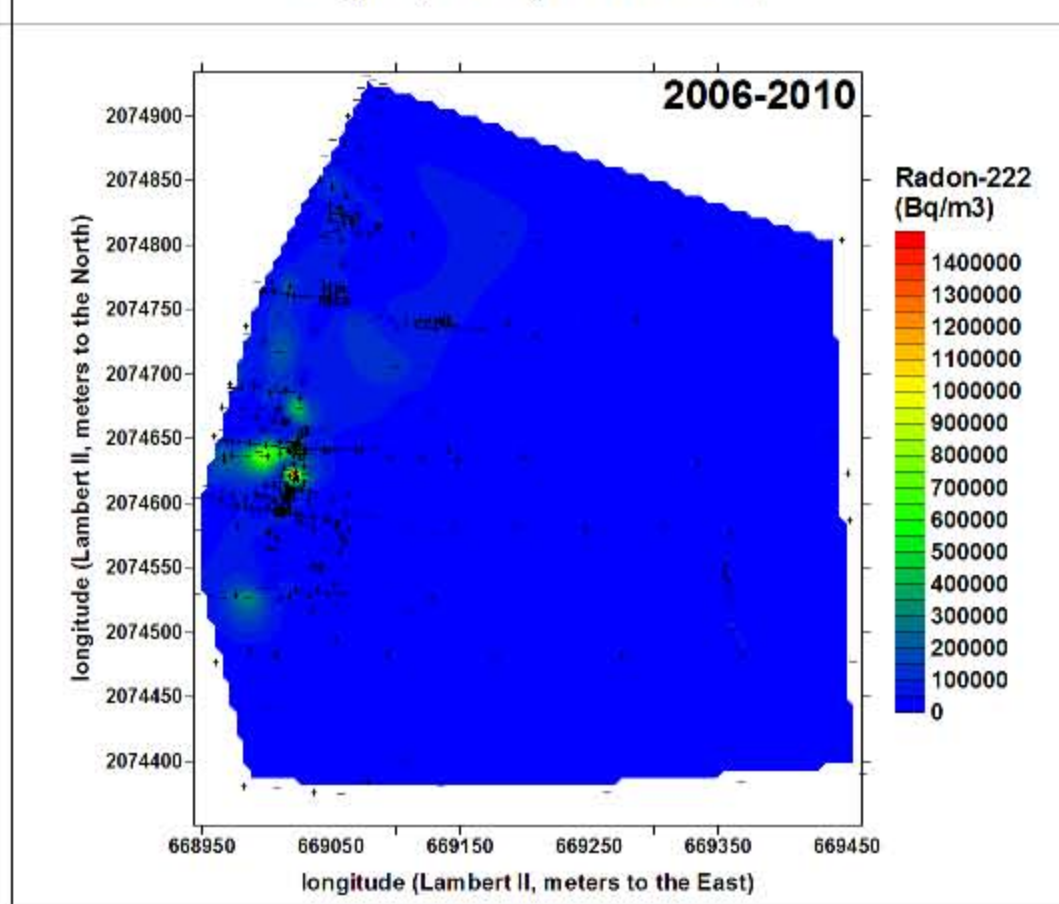
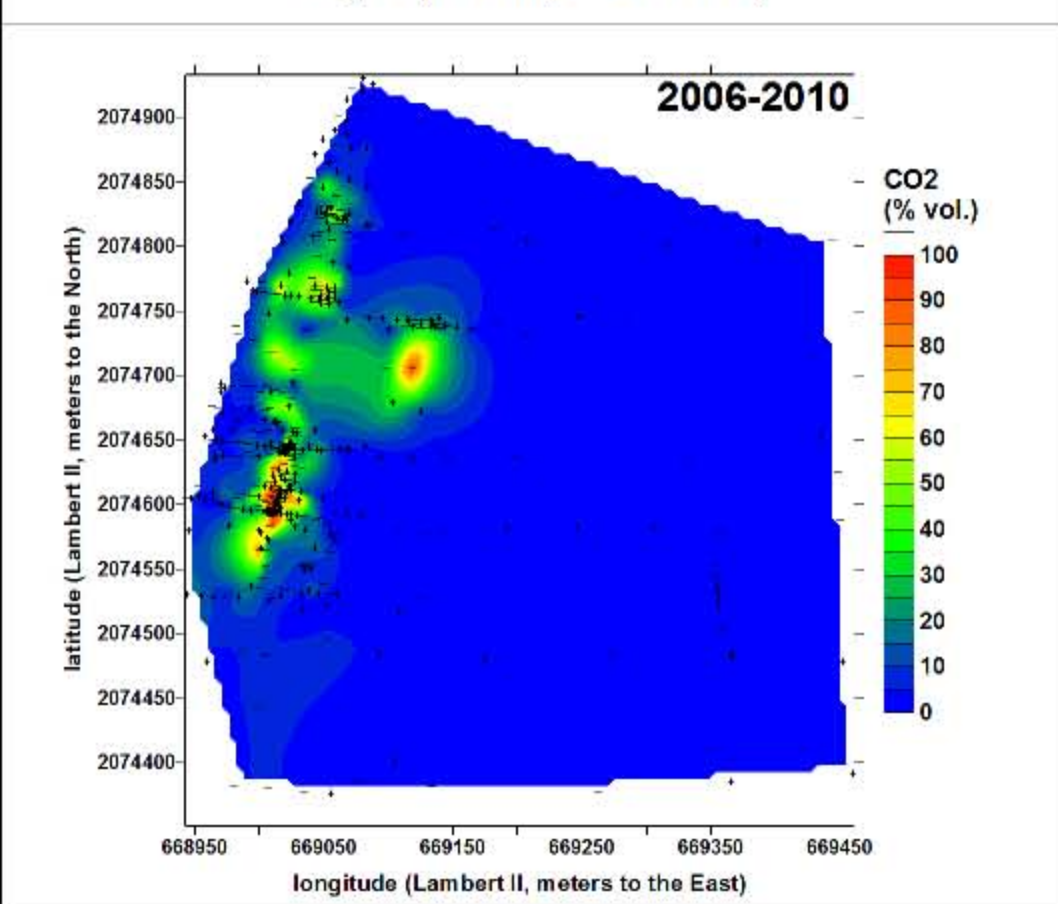
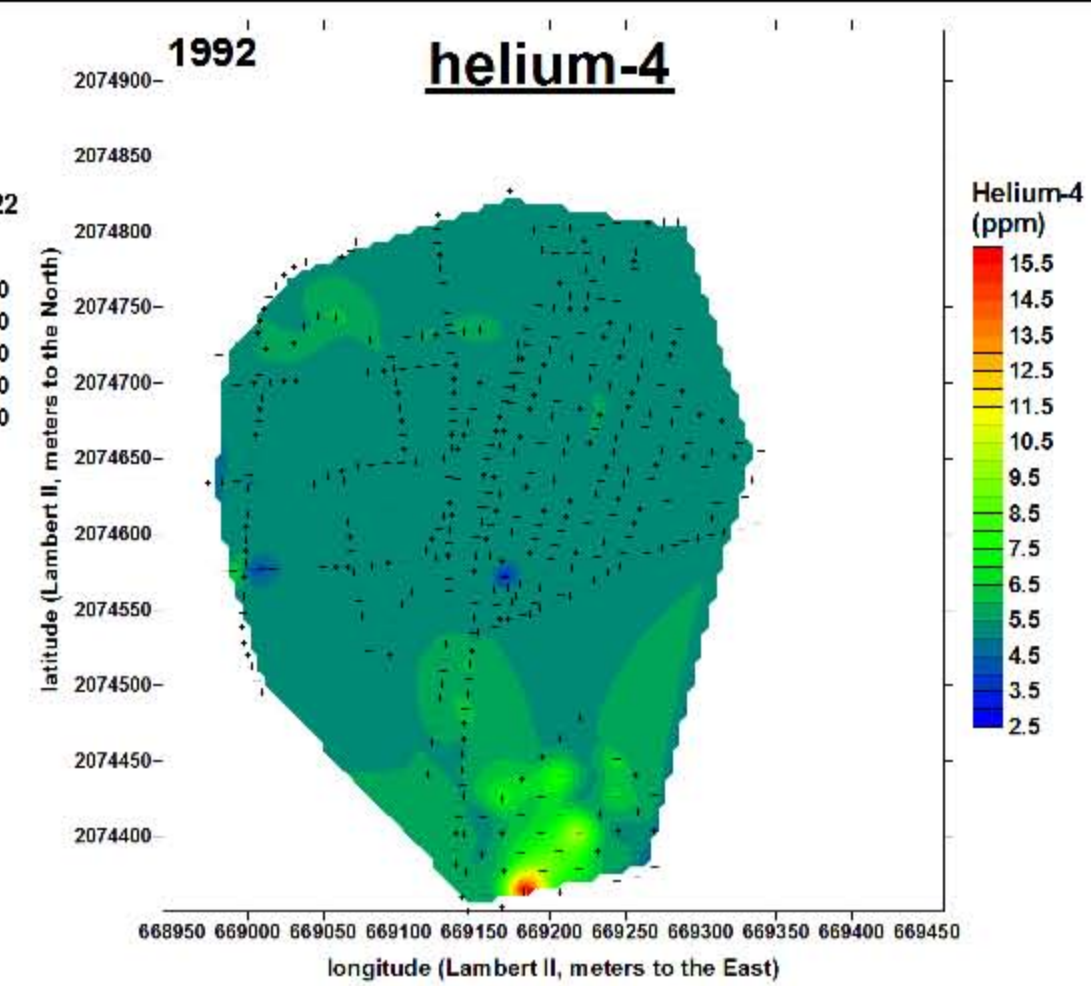
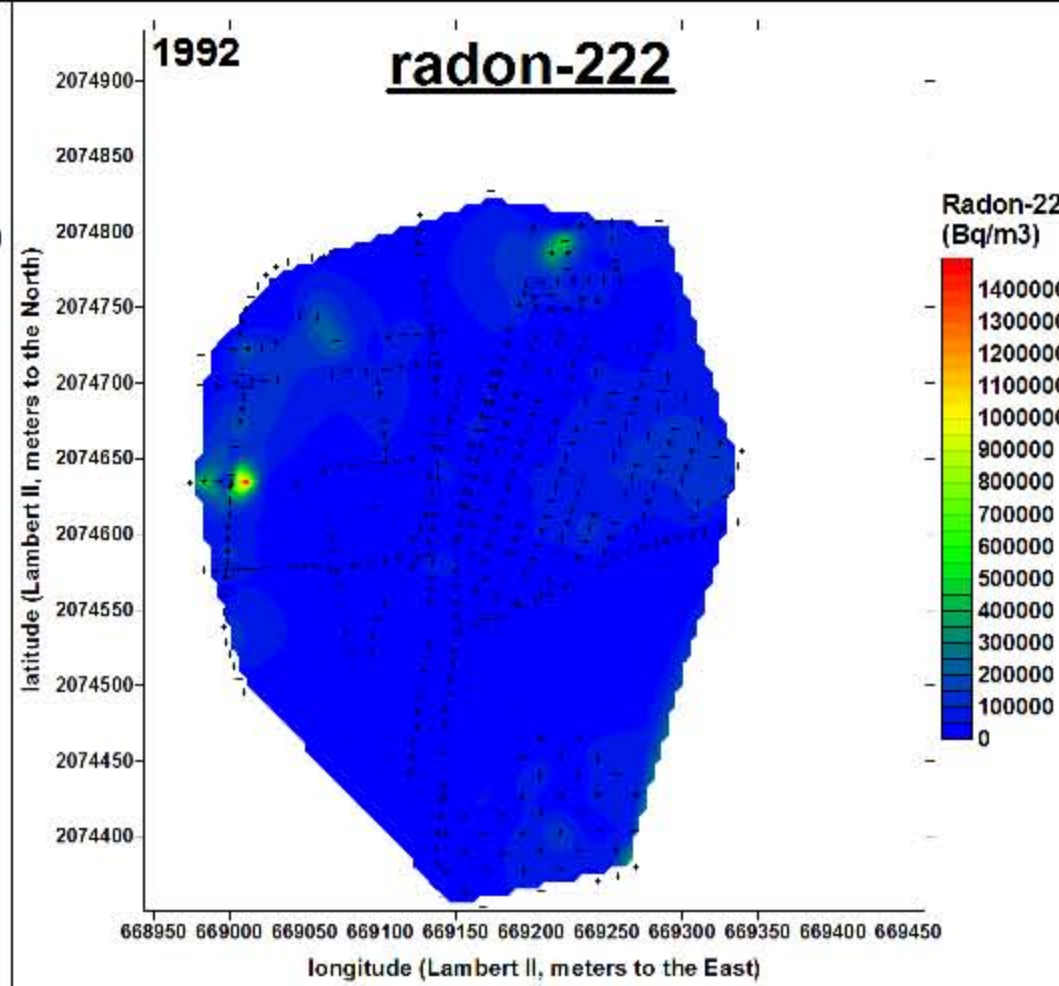
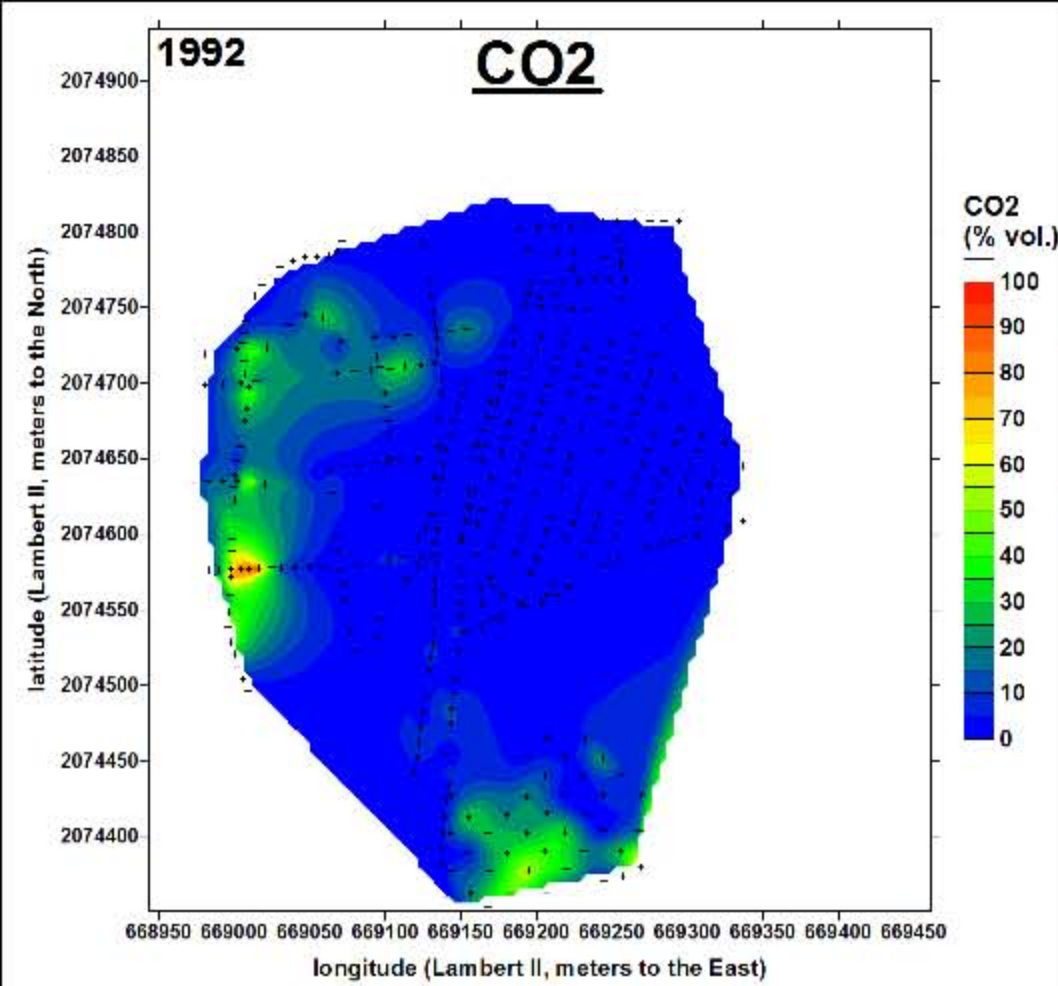


◆ slow  $^{222}\text{Rn}$  enrichment vs.  $\text{CO}_2$  enrichment

■ fast  $^{222}\text{Rn}$  enrichment vs.  $\text{CO}_2$  enrichment

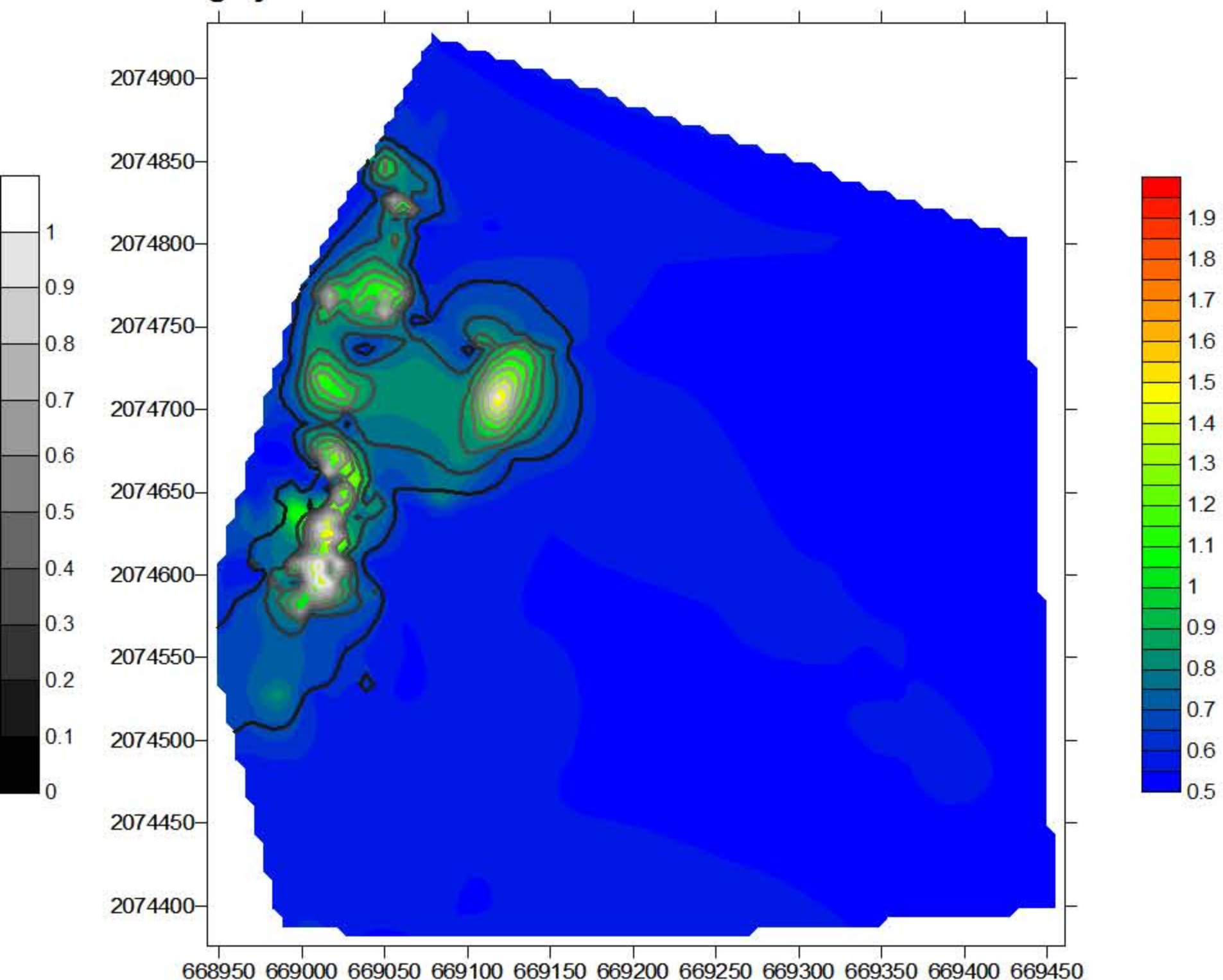
▲ intermediate tendency



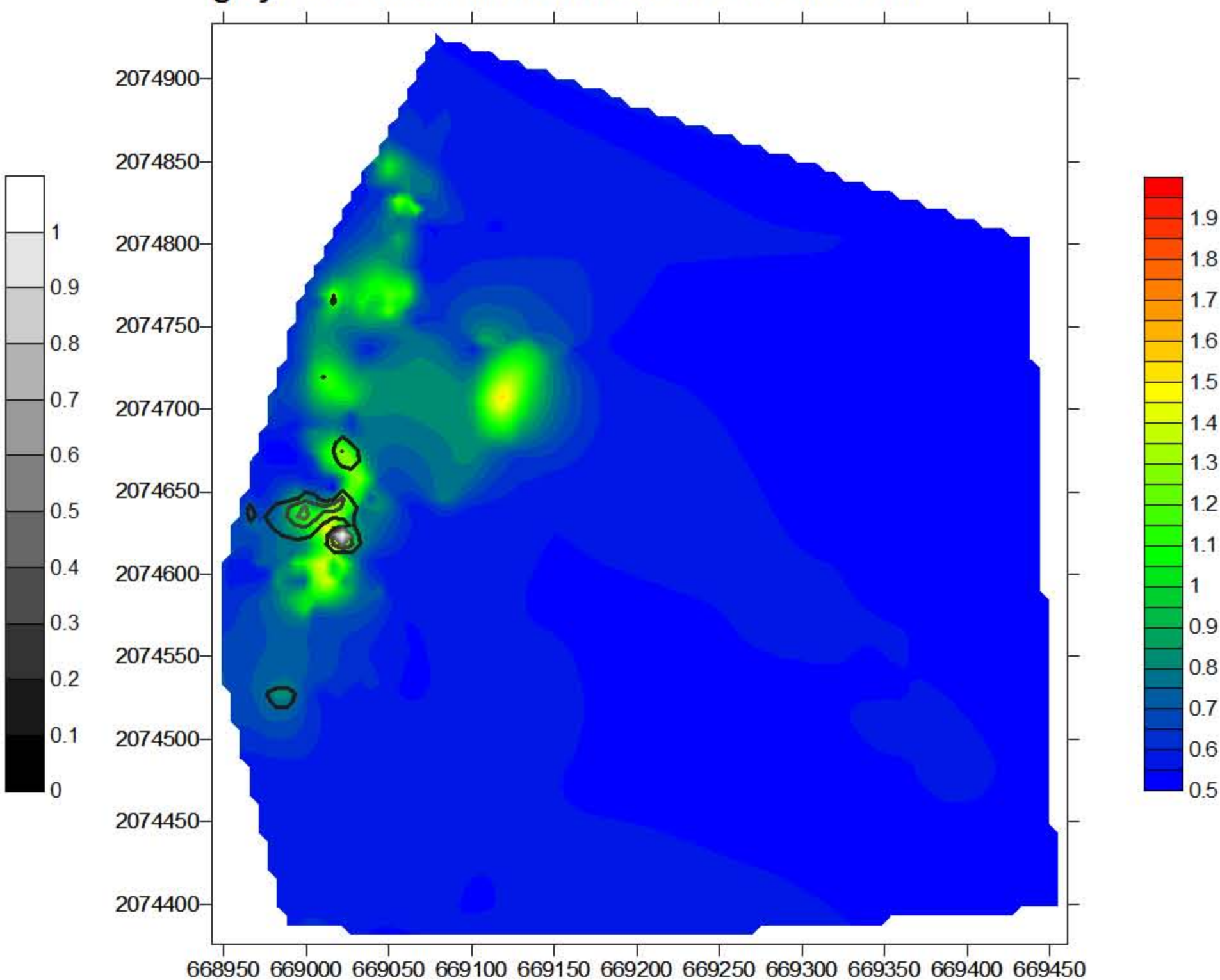




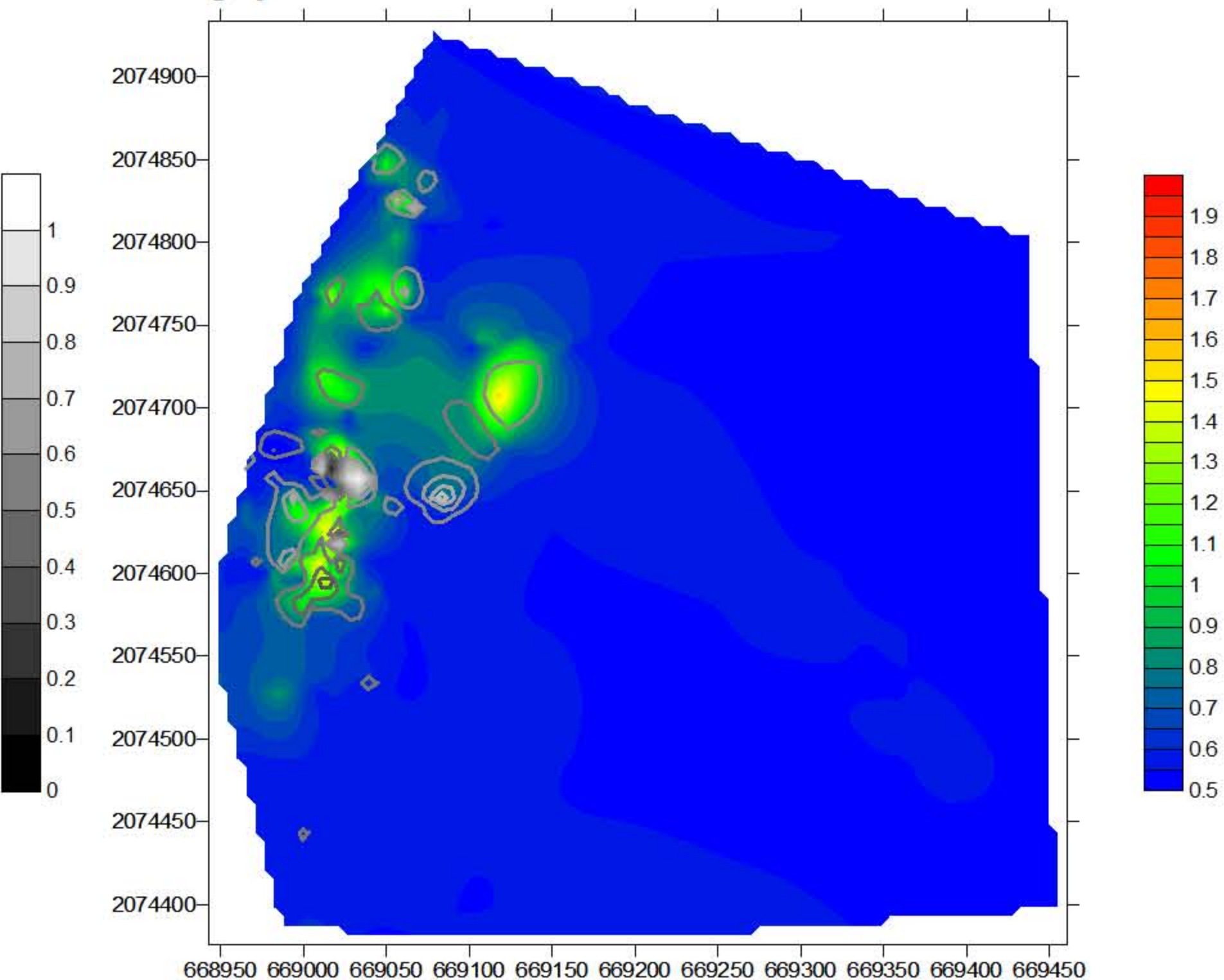
colorscale: sum of CO2 + radon + helium fitted in the 0 - 1 interval  
greyscale: CO2 distribution in the same interval



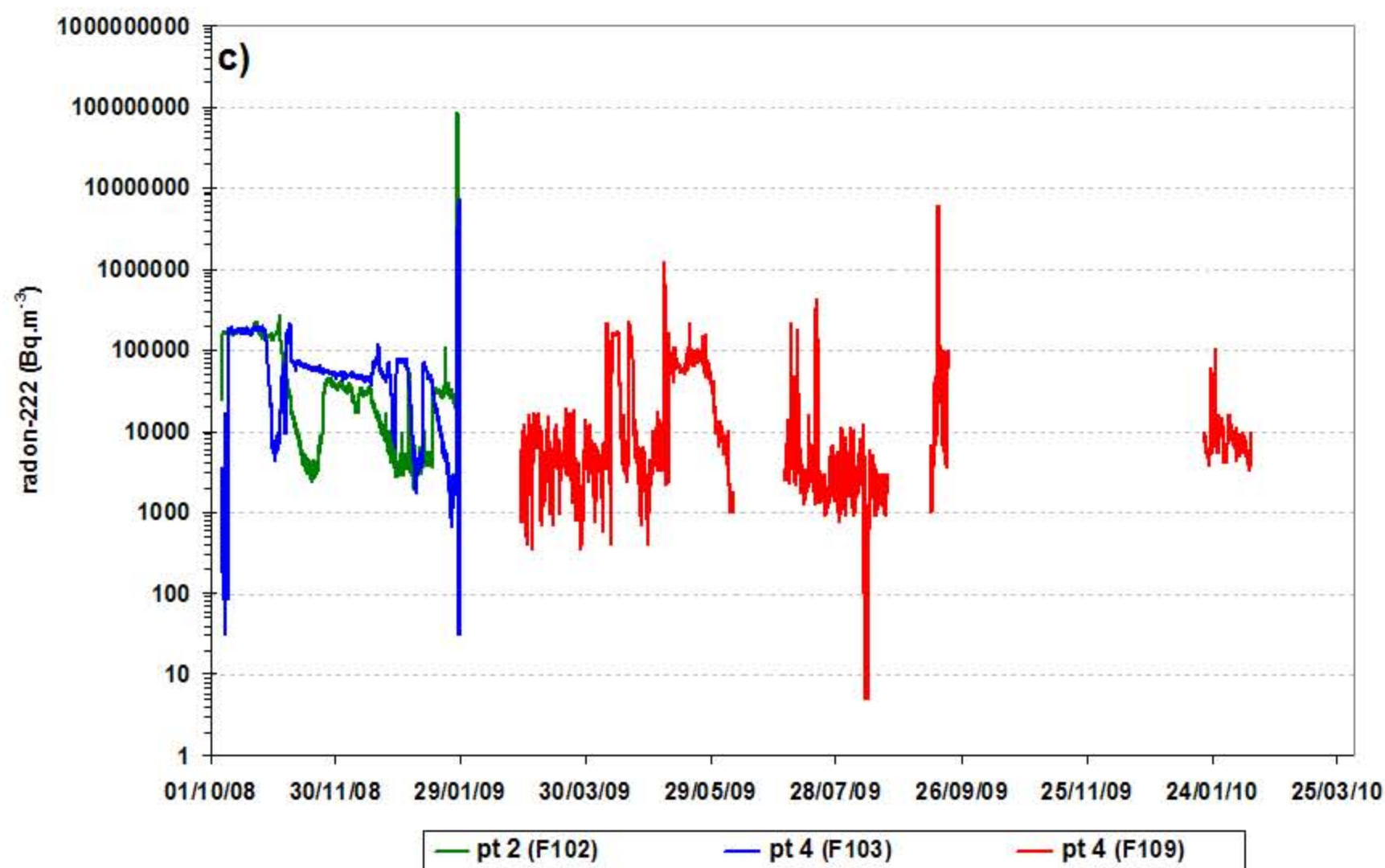
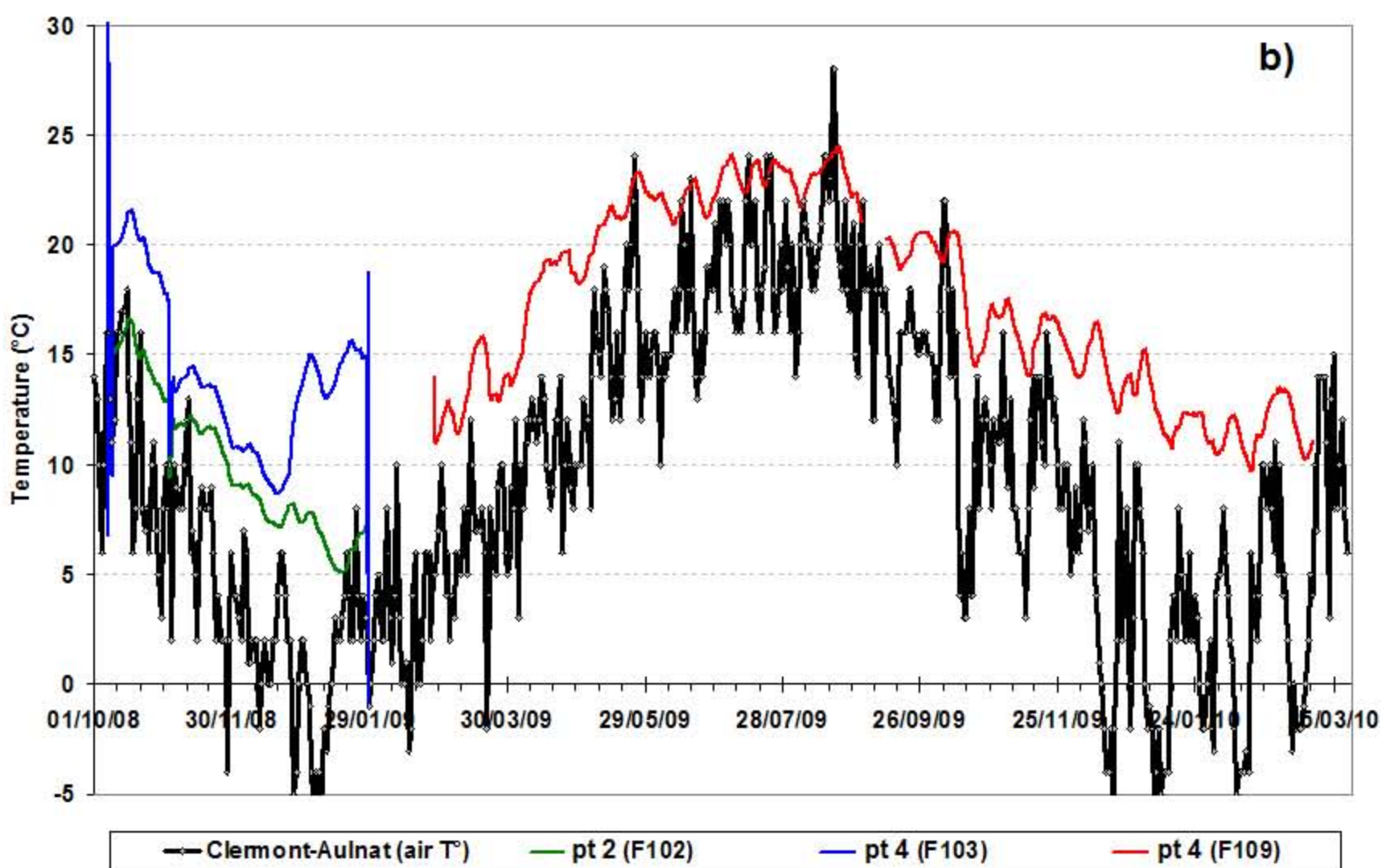
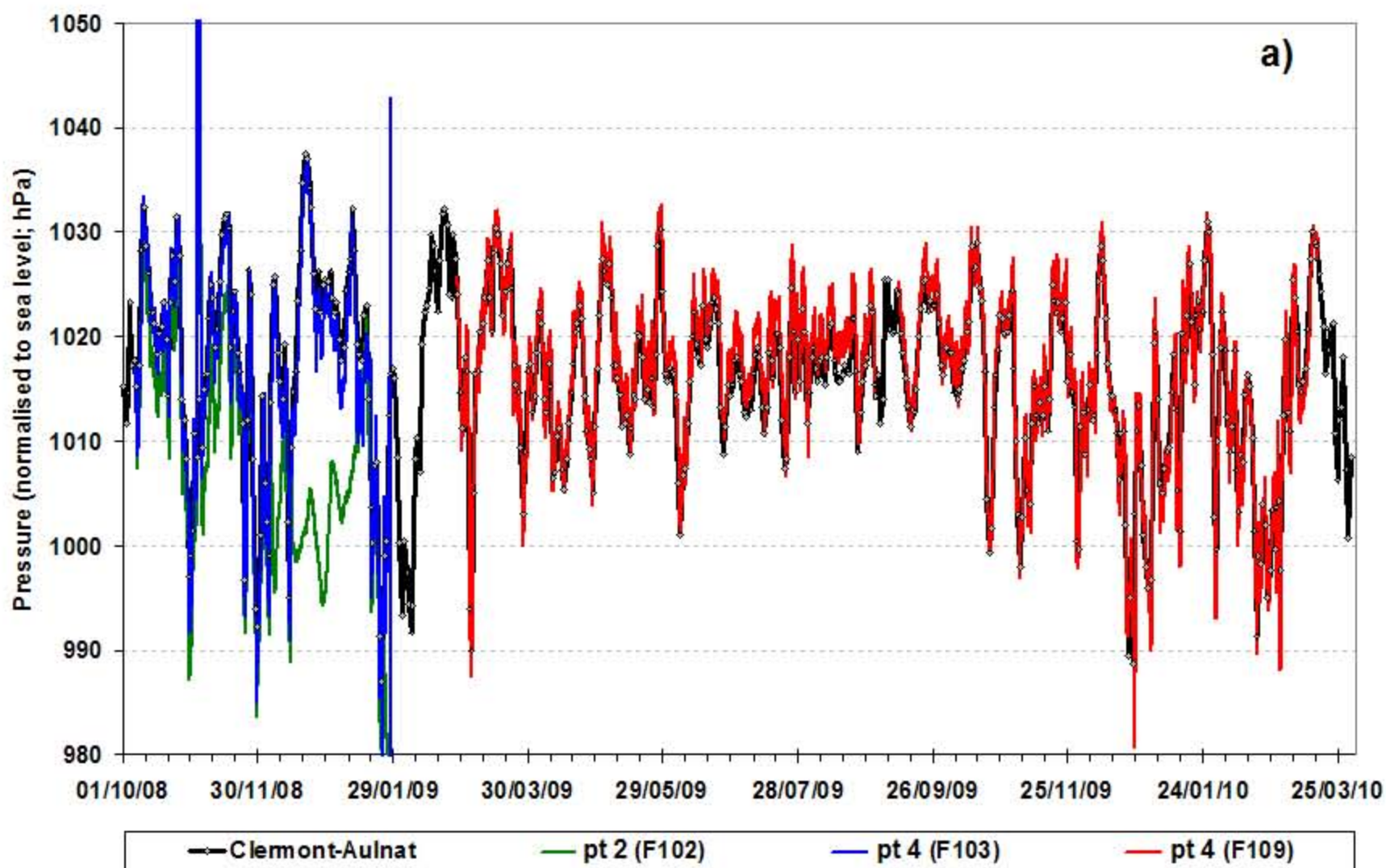
colorscale: sum of CO2 + radon + helium fitted in the 0 - 1 interval  
greyscale: radon distribution in the same interval



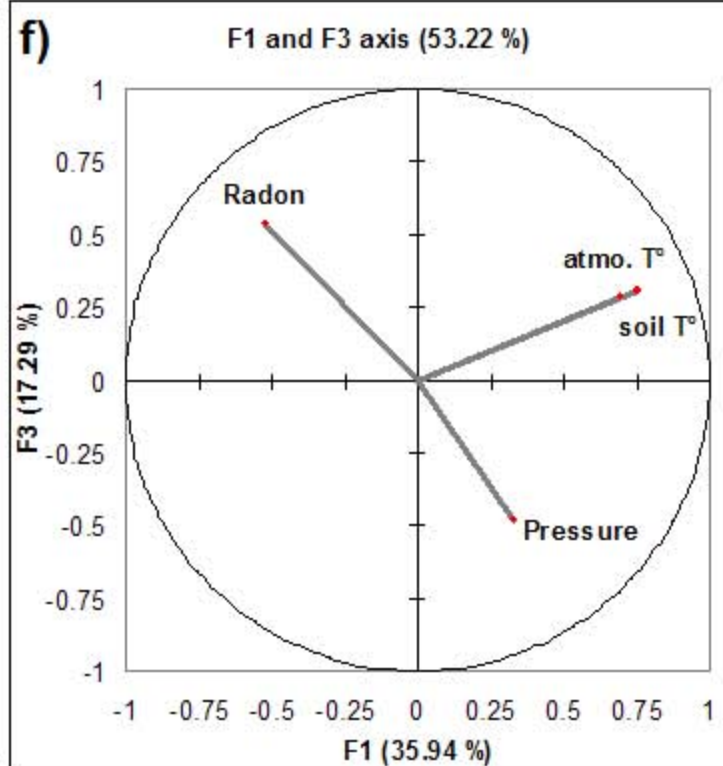
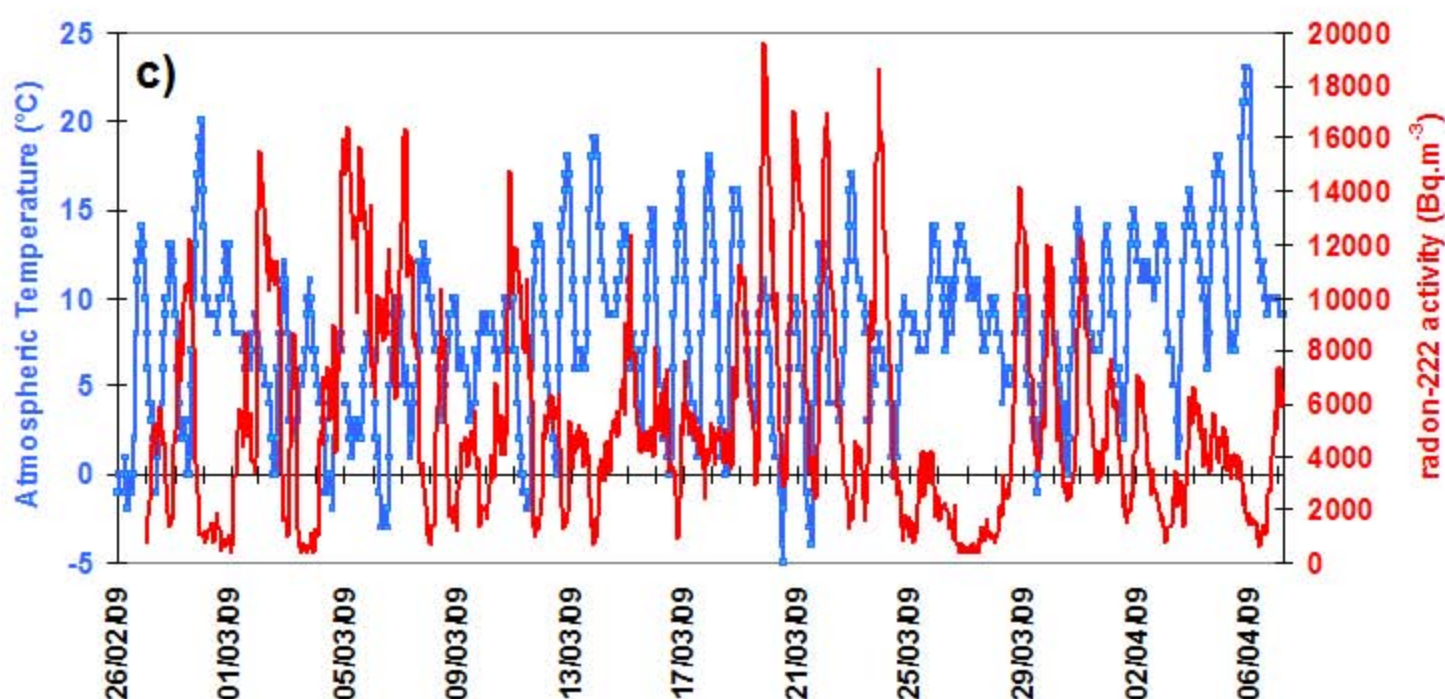
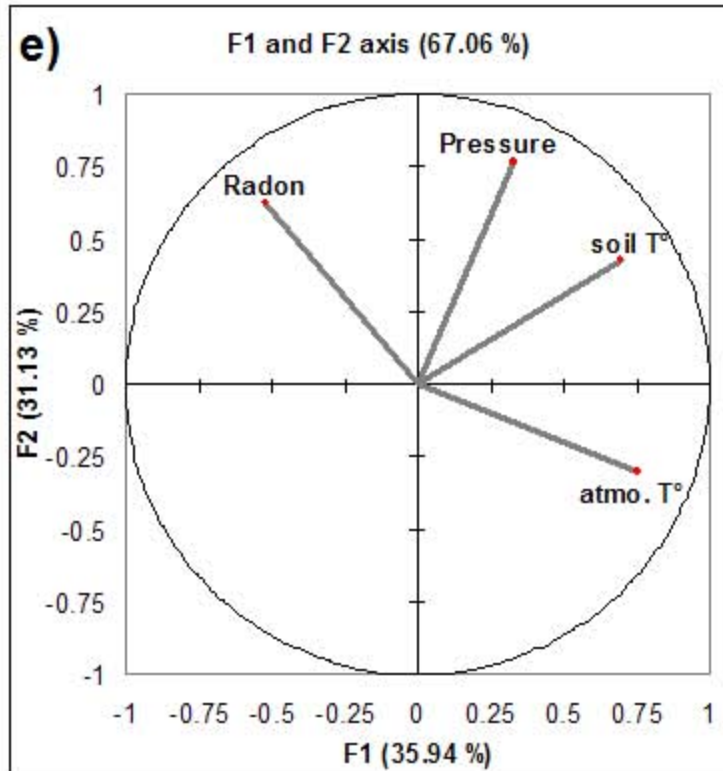
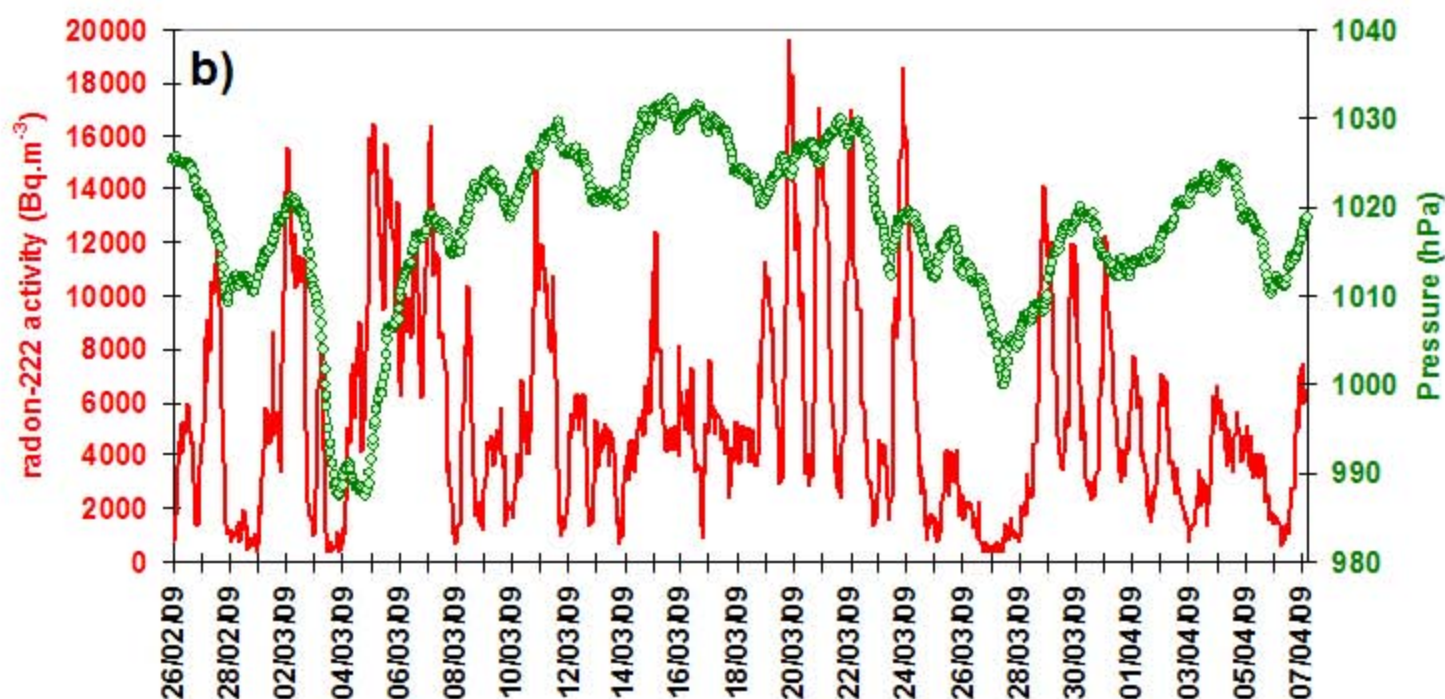
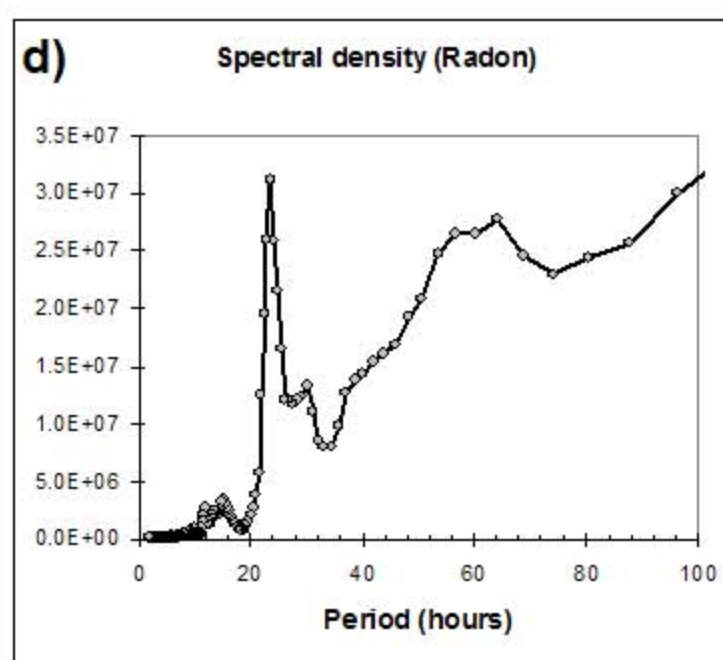
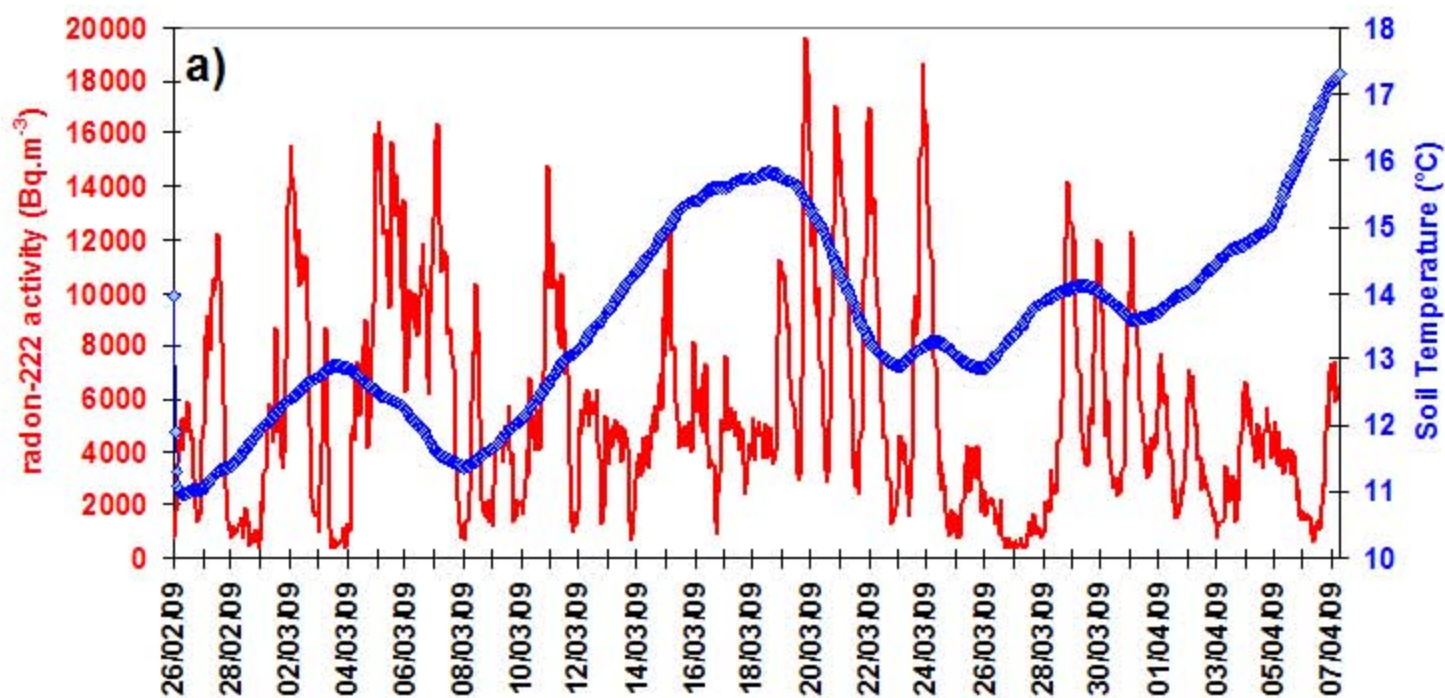
colorscale: sum of CO2 + radon + helium fitted in the 0 - 1 interval  
greyscale: helium distribution in the same interval





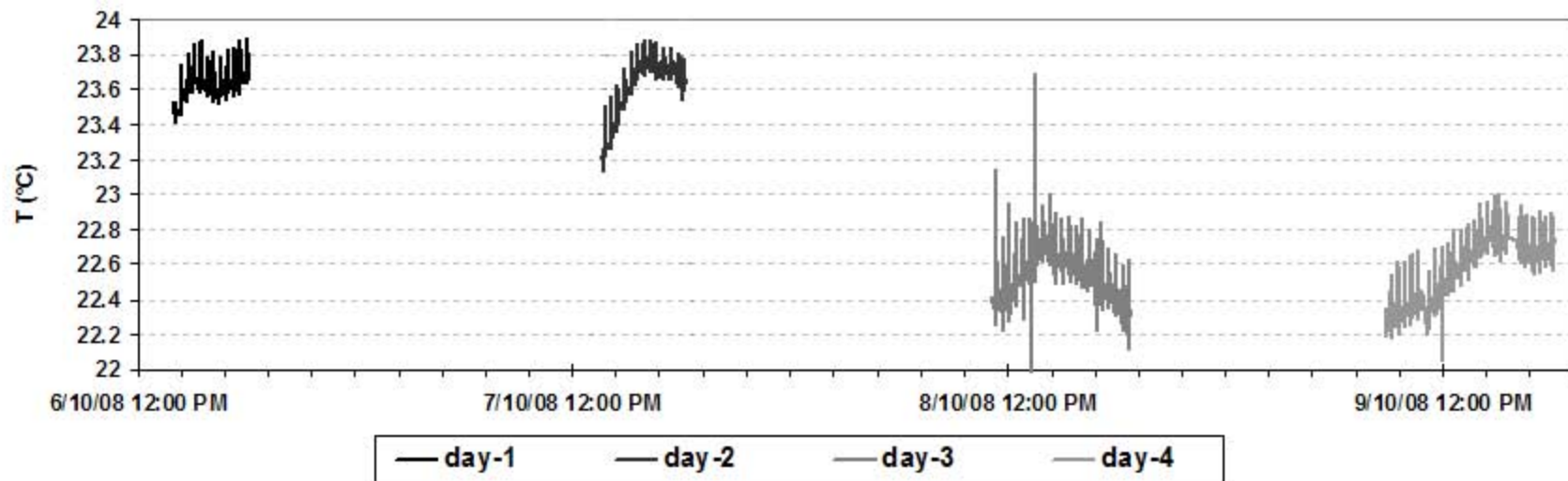
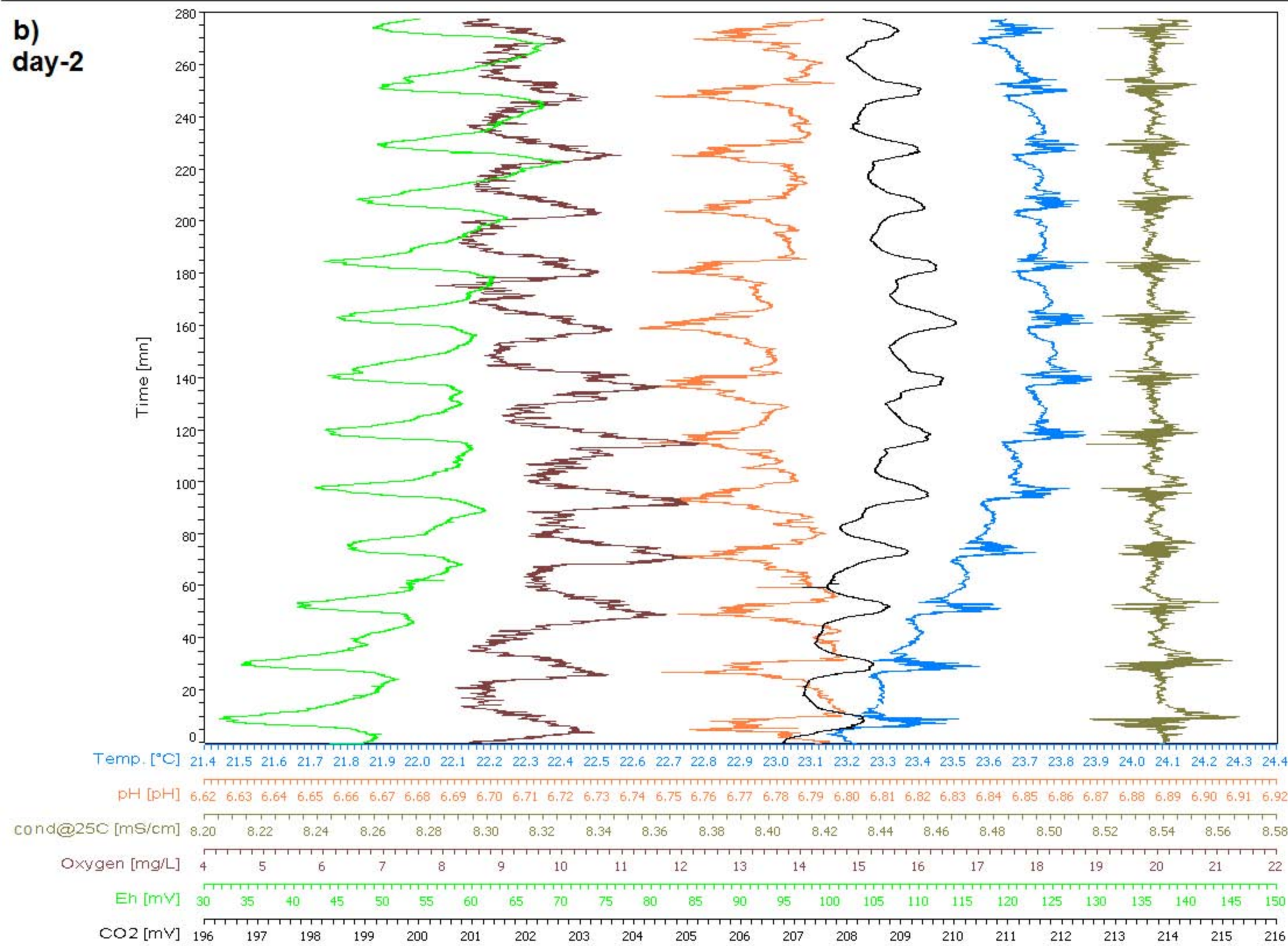








a)

b)  
day-2

	CO <sub>2</sub> (%)	CO <sub>2</sub> (%)	CO <sub>2</sub> (%)	<sup>222</sup> Rn (Bq.m <sup>-3</sup> )	<sup>222</sup> Rn (Bq.m <sup>-3</sup> )	<sup>222</sup> Rn (Bq.m <sup>-3</sup> )	<sup>4</sup> He (ppm)	<sup>4</sup> He (ppm)	<sup>4</sup> He (ppm)
	all data	1992	2006-2010	all data	1992	2006-2010	all data	1992	2006-2010
<b>nb. of measurements</b>	1058	504	554	913	503	410	917	431	486
<b>minimum</b>	0.05	0.08	0.05	144	148	144	< 0.05	2.58	< 0.05
<b>maximum</b>	100	91.40	100	2482000	1930000	2480000	17.68	17.68	9.83
<b>1st quartile</b>	1.40	1.18	3.31	15800	17000	13800	5.19	5.24	5.04
<b>median value</b>	4.64	1.70	15.76	39800	37000	43200	5.24	5.30	5.22
<b>3rd quartile</b>	24.08	5.10	47.00	80000	71000	97400	5.34	5.36	5.26
<b>mean value</b>	18.66	7.07	29.21	81700	57200	112000	5.30	5.42	5.19
<b>standard deviation</b>	27.23	13.48	31.90	189700	105000	250000	0.76	0.81	0.69
<b>coeff. of variation</b>	1.46	1.91	1.09	2.32	1.84	2.28	0.14	0.15	0.13

Sample	T (°C)	pH	cond@25°C ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	Eh (mV)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Fe(III) (mg/l)	Mn (mg/l)	Sr (mg/l)	Li (mg/l)	HCO <sub>3</sub> (mg/l)	Cl (mg/l)	SO <sub>4</sub> (mg/l)	PO <sub>4</sub> (mg/l)	NO <sub>3</sub> (mg/l)	F (mg/l)	Br (mg/l)	SiO <sub>2</sub> (mg/l)	$\delta^{18}\text{O}$ (‰ VSMOW)	$\delta\text{D}$ (‰ VSMOW)	<i>theoretical <math>\delta\text{D}</math> if belonging to LMWL</i>	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{13}\text{C}_{\text{gas}}$ open sys.	
Chapelle 1 (2006)	17.8	6.54	5210	338	237	121	776	81.9			3.74		2288	717	146		4.9				-8.3	-57.4	-53.3	0.712298	-4.6	
Chapelle 1 (2007)	16.6	6.63	4530	391	248	137	875	97.4			4.37	4.48	2465	806	155		2.8	0.7	1.8							-5.1
Chapelle 2 (2006)	18	6.21	3070	336	196	117	304	34.5			2.5		1276	298	192		6.3				-7.5	-53.7	-46.9	0.712818	-2.8	
Chapelle 2 (2007)	16.6	6.33	3130	444	188	127	360	39.1			2.38	1.66	1483	340	202		4.4	0.9	0.7							-3.4
Chapelle 3 (2006)	17.5	6.38	2730	340	178	104	266	34.6		0.02	2.16		1410	230	198		8.3				-7.7	-54	-48.5	0.712035	-3.7	
Chapelle 3 (2007)	15.9	6.51	2410	420	184	126	301	40.7			2.30	1.52	1332	315	209		4.6	1.0	0.6							-4.5
Tennis (2006)	29.2	6.48	7970	91	306	131	1493	163		0.10	6.37		3554	1495	101						-9.6	-63.2	-63.7	0.713388	-3.9	
Tennis (2007)	29	6.46	7970	140	295	135	1486	167			6.66	8.03	3515	1348	129			0.5	3.7							-3.9
Tennis (2008)	28.5	6.58	8440	138	301	133	1461	163	2.75				3527	1370	111	0.4		1.1		107	-9.5	-62.8	-62.9			-4.4
Geyser Brissac (2006)	24.6	6.65	8180	186	307	133	1497	163		0.10	6.33		4135	1429	100						-9.6	-63		0.713387	-4.9	
Geyser Brissac (2007)	23.5	6.62	7990	180	297	136	1485	167			6.88	7.99	3534	1355	126			0.4	3.7							-4.8
Geyser Brissac (2008)	23	6.57	8310	158	299	132	1447	162	2.80				3562	1360	111	0.5		1.1		106	-9.5	-62.7	-62.9			-4.6
Petit Saladis (2007)	21.6	6.58	8190	245	295	136	1498	168			6.29	8.13	3554	1344	125			0.5	3.5							-4.7
Grand Saladis (2007)	16.1	7.24	7920	386	125	139	1579	180			2.60	8.52	3124	1414	108		11.0	0.4	3.9							-7.6
old plant sp. (2008)	29.3	6.7	8270	140	302	133	1457	164	2.41				3147	1390	110	0.4		0.8		105	-9.5	-63	-62.9			-4.9
Valois sp. (2008)	25.3	6.45	7840	105	298	129	1461	163	2.80				3536	1370	109	0.4		1.2		106	-9.5	-62.9	-62.9			-3.9
terrace sp. (2008)	18.6	6.45	8410	197	296	131	1459	163	2.44				3566	1360	111	0.3		1.2		102	-9.6	-62.8	-63.7			-4.1
rainwater (08/10/2008)	12.4	8.45	65	273	4.2	0.9	8.3	1.2	0.03				24	6	2		1.7		0.7		-8.8	-64.7	-57.3			-9.2

radon-222 (Bq.m <sup>-3</sup> ) DATA greater than 10 Bq.m <sup>-3</sup> and lesser than 10 <sup>6</sup> Bq.m <sup>-3</sup>	POINT 2	POINT 4			
	06/10/08 → 28/01/09	06/10/08 → 28/01/09	26/02/09 → 01/09/09	11/09/09 → 16/03/10	06/10/08 → 16/03/10
nb of meas. (hours)	2728	2729	3869	740	7338
hours of deployment	2735	2735	4471	4459	11665
Min. value	60	30	50	1030	30
Max. value	2.69E+05	2.14E+05	9.09E+05	9.80E+05	9.80E+05
1st Quartile	5820	20900	2410	5890	9640
Median value	28500	51700	4810	7500	16800
3rd Quartile	102000	71500	13600	10700	12500
Mean value	56500	65300	28700	26300	31300
std. dev.	66400	57600	73600	93200	66100
PEAK values: nb of meas.	3	4	1		
PEAK values: Max. value	8.57E+07	7.06E+06	1.24E+06		
Cycle analysis	no cycle	7 - 10 - 22 hours 5.5 days	15 - 25 - 39 - 74 hours	24 - 58 hours	

DESCRIPTIVE STATISTICS	day 1 (7400 data)					day 2 (8300 data)					day 3 (13800 data)					day 4 (15800 data)				
	T°	EC	O <sub>2</sub>	pH	Eh	T°	EC	O <sub>2</sub>	pH	Eh	T°	EC	O <sub>2</sub>	pH	Eh	T°	EC	O <sub>2</sub>	pH	Eh
minimum	21.15	8505	7.7	6.75	1.1	23.14	8512	7.9	6.74	31.6	21.98	7621	5.3	6.40	-162.1	22.05	8477	5.9	6.43	-61.4
maximum	23.89	9184	10.8	6.80	29.7	23.88	8567	12.3	6.80	70.1	23.66	8264	18.0	7.28	206.2	23.00	8639	14.5	7.81	128.9
mean value	23.62	8532	9.2	6.78	20.5	23.62	8537	9.7	6.78	54.2	22.54	8061	9.9	6.83	69.2	22.57	8535	9.2	6.84	57.7
standard deviation	0.16	37	0.5	0.01	7.1	0.16	4	0.9	0.01	7.4	0.13	72	1.1	0.03	12.4	0.17	7	0.9	0.02	15.0