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1 **What can be learned from natural analogues studies in view of CO₂ leakage issues in**
2 **Carbon Capture and Storage applications? Geochemical case study of Sainte-**
3 **Marguerite area (French Massif Central).**

4

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18 **Abstract**

19 Natural analogue studies have received much interest over past years through the CO₂
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 (CO₂, ²²²Rn and ⁴He) 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 CO₂.

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂FieldLab ones (<http://www.sintef.no/Projectweb/co2fieldlab/>).

59 The Sainte-Marguerite site allows the study of both CO₂ 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 CO₂ escapes as a gas phase may consist in the ultimate
64 warner 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. CO₂ 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 CO₂ 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 CO₂ 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 - CO₂, O₂ and CH₄ 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. CO₂ and CH₄ contents were determined by non-dispersive infrared absorption
112 and O₂ contents by electrochemistry. No CH₄ was found during the successive surveys
113 indicating concentrations lesser than 0.01% volume in the gas phase. As the CO₂
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 - ^4He and ^{222}Rn concentrations were also systematically determined using samples
118 collected in Tedlar bags for ^4He and vacuumed scintillating flasks for ^{222}Rn ,
119 respectively. Concentrations were obtained using mass spectrometry for ^4He (Adixen
120 ASM102S leak detector, France) and scintillation counting for ^{222}Rn (Calen, Algade,
121 France).

122 - Some additional grab samples were collected for laboratory determination of the $\delta^{13}\text{C}$
123 of the 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 N_2 , Ar, O_2 , CO_2 and $\text{C}_n\text{H}_{2n+2}$ (n
126 = 1 to 6).

127 - Continuous data acquisition was also performed on ^{222}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 (^4He), from poorly mobile
134 elements that may help highlight areas with significant gas fluxes (^{222}Rn) and from a widely
135 existing gas (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 δD 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 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 (CO_2 , ^{222}Rn and ^4He) 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 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 CO_2 concentration is significantly
161 greater for the 2006-2010 dataset than for the 1992 dataset.

162 Radon-222 (^{222}Rn) concentrations also fall within similar ranges during the two periods,
163 minimum values being close to 150 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 CO₂ concentrations.
167 Helium-4 (⁴He) 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 (≥ 10 ppm).

171

172 Most of the CO₂ measurements made between 2006 and 2010 were also supplemented by
173 measurements of the O₂ concentrations in soils. A very homogeneous inverse behaviour exists
174 between those species (Figure 2). Almost all data exhibit an O₂ decrease that is not
175 proportional with the increase of the CO₂ content on a per mole basis. Depletion of O₂ is
176 much faster with a factor close to 5. This suggests that CO₂ 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 O₂ 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 CO₂ end-member and the N₂-
185 O₂-Ar triptych, with CO₂ 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% N₂; 0.023% O₂; 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 N₂ 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 O₂, which is subject to a more active
192 kinetic of replacement, N₂ and Ar are diluted in the soil gas by equimolar replacement with
193 CO₂.

194

195 Figure 3

196

197 Finally, the δ¹³C isotope ratio of the CO₂ gas was also evaluated on these samples and ranged
198 between -3 to -5.1‰ VPDB for CO₂ 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⁻¹, Chapelle springs (used for bottling) having total mineralization approximately half
208 of other sampled waters. The mineralization is dominated by HCO₃ (1.3 to 4 g.L⁻¹), Na (0.3 to
209 1.5 g.L⁻¹) and Cl (0.2 to 1.5 g.L⁻¹). If this Na-Cl-HCO₃ facies predominates, the Ca and Mg
210 amounts, less variable (respectively 120 to 310 mg.L⁻¹ and 100 to 140 mg.L⁻¹), 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 be considered for highlighting a potential leakage at a CCS site is to
224 characterise the CO₂ 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 CO₂ 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, CO₂ 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, CO₂-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% CO₂ with no ⁴He (< 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 CO₂ 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 ²²²Rn and ⁴He. As ²²²Rn and ⁴He are only present as
248 trace levels in the free atmosphere (respectively around 50 Bq.m⁻³ 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 (²²²Rn) or deeper in the ground (⁴He; Battani *et al.*, 2010; Gilfillan *et al.*, 2011).
251 Relationships between CO₂, ²²²Rn and ⁴He are presented in Figure 4.

252

253 Figure 4

254

255 For ²²²Rn/CO₂ and ⁴He/CO₂ couples, graphical relationships (Figure 4A) confirm the different
256 origin of these two gases and highlight that the genesis of ⁴He from radioactive decay of
257 uranium in the near surface has little influence on the ⁴He concentrations. This should also
258 result in an increase of the ⁴He concentration when ²²²Rn activities are high. This is not the
259 case, since there is rather a gradual depletion when the ²²²Rn activities exceed 10⁶ Bq.m⁻³
260 (Figure 4A). Moreover, these high ²²²Rn 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 ²²²Rn 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 CO₂ source
265 is not strong enough to dilute the ²²²Rn as may occur farther from travertine deposits. As a
266 consequence, perennial ²²²Rn high concentrations exist locally.

267 The behaviour of ²²²Rn and CO₂ is also complex for ²²²Rn concentrations lesser than 300,000
268 Bq.m⁻³ (Figure 4B). Two distinct trends seem to exist, one with fast ²²²Rn enrichment with
269 low CO₂ concentrations (red squares), and the other with weaker ²²²Rn enrichment when CO₂
270 concentrations rise (blue lozenges). These two behaviours correspond to various spatial
271 locations (Figure 5). Most of the “high ²²²Rn – low CO₂” 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 ²²²Rn – high CO₂” 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 CO₂ gas interacts to a lesser extent
277 with surface formations, leading to moderate ²²²Rn enrichment. On the contrary, on the
278 eastern part of the site, CO₂ has to go through thicker formations (alluvial and Oligocene
279 formations), leading to smaller CO₂ amounts and also to ²²²Rn enrichment due to the
280 percolation of the CO₂ into these formations. An intermediate behaviour occurs above
281 travertines deposits (Figures 4 and 5) where the ²²²Rn content is also dependent from the
282 uranium content of these formations. An additional process can also act in a complementary
283 fashion. Deep CO₂ 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 ⁴He/CO₂ couple except from a very weak tendency
287 of having slightly lower ⁴He concentrations when CO₂ 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 ^4He depleted. A strong CO_2 flux can act as a flushing
290 agent on ^4He . For lesser CO_2 amounts, flushing effect may be less important and ^4He
291 concentrations are higher or even enriched depending on the amounts of ^4He 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 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 CO₂ distribution in soils is not restricted to this gas phase. A well characterised
325 time coherence for ²²²Rn 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 CO₂ but with
328 increased nugget effect (50% of the variability). This may be linked to the location of the area
329 of maximum ²²²Rn concentrations, close to the high CO₂ 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 CO₂ in the present case.

332

333 The evolution of ⁴He concentrations in the area where ²²²Rn and CO₂ 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 ⁴He emanations is remarkably stable over time.
337 Low ⁴He 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 CO₂, ²²²Rn and ⁴He, 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, CO₂ and ⁴He are considered as
344 deep end-members and ²²²Rn 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 CO₂. This strengthens previous results indicating
347 that CO₂ and ⁴He amounts are not directly proportionally linked. The linearization process is
348 then intended to lower the influence of ²²²Rn and to over-estimate the one of ⁴He by assigning
349 a value between 0 and 1 to each of the gas specie. The 0.05 to 100% CO₂ range is restricted in
350 the 0 – 1 interval and so on for ²²²Rn (140 to 248,000 Bq.m⁻³) and ⁴He (0.05 to 9.83 ppm).
351 Using this procedure, ⁴He concentrations account for *c.a.* 75% of the total variability, CO₂ for
352 22% and ²²²Rn 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 CO₂
354 concentrations, the influence of ⁴He been of second order. Consequently, it is the deep CO₂
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 CO₂ flux data available in the area (Battani *et*
362 *al.*, 2010). The most anomalous CO₂ 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 (CO_2 , ^{222}Rn and ^4He) and continuous measurements (on the 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 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 CO_2 and
375 200 for ^{222}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}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}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 80×10^6 Bq.m⁻³). Such
413 concentrations remain under saturation threshold of the probe (10^9 Bq.m⁻³) but are far greater
414 than maximum values found during spot sampling (2.5×10^6 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 ²²²Rn 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 ²²²Rn and a subsequent strong depletion.
419 Concentrations remained low until radioactive decay produced again a sufficient amount of
420 ²²²Rn. 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 ²²²Rn 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 ²²²Rn 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}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}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}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}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}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}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}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}Rn peak) and February 13 (17 days after the ^{222}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}Rn
466 measurements for low seismic magnitudes, no clear relationship exists in the present case
467 between ^{222}Rn peaks and tectonic activity.

468 Such excursions of ^{222}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}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}Rn phase but mostly on CO_2 and/or 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-HCO₃ 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 δD 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 ¹³C 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 (⁸⁷Sr/⁸⁶Sr) 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). ⁸⁷Sr/⁸⁶Sr 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}O , ^2H or ^{13}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 CO₂ 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 CO₂ 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 CO₂, slight decrease
567 of the pH value (-0.05 pH unit) and decreases of the dissolved O₂ concentration and of the
568 redox potential. Such evolutions are self-consistent and reflect the progressive replacement of
569 O₂ by CO₂ in the bowl as the eruption takes place. Specific conductance is also affected, CO₂
570 inflows leading to harmonic variations of the record. Nevertheless, diurnal heating affects the
571 dissolved CO₂ 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 O₂, 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 CO₂ storage. Monitoring performed at Sainte-Marguerite natural analogue shows
581 that this method is sensitive to strong CO₂ 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 CO₂ 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 CO₂ 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 CO₂-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 ²²²Rn 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 ²²²Rn 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 ^4He (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 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 CO₂ 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

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699

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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: O₂ – CO₂ relationship for the 2006-2010 soil gas measurements; the equimolar
865 replacement line (1 mole CO₂ ⇌ 1 mole O₂) 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, N₂, O₂ and CO₂ concentrations (% vol.) on samples
870 analysed using laboratory gas chromatography (samples from year 2007).

871

872 Figure 4: A: Relationships between CO₂, ²²²Rn and ⁴He in soil gas (2006-2010 dataset); B:
873 detail of the CO₂ - ²²²Rn relationship for low ²²²Rn concentrations (lesser than 300,000 Bq.m⁻³).
874 ³).

875

876 Figure 5: Relationships between CO₂, ²²²Rn and ⁴He in soil gas.

877

878 Figure 6: spatial distribution of soil gas species (from left to right: CO₂, ²²²Rn and ⁴He) along
879 with time (from top to bottom). Interpolation is done using natural neighbour contouring.

880

881 Figure 7: CO₂, ²²²Rn and ⁴He concentrations (2006 to 2010 measurements) recalculated in the
882 0 – 1 interval to lower the influence of ²²²Rn and strengthen the one of ⁴He (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: ²²²Rn concentrations over time; blanked areas (F109
889 probe) correspond to power supply deficiency or to electronical malfunctioning of the ²²²Rn
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 ²²²Rn concentrations; b: temporal
894 evolution of atmospheric pressure and ²²²Rn concentrations; c: temporal evolution of
895 atmospheric temperature and ²²²Rn concentrations; d: spectral densities of ²²²Rn
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⁻¹),
900 dissolved oxygen content (mg.L⁻¹), redox potential (Eh, mV) and dissolved CO₂ (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 CO₂, ²²²Rn and ⁴He 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). δ¹⁸O and δD isotope ratios are reported as well
911 as the δD difference to the local meteoric water line (δD = 8 δ¹⁸O + 13.1; Fouillac *et al.*,
912 1991). Equilibrium partial CO₂ pressure is computed using Diagrammes software
913 (<http://www.lha.univ-avignon.fr/>).

914

915 Table 3: descriptive statistics for ²²²Rn concentrations acquired using Barasol probes.

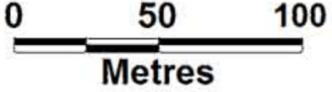
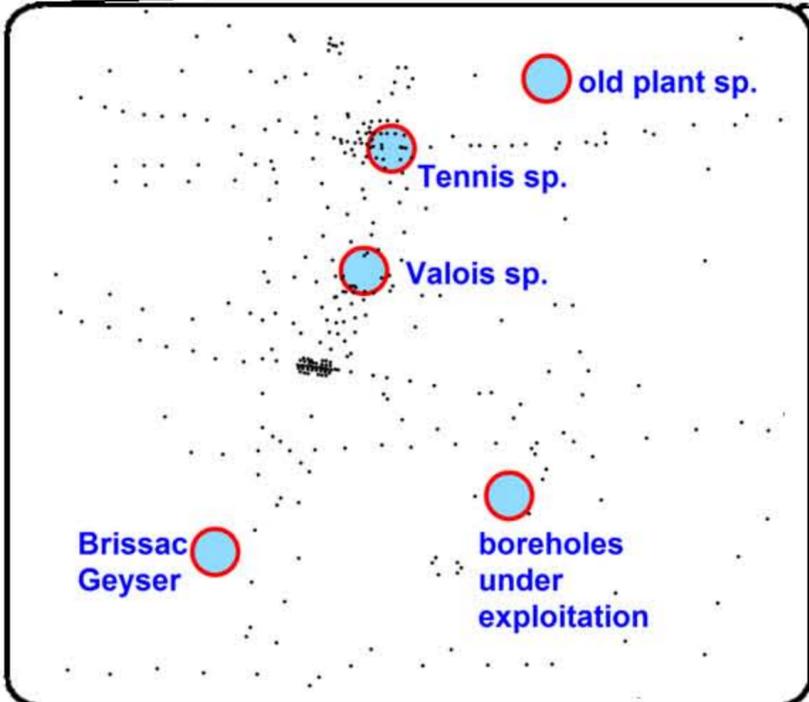
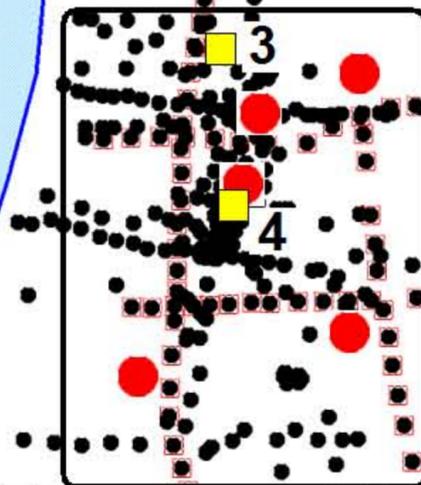
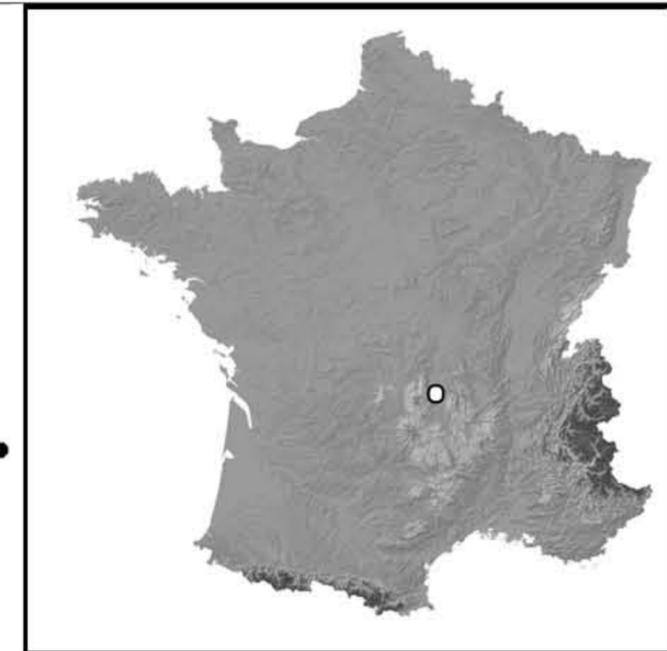
916

917 Table 4: top: evolution of temperature (°C), pH, specific conductance at 25°C (EC, mS.cm⁻¹),
918 dissolved oxygen content (mg.L⁻¹), redox potential (Eh, mV) and dissolved CO₂ (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).

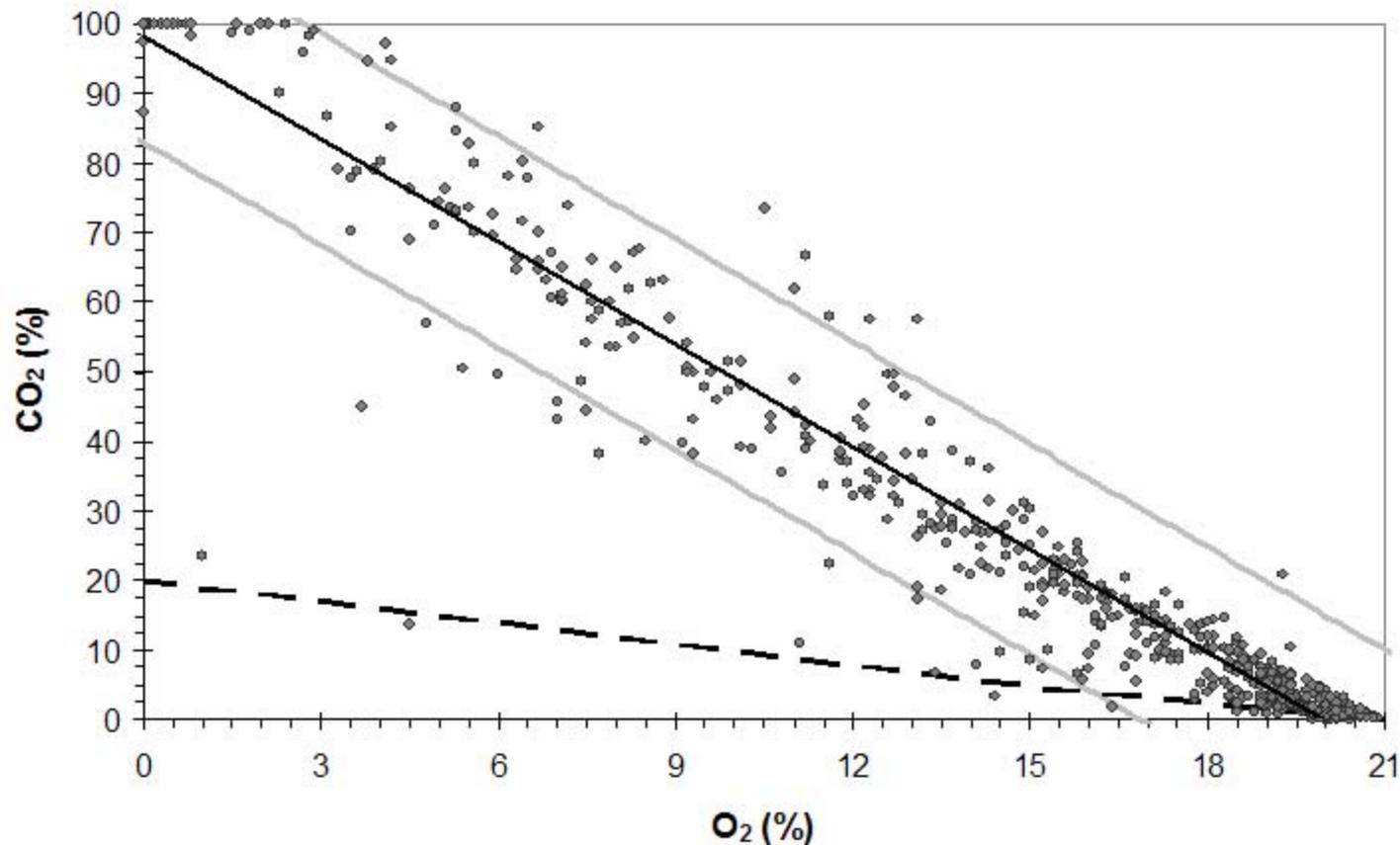


Saladis
springs

Allier River



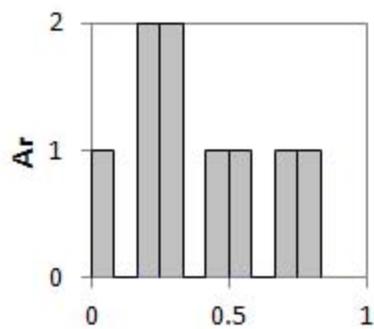
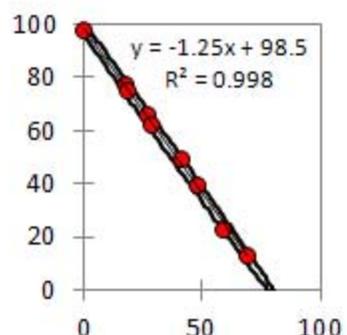
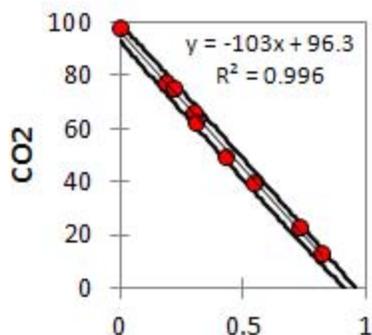
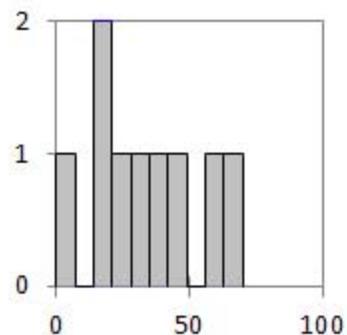
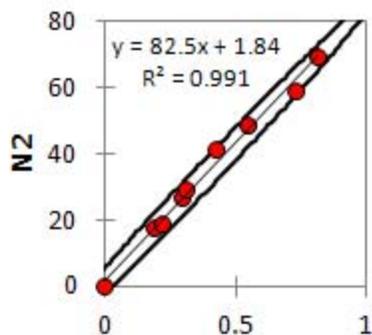
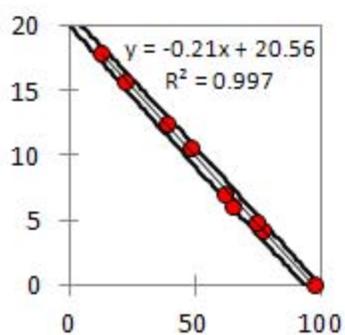
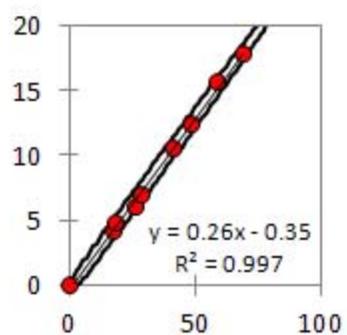
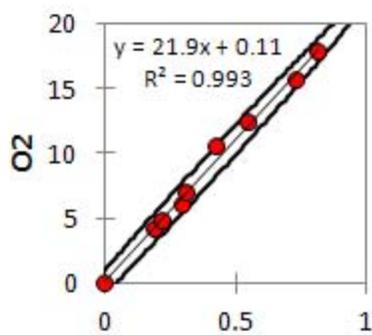
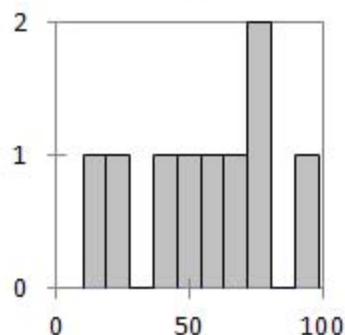
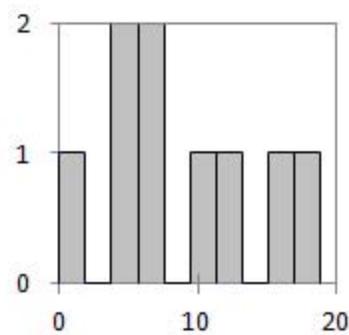
$$\text{CO}_2 (\%) = 98.2 - 4.92 \times \text{O}_2 (\%) \quad (R^2=0.943; n = 566)$$



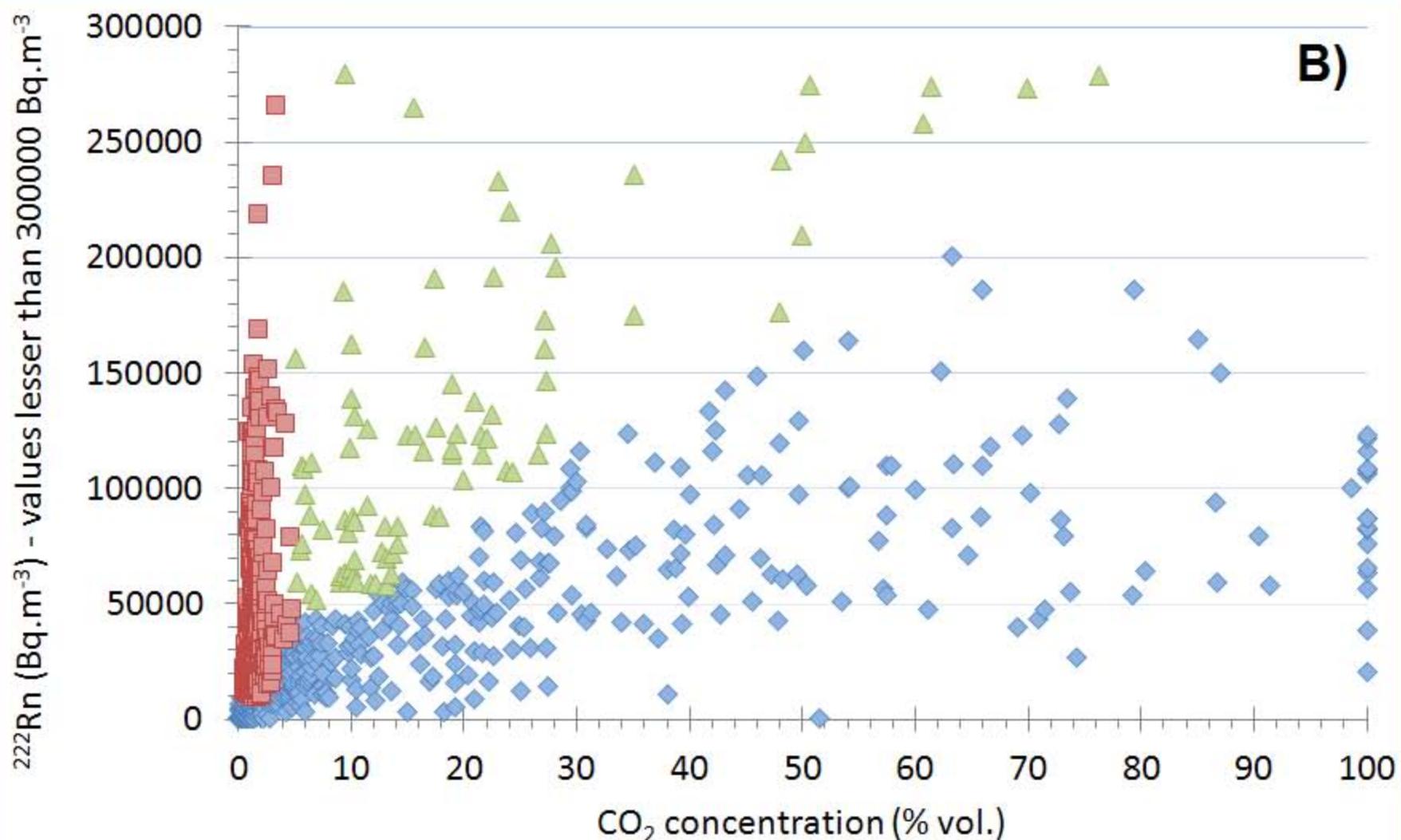
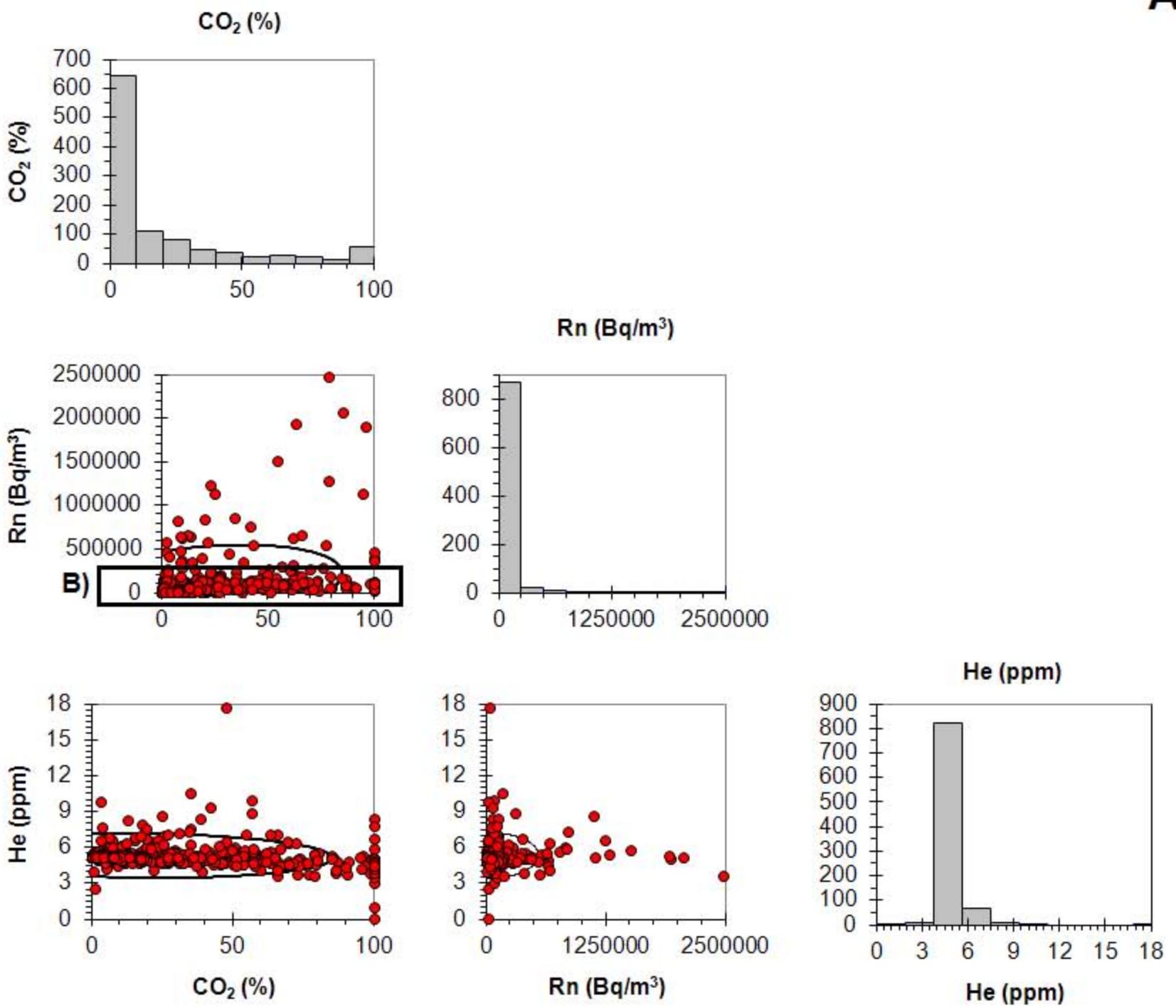
— Model

— Conf. int. (Obs. 95%)

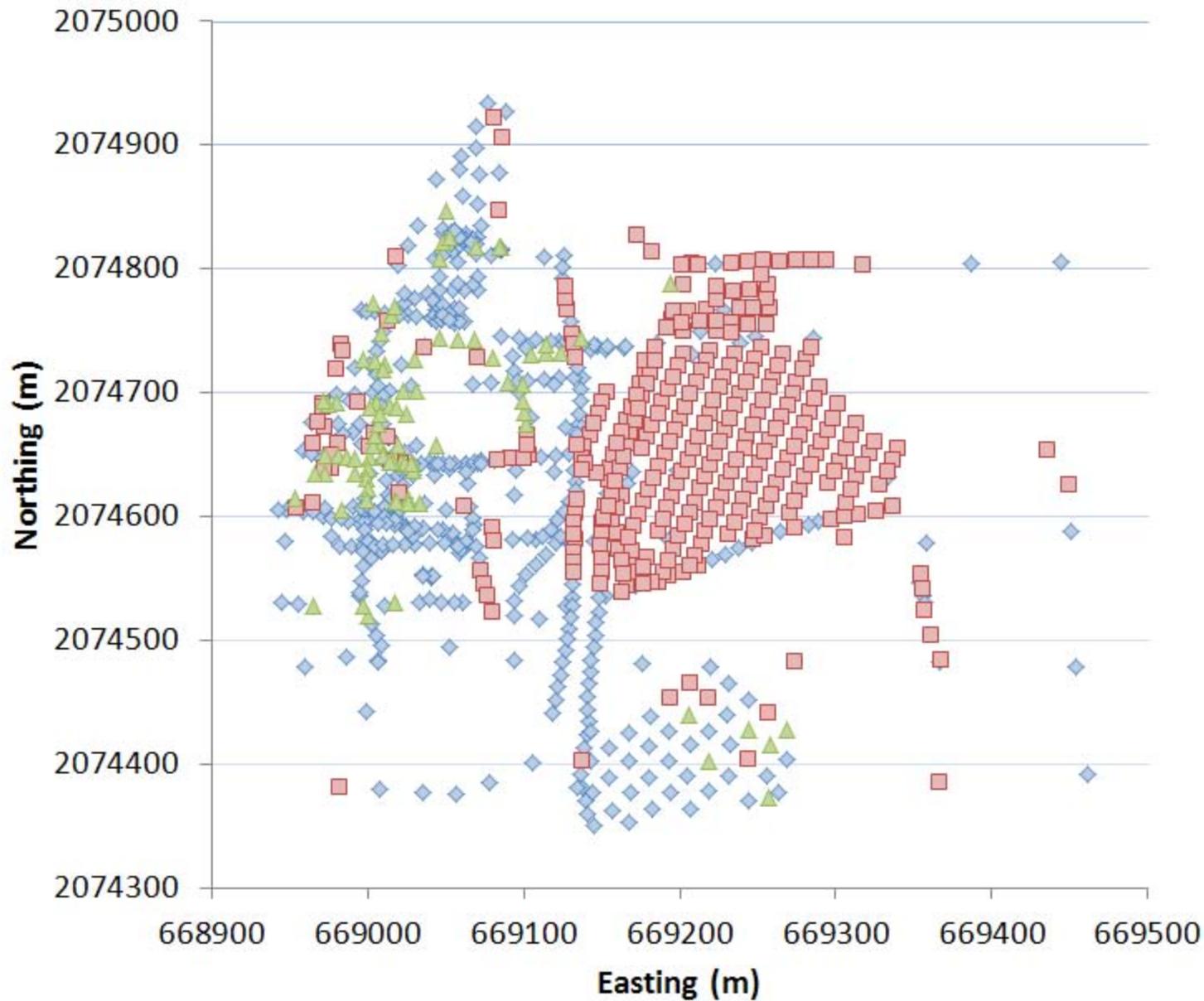
- - 1:1 replacement

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

A)

◆ slow ²²²Rn enrichment vs. CO₂ enrichment■ fast ²²²Rn enrichment vs. CO₂ enrichment

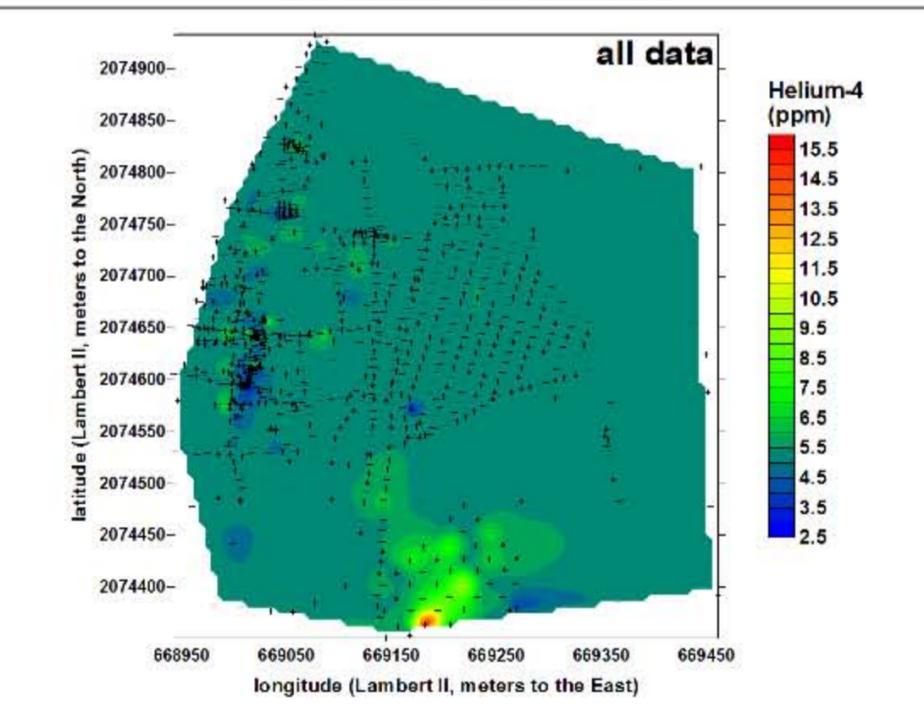
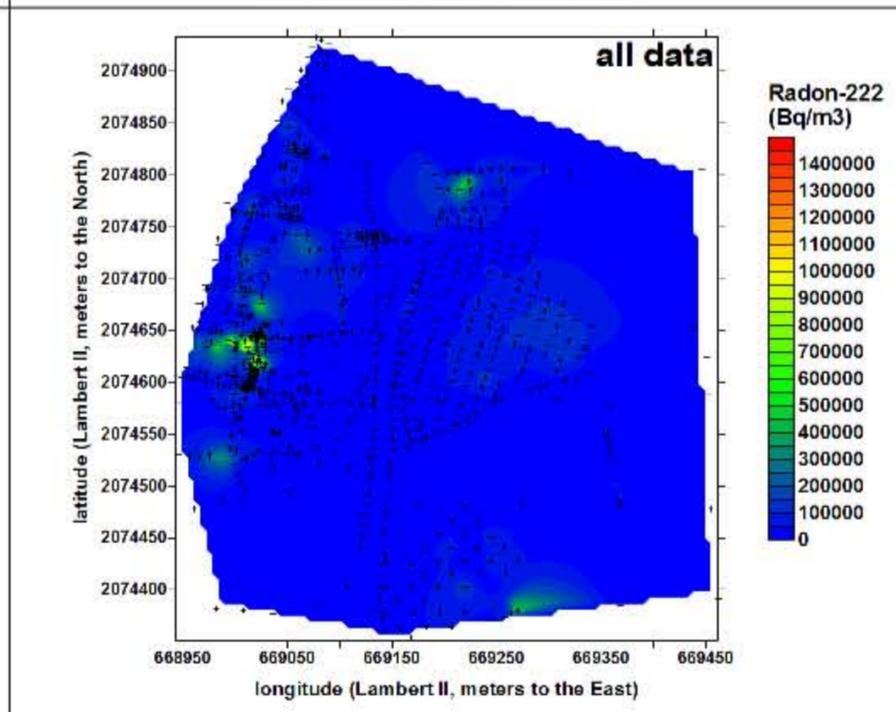
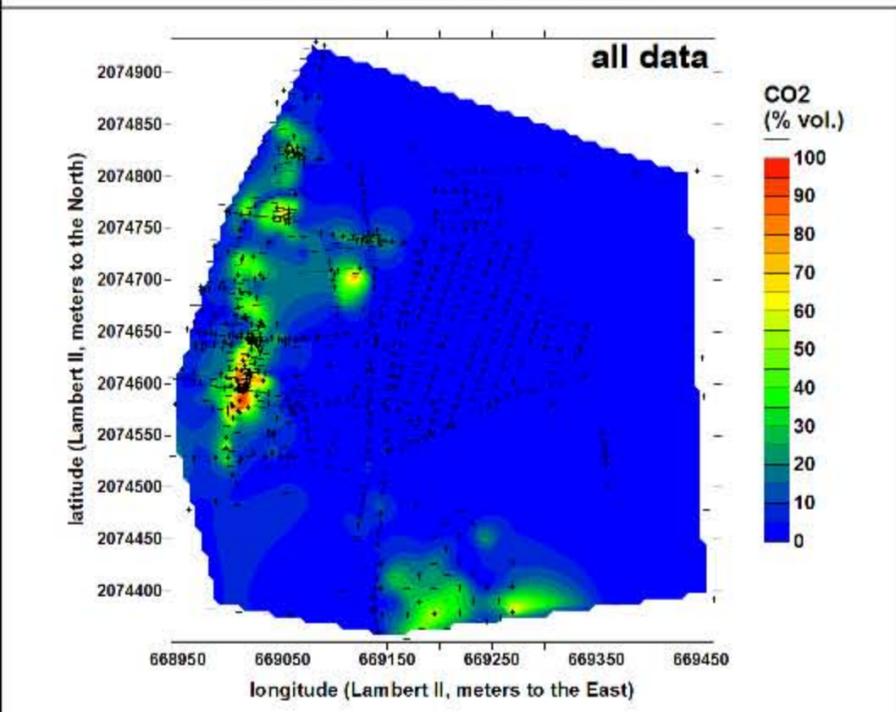
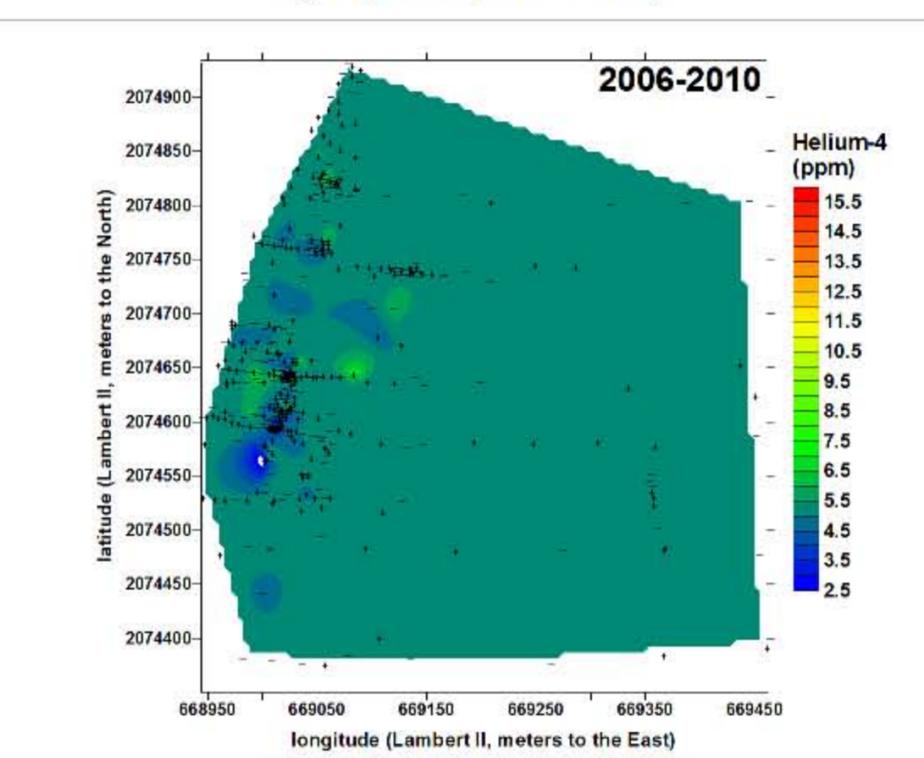
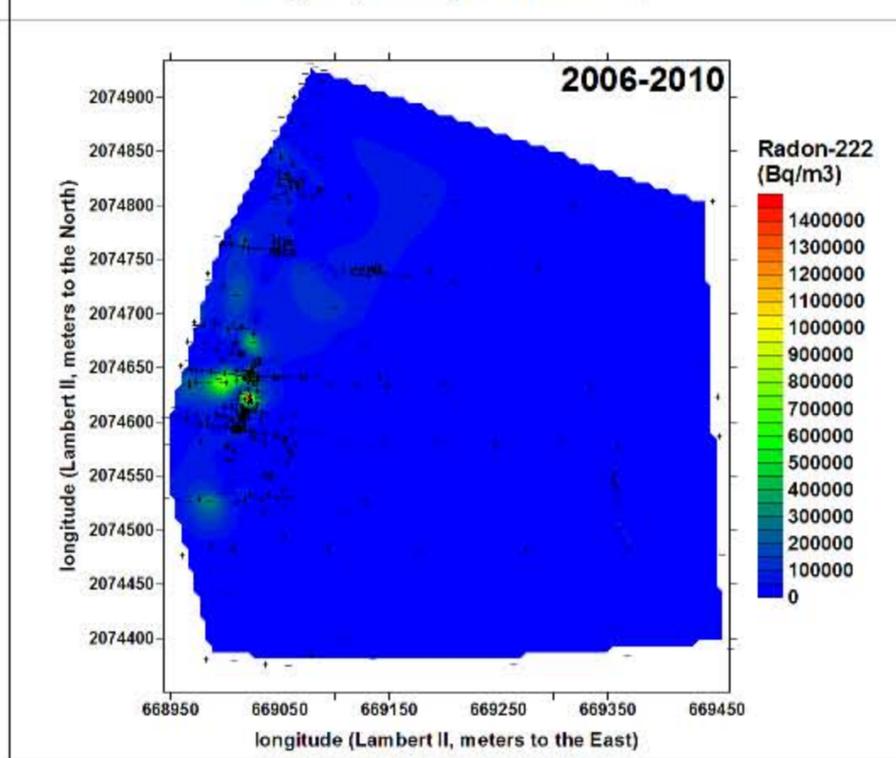
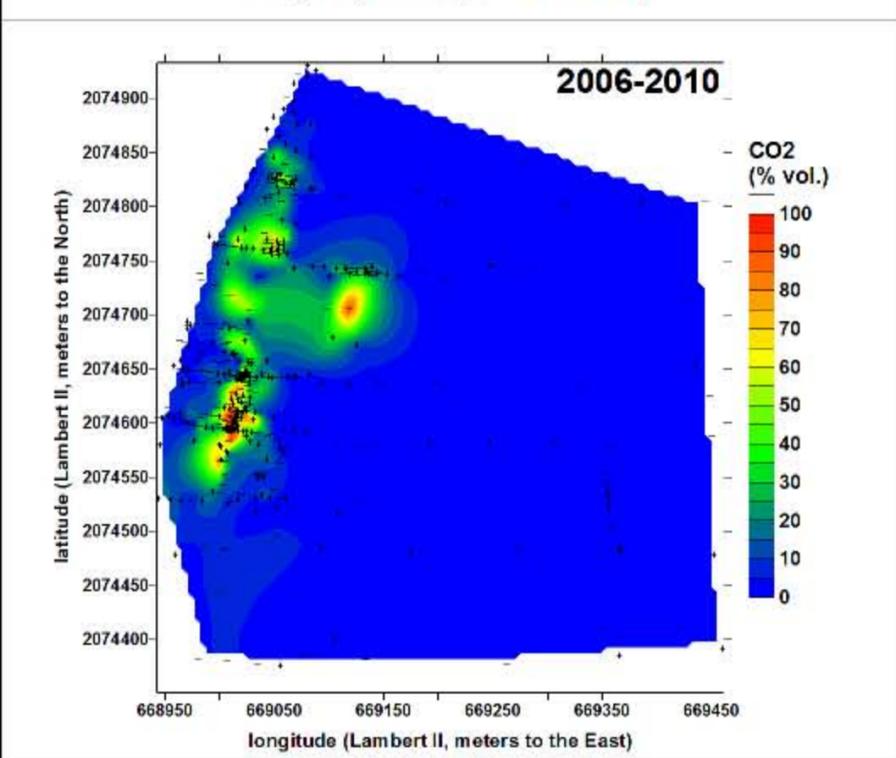
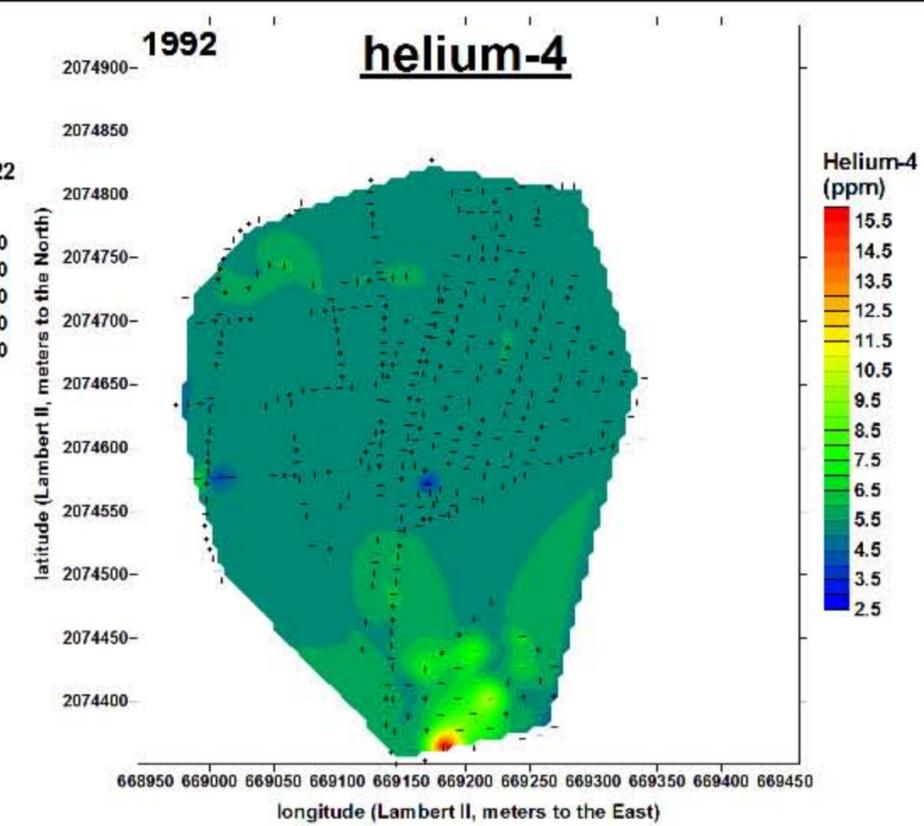
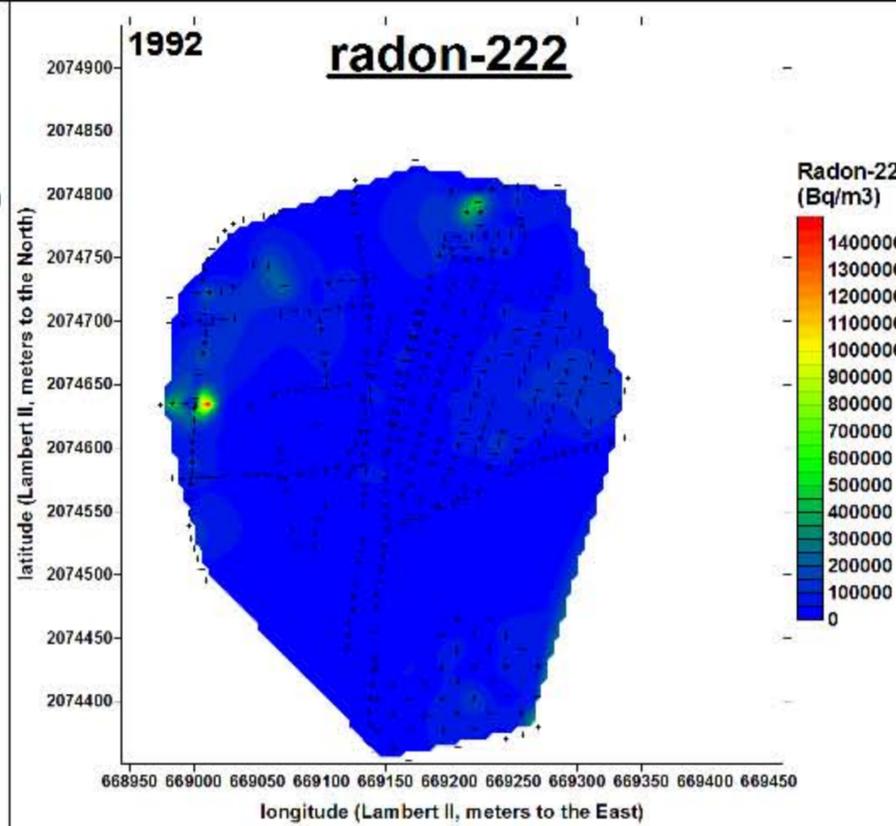
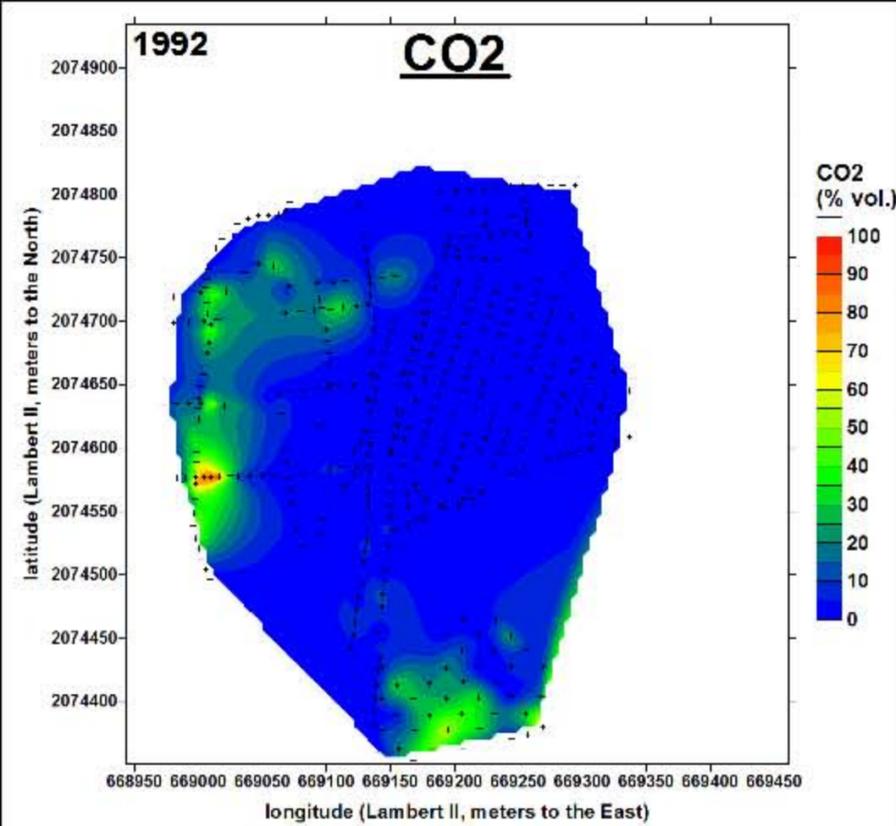
▲ intermediate tendency



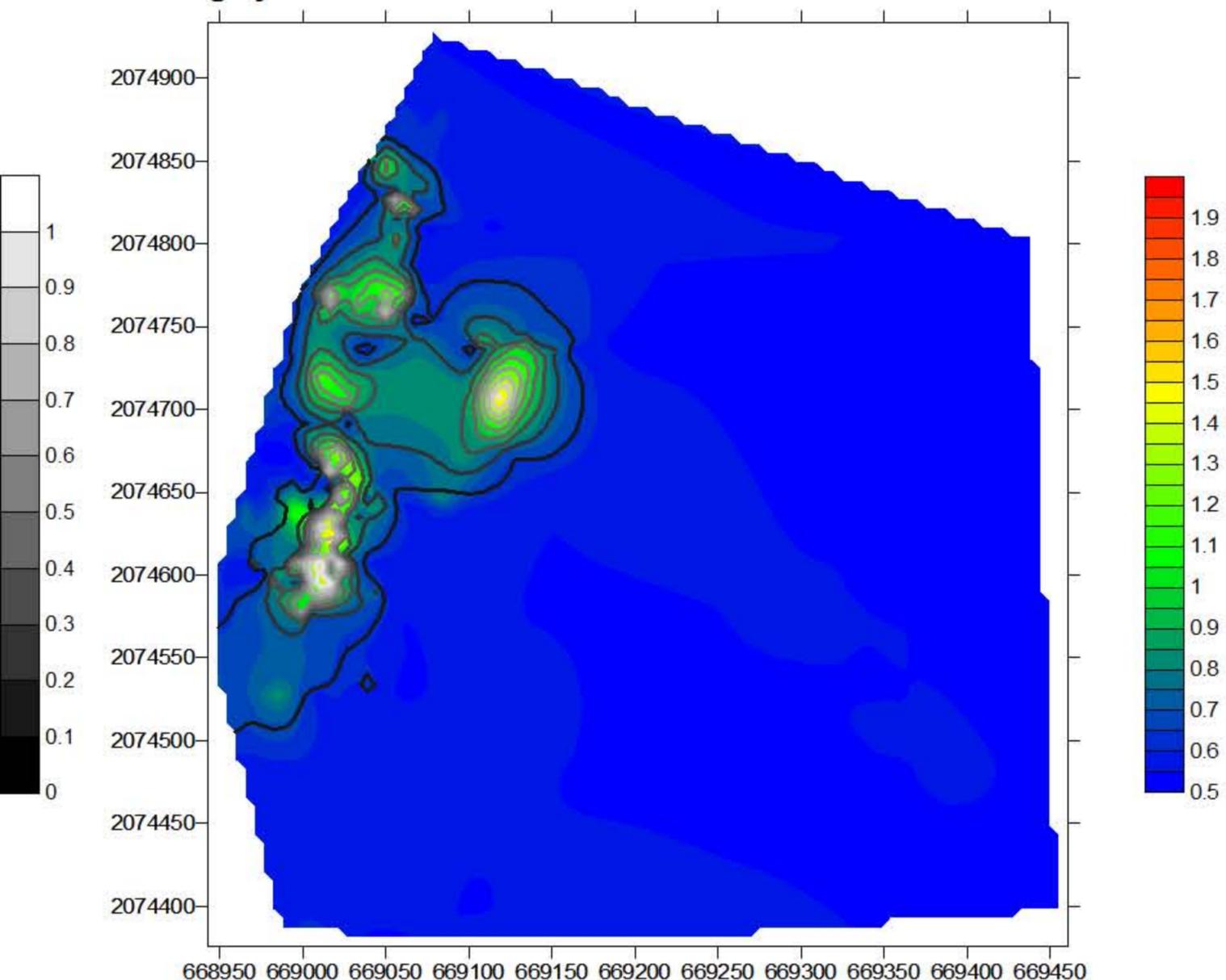
◆ slow ^{222}Rn enrichment vs. CO_2 enrichment

■ fast ^{222}Rn enrichment vs. CO_2 enrichment

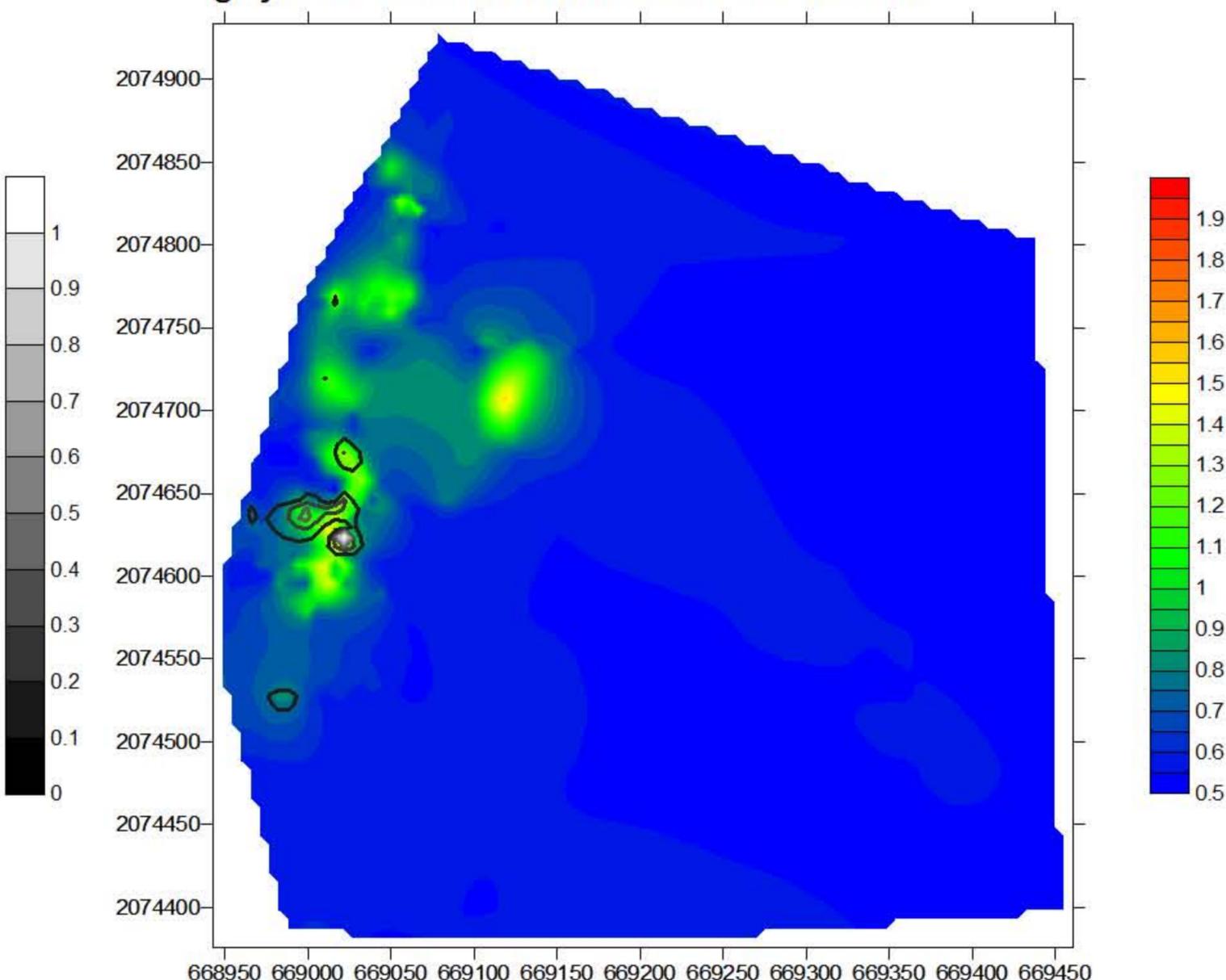
▲ intermediate tendency



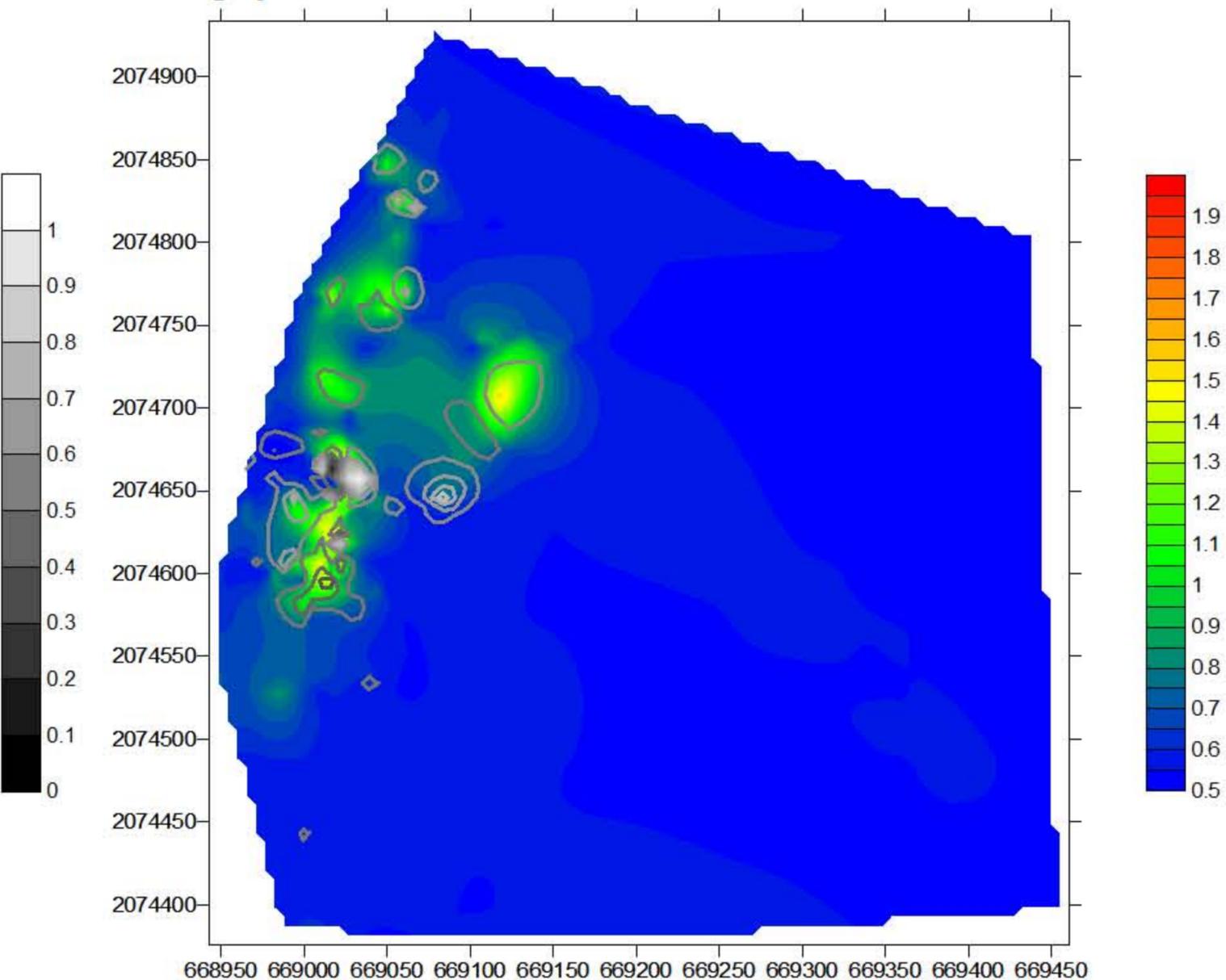
colorscale: sum of CO2 + radon + helium fitted in the 0 - 1 interval
greyscale: CO2 distribution in the same interval

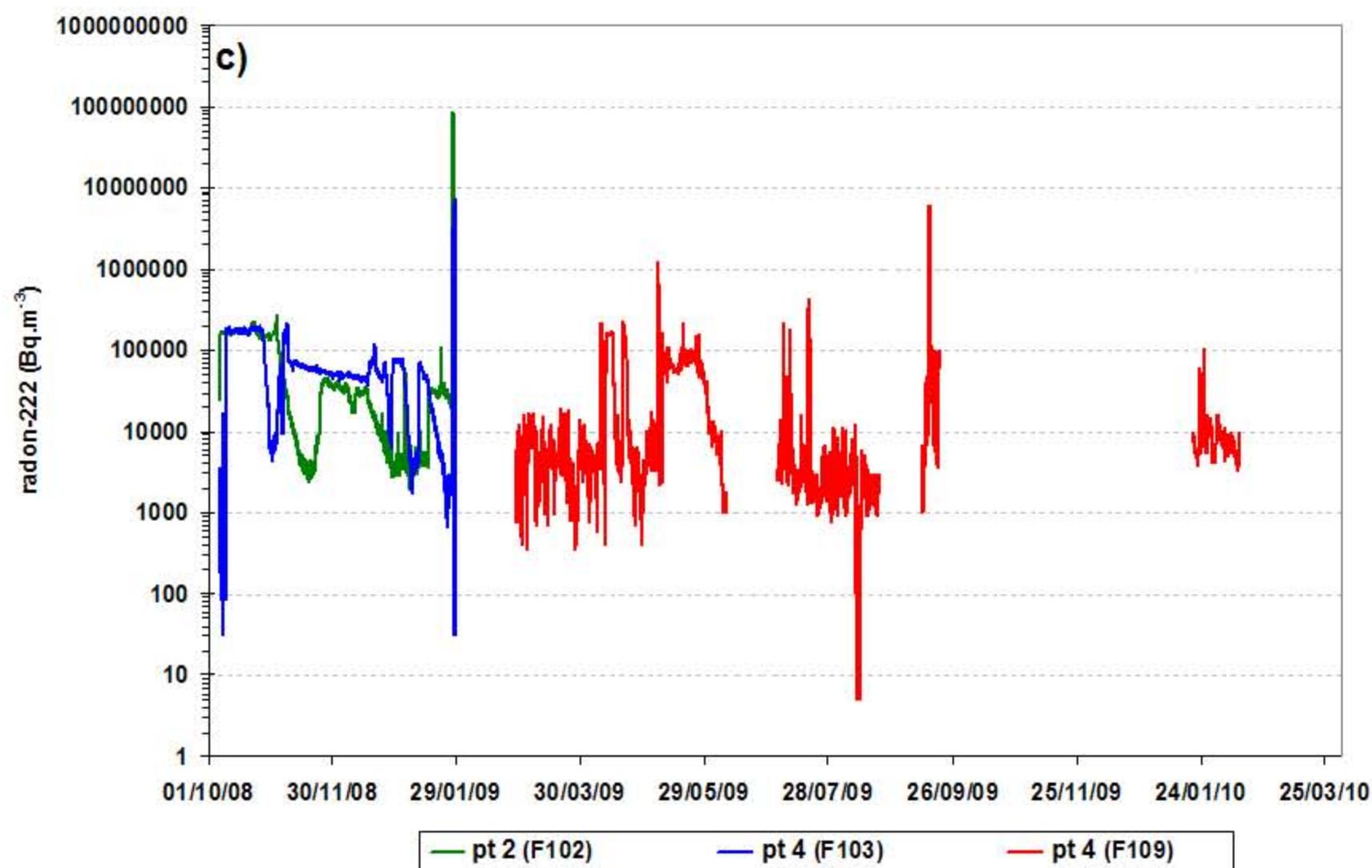
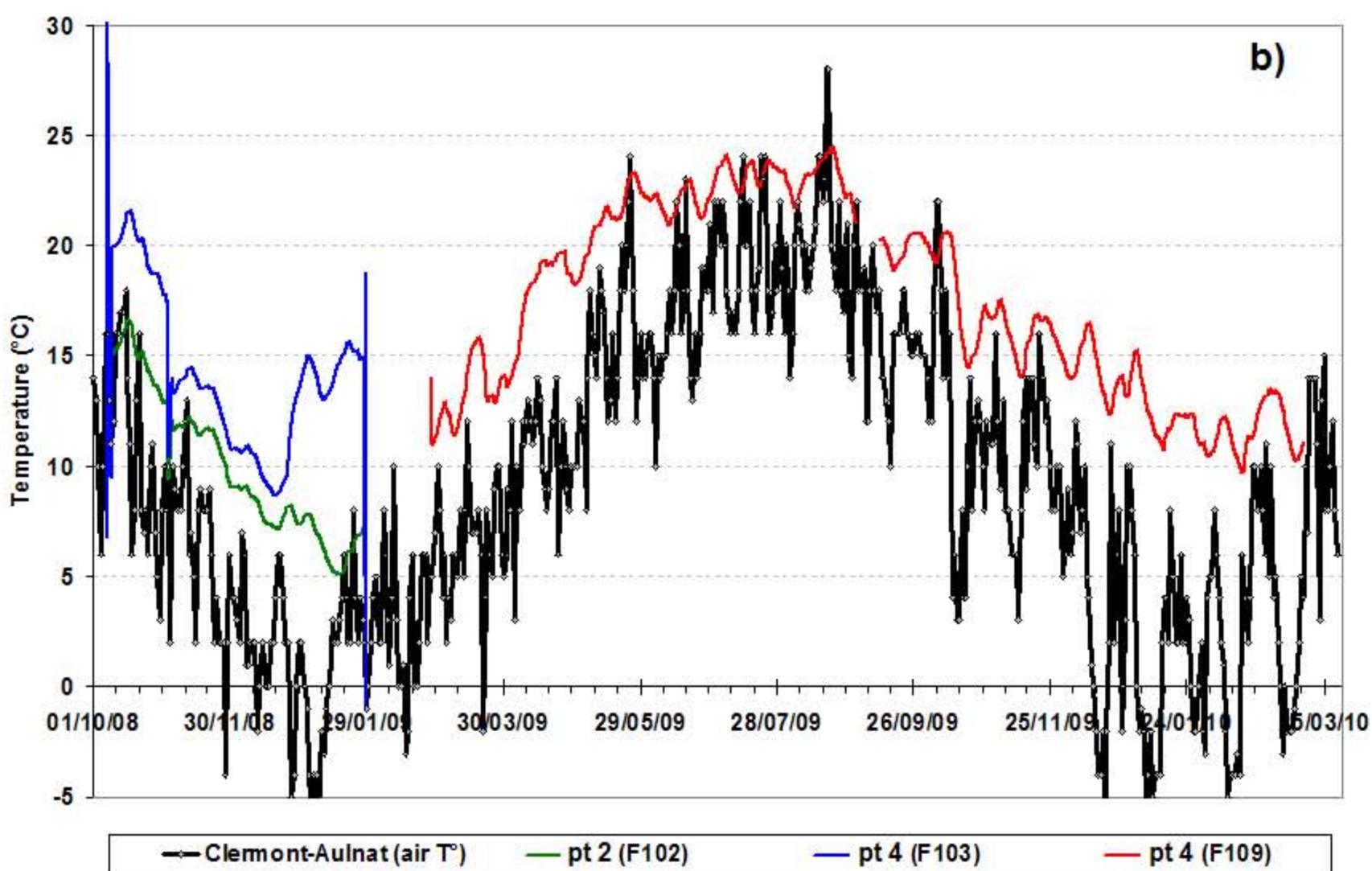
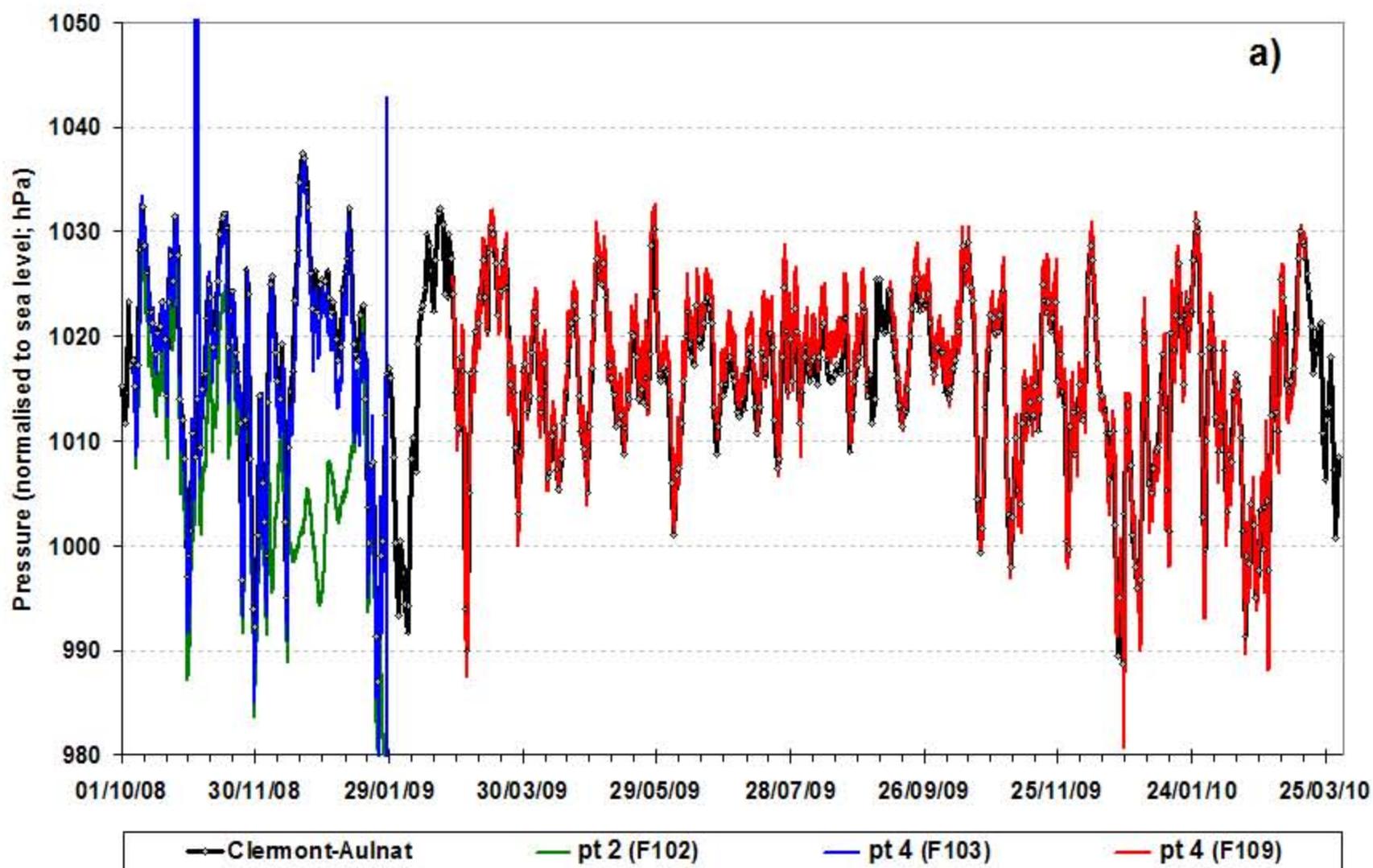


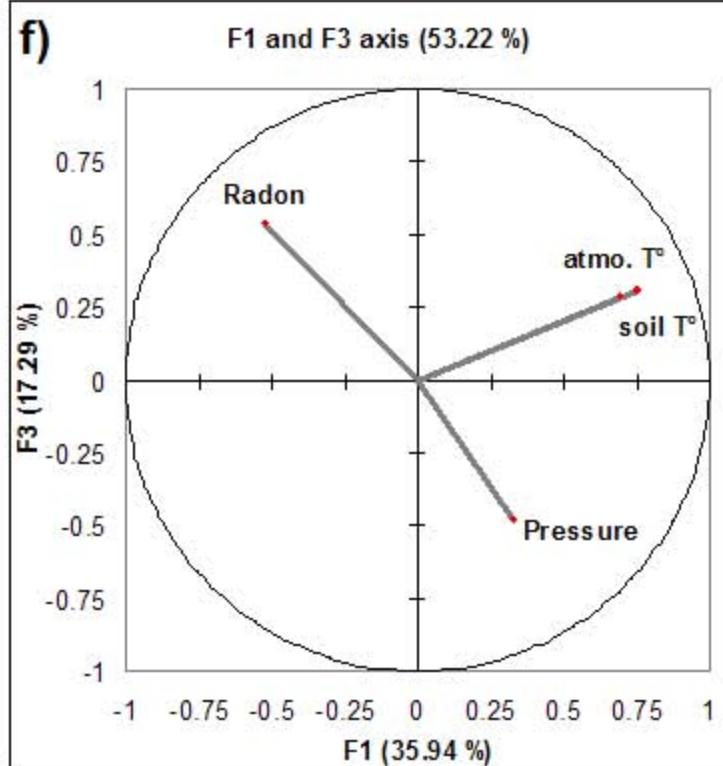
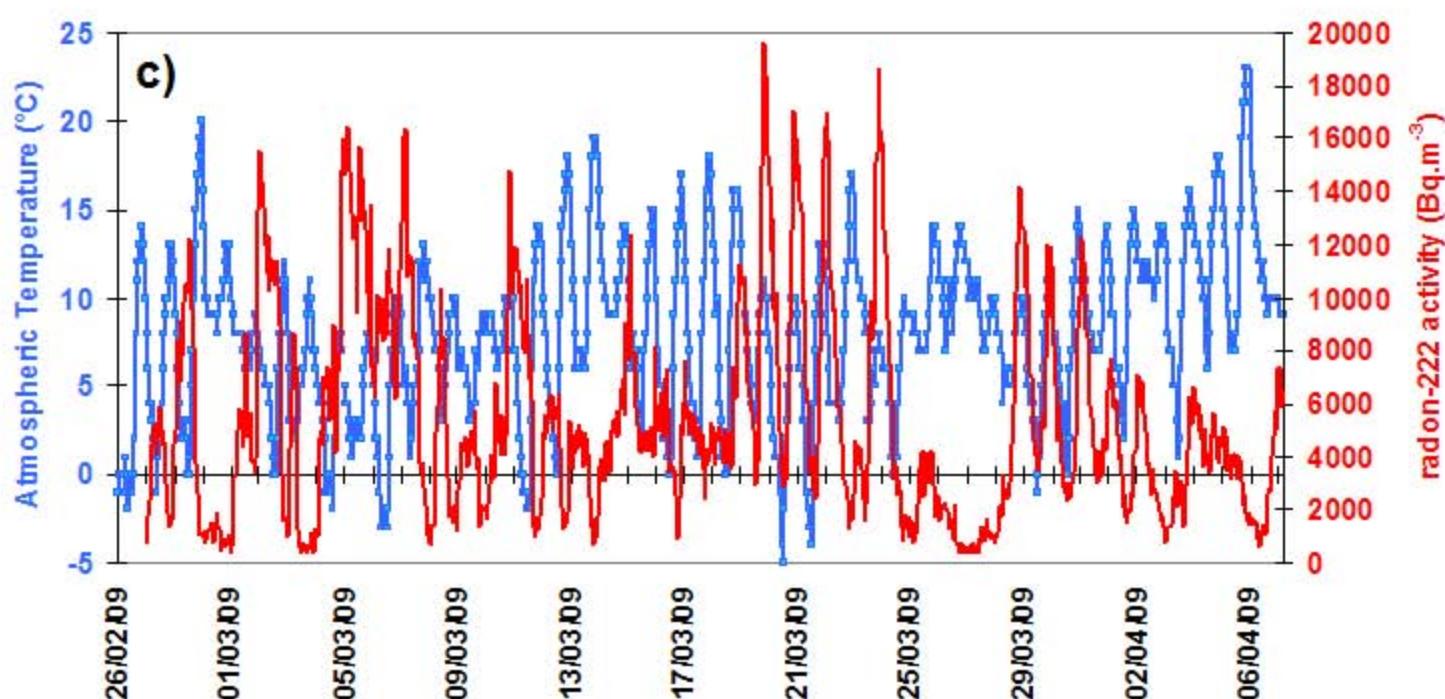
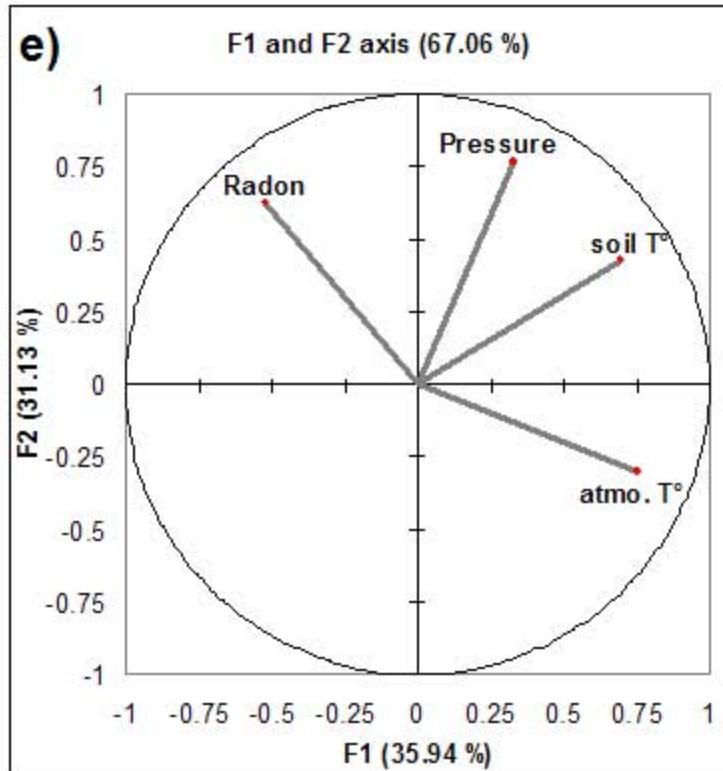
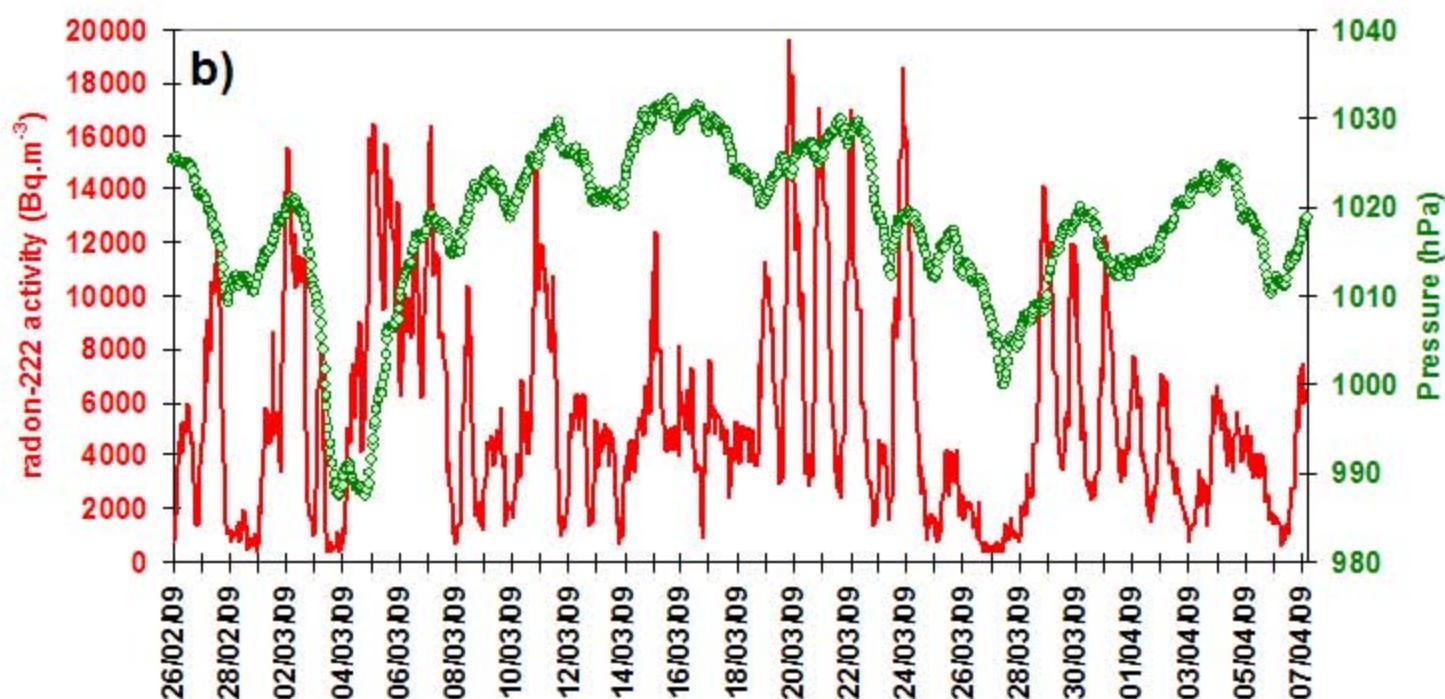
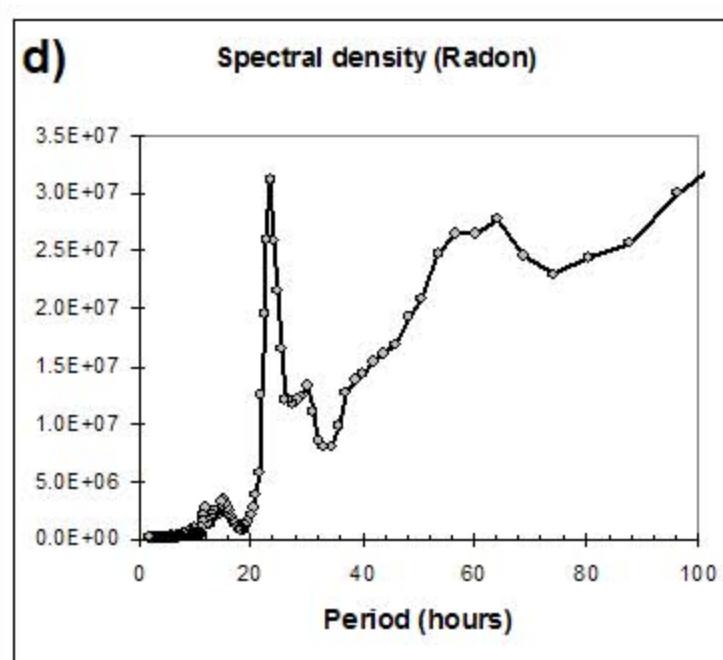
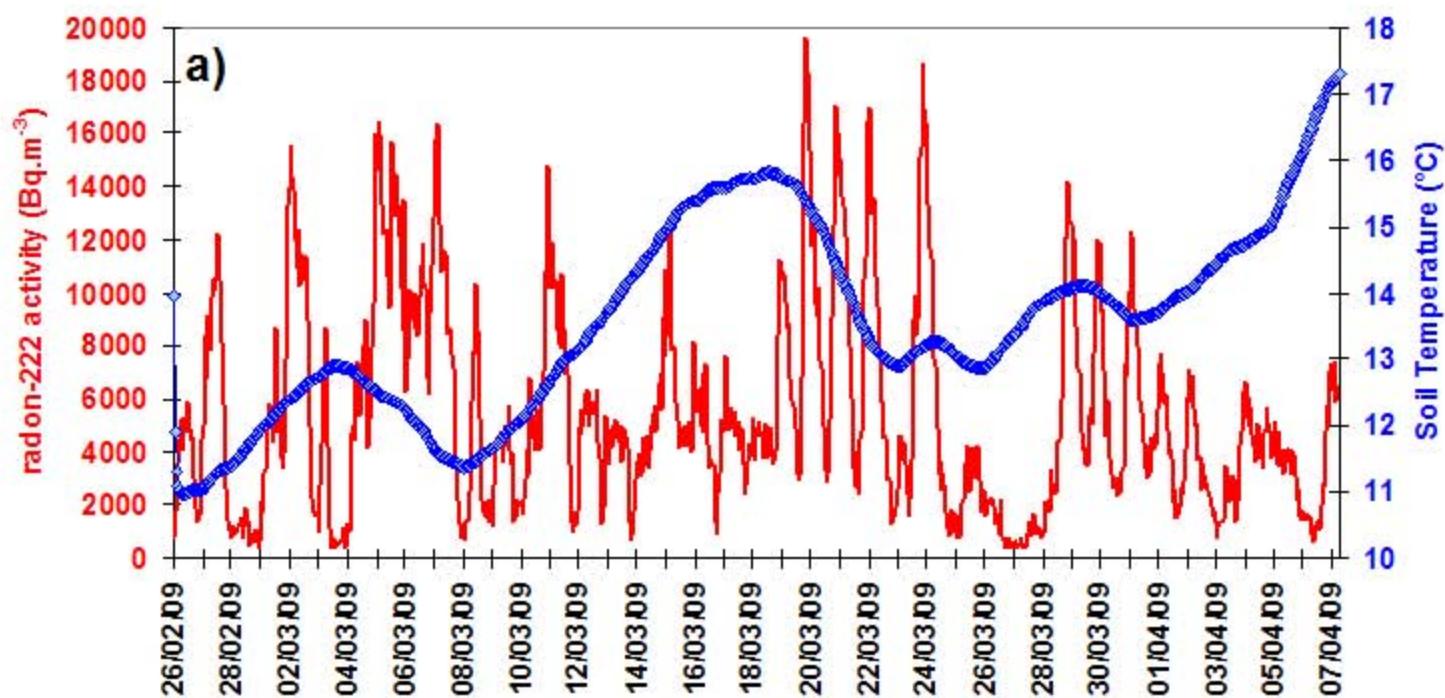
colorscale: sum of CO2 + radon + helium fitted in the 0 - 1 interval
greyscale: radon distribution in the same interval



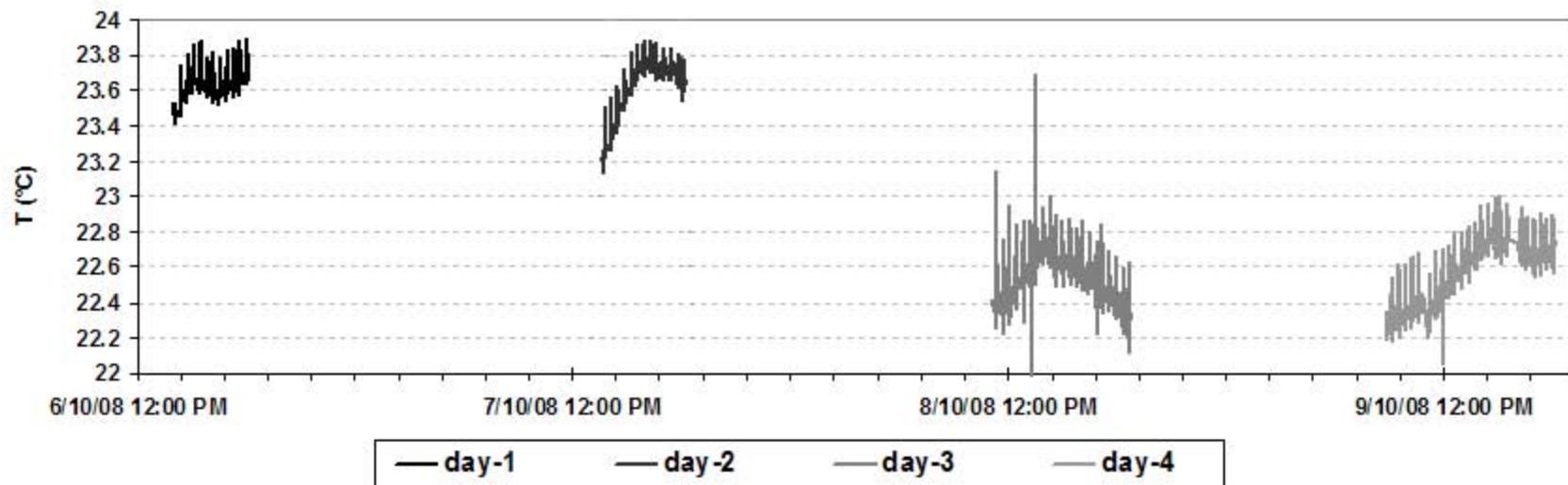
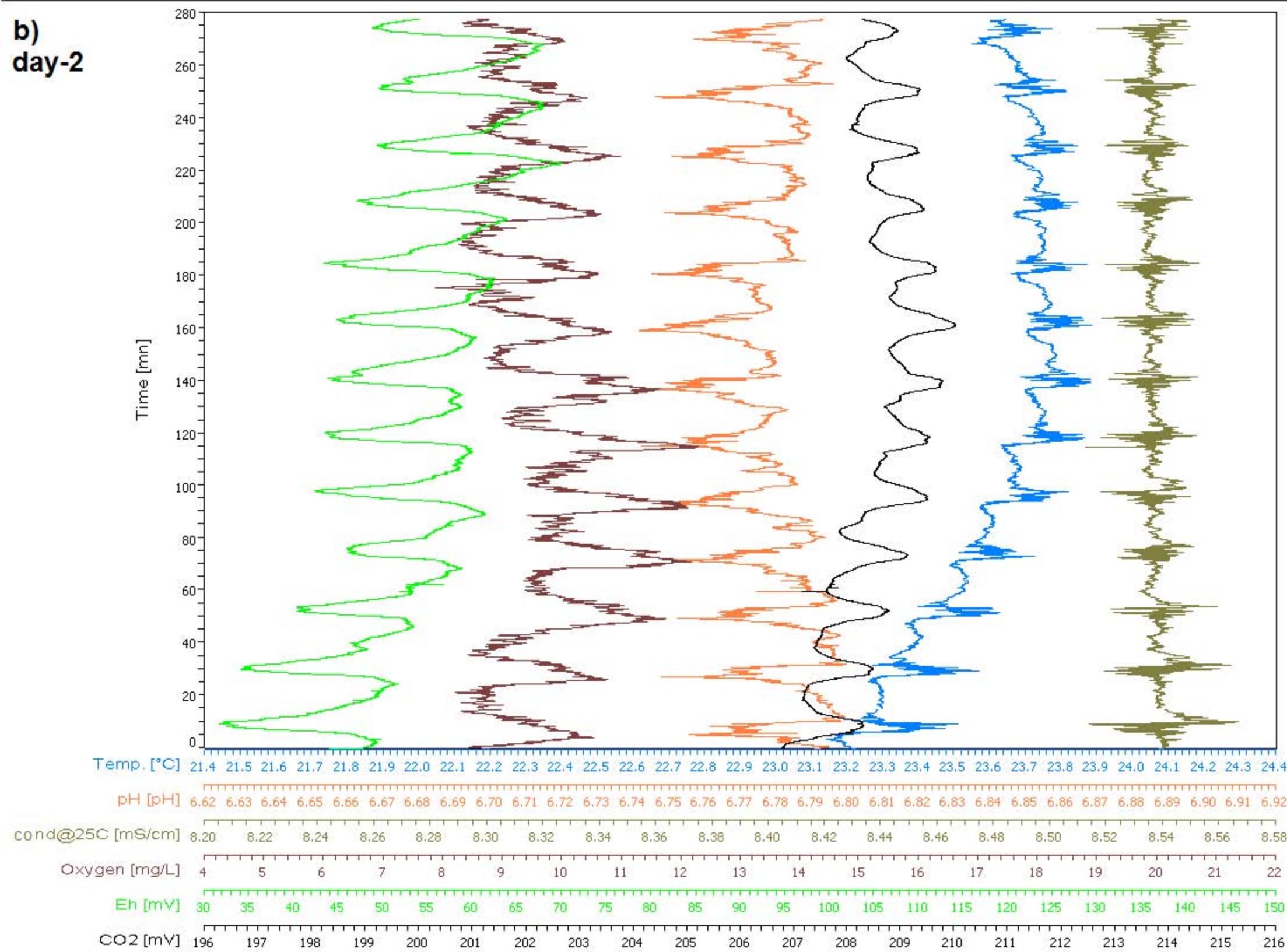
colorscale: sum of CO2 + radon + helium fitted in the 0 - 1 interval
greyscale: helium distribution in the same interval







a)

b)
day-2

	CO ₂ (%)	CO ₂ (%)	CO ₂ (%)	²²² Rn (Bq.m ⁻³)	²²² Rn (Bq.m ⁻³)	²²² Rn (Bq.m ⁻³)	⁴ He (ppm)	⁴ He (ppm)	⁴ He (ppm)
	all data	1992	2006-2010	all data	1992	2006-2010	all data	1992	2006-2010
nb. of measurements	1058	504	554	913	503	410	917	431	486
minimum	0.05	0.08	0.05	144	148	144	< 0.05	2.58	< 0.05
maximum	100	91.40	100	2482000	1930000	2480000	17.68	17.68	9.83
1st quartile	1.40	1.18	3.31	15800	17000	13800	5.19	5.24	5.04
median value	4.64	1.70	15.76	39800	37000	43200	5.24	5.30	5.22
3rd quartile	24.08	5.10	47.00	80000	71000	97400	5.34	5.36	5.26
mean value	18.66	7.07	29.21	81700	57200	112000	5.30	5.42	5.19
standard deviation	27.23	13.48	31.90	189700	105000	250000	0.76	0.81	0.69
coeff. of variation	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 ₃ (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	PO ₄ (mg/l)	NO ₃ (mg/l)	F (mg/l)	Br (mg/l)	SiO ₂ (mg/l)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	<i>theoretical δD 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 ⁻³) DATA greater than 10 Bq.m ⁻³ and lesser than 10 ⁶ Bq.m ⁻³	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	day 1 (7400 data)					day 2 (8300 data)					day 3 (13800 data)					day 4 (15800 data)				
STATISTICS	T°	EC	O ₂	pH	Eh	T°	EC	O ₂	pH	Eh	T°	EC	O ₂	pH	Eh	T°	EC	O ₂	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