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1 **LITHIUM ISOTOPES AS TRACERS OF GROUNDWATER CIRCULATION**
2 **IN A PEATLAND**

3
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7

8 **Abstract**

9
10 Water circulation in the peat bog of a maar depression in the Massif Central (France) was traced with
11 lithium isotopes on water samples collected in the area from springs, surface- and groundwaters, as
12 well as on solid samples taken from peat bogs.

13 Lithium contents fluctuate significantly in the groundwaters, ranging from 0.01 $\mu\text{mol. L}^{-1}$ in springs
14 feeding the peat bog, up to 28 $\mu\text{mol. L}^{-1}$ in the groundwater collected in the peat bog. Lithium-isotope
15 compositions ($\delta^7\text{Li}$, ‰) are extremely variable within the site, ranging from +12‰ in the stream
16 draining the area up to a ^7Li -rich value of +1226‰ in groundwater from the peat bog. The $\delta^7\text{Li}$ values
17 in the streams agree with those reported in the literature for surface waters, while those of groundwater
18 are far beyond the range of values measured in nature.

19 In the present study, we explain the extremely enriched ^7Li signature of the groundwaters by an
20 external input due to Ca-amendment, used in local agriculture. The relationships between Li content
21 and Ca, Mg and HCO_3 as well as the lack of a relationship between Li and Na plead in favour of ^7Li -
22 enriched carbonate amendments. This hypothesis was tested by Li-isotope analyses on the peat and on
23 several amendment samples (carbonates and NPK fertilizers), confirming the potential role of
24 amendments in the control of Li isotopes in peatland groundwater and showing high $\delta^7\text{Li}$ values in
25 fertilizers. Application of $\delta^7\text{Li}$ ratios to peatland waters provides a unique perspective on the
26 hydrogeochemical dynamics at the scale of this site, as the $\delta^7\text{Li}$ values for the surface water were quasi
27 constant throughout the survey period, and the peatland groundwater does not supply the surface-water
28 runoff and may evolve as a stagnant system. To conclude, the water within the peatland exhibits very
29 high $\delta^7\text{Li}$ values consistent with artificially enriched ^7Li associated with Ca amendments. This study
30 open a new field for Li isotope investigations in hydro-systems and potential utility of Li isotopes as
31 environmental tracers.

32 **Keywords:** peatland, groundwater, Li isotopes, Massif Central
33

* corresponding author

34 **1 – Introduction**

35
36 A wetland is an area covered at least part-time by usually quite shallow water. Wetlands can
37 be natural or artificial, permanent or temporary, and the water in them can be static or
38 flowing, and fresh, brackish or salty. Wetlands form where water collects in a low-lying area
39 with poor drainage. The water filling a wetland can have many origins: precipitation is a
40 major source of water for many wetlands, but others are maintained by water that periodically
41 overflows from rivers, lakes, etc., whereas a third source of water for wetlands is
42 groundwater. All three sources generally deliver water to wetlands in regular cycles, based on
43 the natural cycle of water through the hydrosphere. It is also worth noting that understanding
44 the hydrology of a wetland is primordial for efficient flood control, paleoclimate analyses,
45 and studying its role in the overall ecology.

46 The present study investigates the use of Li and its isotopes as a proxy of ground-to-surface
47 water exchanges in a peatland from a mire-lake complex in the French Massif Central, as the
48 capability of Li isotopes as hydrogeological tracers was earlier demonstrated by Hogan and
49 Blum (2003). As one aim of the work was to determine geochemical constraints on the
50 hydrological functioning of a peatland, our primary objective was to constrain hydro-reservoir
51 signatures and the exchanges of water and solutes with adjacent ground and uplands. One
52 particularly important aspect of this work was to evaluate the mechanisms of water and solute
53 transfer between the reservoirs by applying Li as a new isotopic tracer.

54 Lithium has two stable isotopes of mass 6 and 7, with natural abundances of 7.5% and 92.5%
55 respectively. Lithium is a mobile element that tends preferentially to go into the fluid phase
56 during water/rock interactions. The relative mass difference between the two isotopes is
57 considerable at 17%, generating significant mass-dependant fractionation during geochemical
58 processes. The range of variation in lithium-isotope compositions is more than 50‰ in
59 geological materials (see Coplen et al., 2002; Tomascak, 2004 for data compilation). As Li is

60 a recently developed isotopic tracer, not all the processes that could induce and control
61 isotopic fractionation are as yet well constrained. However, in the context of water/rock
62 interactions, numerous studies (Huh et al., 1998, 2001; Pistiner et al., 2003; Kisakurek et al.,
63 2004, 2005; Pogge von Strandmann et al., 2006; Millot et al., 2007, 2010a, 2010b) have
64 clearly shown that isotopic fractionation supports the enrichment of the heavy isotope (^7Li) in
65 solution, the light isotope (^6Li) being preferentially retained in secondary weathering
66 minerals. Silicate rocks display Li isotope compositions ranging from -2 to $+10\text{‰}$ (Coplen et
67 al., 2002; Teng et al. 2004), that of seawater is $\sim +31\text{‰}$ (Millot et al., 2004), river water has
68 intermediate isotopic compositions ($+6$ to $+23\text{‰}$, Huh et al., 1998), and saline (thermo-
69 mineral) water generally has isotopic compositions in the range of 0 to $+15\text{‰}$ (Millot and
70 Négrel, 2007, Millot et al., 2010b) although Falkner et al. (1997) found Li isotopic
71 compositions in the range of $+17$ to $+35\text{‰}$ in hot spring water from Lake Baikal.
72 Here, we present the first results of Li and its isotopes in all reservoirs of a peatland
73 (groundwater, surface water, rainwater, wastewater, and solid peat samples) in order to
74 evaluate the potential of Li isotopes as effective tracers of the connections between ground-
75 and surface waters in a wetland. We also explore the role of groundwater in supplying
76 surface-water output from a peatland, using Li isotopes as a new probe for such
77 characterization.

78 **2 - General setting**

79
80 The Narces de la Sauvetat peatland is located in the French Massif Central, which is the main
81 volcanic province in France (Brousse and Lefevre, 1990) and the largest magmatic province
82 of the West-European Rift system (Michon and Merle, 2001). Alkali basaltic volcanism is
83 widespread in the Massif Central, occurring as numerous small centres clustered into several
84 fields (Fig. 1). The Narces de la Sauvetat peatland occupies a maar depression with lapilli tuff
85 deposited on the flanks (Boivin and Gourgaud, 1978), one of the biggest maars in the Velay in

86 view of its 1.5-km diameter and 90-m depth (Fig. 1) (Cubizolle et al., 2007; Tourman, 2007).
87 A 37-m drill-hole on the edge of the peatland revealed 2 m of black peat with increasing clay
88 content at depth. Below this lie sandy clay with peat debris from 2 to 3 m, sandy gravel with
89 variable clay content, and basalt debris from scoria and lava from 3 to 6.4 m, and finally
90 alternating sandy silt, sandy gravel and some clay layers from 6.4 to 37 m.

91 Recent coring as part of this work in the central part of the peatland (Fig. 1), revealed 3.5 to
92 4 m of black peat overlying 1.5 to 2 m of lighter peat and then a clayey layer that forms an
93 impervious barrier for groundwater. This recent coring showed around 6 m of peat deposits in
94 the site and revealed the heterogeneity of the peat in the maar. The limit between the saturated
95 and unsaturated zones lies around -1.5 m in piezometer well Q1 and -0.5 m in piezometer Q2,
96 and the aquifer is everywhere unconfined (Fig. 1), Q2 being up-slope compared to Q1. All
97 deposits (sand, gravel, etc.) are linked to the maar origin and, contrary to other maars in the
98 Deves (Tourman, 2007), there are no lacustrine deposits.

99 The Narces de la Sauvetat is drained by a small stream, the Fouragettes, that represents the
100 outlet of the area (Fig. 1: R1, altitude 1056 m). One other surface water exists in the peatland
101 (R2) with a very low discharge and a non perennial functioning (particularly during summer
102 time). Several diffusive springs occur around the maar (Fig. 1), but most of them emerge on
103 the western side (e.g. S5, altitude of about 1080 m), reflecting the basal level of a basaltic
104 aquifer. Other springs are S1 and S6. S1 emerges at an altitude of 1120 m, but lies farther
105 outside the maar; S6 emerges at an altitude of 1056 m and is more diffuse and may not be
106 related to the maar, but could also reflect another basalt aquifer. A wastewater collector (EU)
107 for two houses is located in the peatland (Fig. 1).

108 **3 – Material and methods**

109 **3.1. Material**

110

111 The site survey was carried out during one year, with a complete sampling of all selected
112 points once a month (Fig. 1). The piezometer wells were pumped before sampling when
113 approximately twice the well volume was removed before water sampling, the key parameter
114 being the stability of electrical conductivity. Surface- and ground-water samples were
115 collected in polyethylene bottles and separated into aliquots. Two of these were filtered
116 through pre-cleaned 0.45 μm acetate filters using a pre-cleaned Nalgene filter apparatus; the
117 filtrate of one of the aliquots was further separated into two additional aliquots (100 and
118 1000 ml). The latter was acidified with Suprapur HNO_3 (pH \sim 2) and stored in pre-cleaned
119 polyethylene bottles for major-cation analysis and lithium-isotope and Li-content
120 determinations.

121 For the Li-isotope investigation, groundwater samples from Q1 and -Q2 were analysed for
122 eight months (June to November, January and April), spring waters from S1, S5 and S6 were
123 analysed once (August), wastewater was analysed once (June) and surface water (R1) was
124 analysed for six months (June to November).

125 Solid samples of brown and black peat were collected near the two piezometers Q1 and Q2
126 (Table 1). Near Q1, three samples were collected at 0-0.6 m, 1 m and 2 m depth, and a further
127 three samples were collected near Q2 (at surface, 0.3 m and 1 m depth). The samples were
128 oven-dried at 70 $^{\circ}\text{C}$ and powdered prior to analysis. In order to obtain representative aliquots
129 for the analyses, the samples were homogenized, quartered and dry-sieved through a 65 μm
130 nylon mesh.

131 In addition, several samples of fertilizers (carbonaceous additives and NPK), carbonate matrix
132 (Mäerl) and agricultural additives (borax, Li-Cl, Li-OH) were collected and analysed for Li
133 contents and Li isotopes (Table 2). Carbonaceous additives consist either of fine white
134 powder or small grains (3-5 mm in size), while NPK consists only of small grains. The white

135 powder was directly dissolved in an HCl-HNO₃ mixture, but the small grains were first
136 crushed and then dissolved in HCL-HNO₃ at ambient temperature in the laboratory.

137 **3.2. Methods**

138
139 The water samples were analysed by ion chromatography for major ions (accuracy 5-10%),
140 by inductively coupled plasma mass spectrometry for Li (accuracy 5%), and by Gran's
141 method (HCl titration) for alkalinity (Négreel and Petelet-Giraud, 2005).

142 Lithium-isotope compositions were measured with a Neptune Multi-Collector ICP-MS
143 (Thermo Fisher Scientific) used in the BRGM Isotope Geochemistry Laboratory (see Millot et
144 al., 2004 for more details) and are reported in delta units as follows:

$$145 \quad \delta^7\text{Li} (\text{‰}) = \left(\frac{\left(\frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{sample}}}{\left(\frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{L-SVEC}}} - 1 \right) \times 10^3$$

146 The ⁷Li/⁶Li ratios were normalized to the L-SVEC standard solution (NIST SRM 8545)
147 following the standard-sample bracketing method. Typical in-run precision on the
148 determination of δ⁷Li is about 0.1-0.3‰ (2σ_m, Millot et al., 2004; 2010a), but can be higher
149 (up to 1‰ for one analysis due to the low signal for this sample, Table 3). Chemical
150 separation of lithium from the matrix was achieved before mass analysis using 3 mL of
151 cationic resin (BioRad AG® 50W-X12, 200-400 mesh) and HCl acid media (0.2N) for 30 ng
152 of lithium. Blanks for the total chemical extraction were less than 20-30 pg of Li, which is
153 negligible since it represents a 10⁻³ blank/sample ratio. The accuracy and reproducibility of
154 the total method (purification procedure + mass analysis) were tested by repeated
155 measurement of a seawater sample (IRMM BCR-403) after separation of lithium from the
156 matrix, for which we obtained a mean value of δ⁷Li = +30.8‰ ± 0.4 (2σ, n = 15) over the
157 duration of the analyses. This mean value is in good agreement with our long-term
158 measurement (δ⁷Li = +31.0‰ ± 0.5, 2σ, n=30, Millot et al. 2004).

159 The $\delta^7\text{Li}$ ratios and Li contents were measured on the solid peat samples and on the different
160 fertilizers and additives, using standard acid-dissolution procedures and chemical separation
161 of lithium from the matrix. For solid peat samples, a total digestion of the sample is necessary
162 before separation of Li from the matrix. About 50 mg of crushed sample was dissolved in a
163 closed beaker with an ultrapure mixture of three acids - 4 ml HF (23N), 1 ml HNO₃ (14N) and
164 0.1 ml HClO₄ (12N) - for 4 days at 100 °C. After evaporation of the acid mixture, 4 ml HCl
165 acid (6N) was added for 4 days at 100 °C. Once this had evaporated, the residue of the acid
166 dissolution was dissolved in 0.5 ml HCl (0.2N) and a sample aliquot (30ng of Li) was placed
167 in a column containing cationic resin for Li separation. Blanks for the total digestion of the
168 solid samples by acids (HF, HNO₃, HClO₄ and HCl) were less than 300 pg of Li. Considering
169 a lithium concentration in the solid samples from 5 to 50 $\mu\text{g. g}^{-1}$ and the sample quantity taken
170 for acid digestion (50 mg), it appears that the quantity of lithium ranges from 250 to 2500 ng.
171 Consequently, the blanks account for only 0.01 to 0.1% of the sample, which is negligible.
172 The accuracy and the reproducibility of the procedure for solid samples (dissolution +
173 purification procedure + mass analysis) were tested by repeated measurement of the JB-2
174 basalt standard (Geological Survey of Japan), giving a mean value of $\delta^7\text{Li} = +4.9\text{‰} \pm 0.6$ (2σ ,
175 $n=17$) which is in good agreement with published values (see Carignan et al., 2007, and
176 Tomascak, 2004, for data compilation). Consequently, based on long-term measurements of
177 both seawater and JB-2 basalt standards, we estimate the external reproducibility of our
178 method to be around $\pm 0.5\text{‰}$ (2σ).

179

180 **4 – Results and comments**

181

182 Measured Li contents and Li isotopes for peat samples and fertilizers are reported in Tables 1
183 and 2, Table 3 reports ground- and surface-water data from the Narces de la Sauvetat
184 peatland, and Table 4 reports surface-water data from previous work.

185 **4.1. Ground- and surface waters**

186
187 Lithium contents in the groundwater fluctuate strongly, between 0.014 $\mu\text{mol L}^{-1}$ (S1, May
188 2007) and 28.260 $\mu\text{mol L}^{-1}$ (Q2, July 2007) as shown in Table 3. Two different sets of Li
189 contents are observed. The groundwaters in the peat bog display the highest content, over 1
190 $\mu\text{mol L}^{-1}$, but the Q2 piezometer showed higher Li contents than the Q1 one. Spring waters
191 generally display a lower Li content, around 0.015 $\mu\text{mol L}^{-1}$ with the exception of S6 with a
192 Li content of around 0.317 $\mu\text{mol L}^{-1}$. The surface water of the Fouragettes stream (R1) has a
193 roughly constant Li content of around 0.4 $\mu\text{mol L}^{-1}$, which corresponds to the lower value
194 observed in streams draining the Massif Central, from volcanic catchments (Table 4) that
195 have Li contents in the range 0.55 to 2.35 $\mu\text{mol L}^{-1}$. Only the water of the Fouragettes (R1)
196 stream agrees with the Li content in peat soil solution as reported by Pokrovsky et al. (2005,
197 0.22–0.34 $\mu\text{mol L}^{-1}$), while the groundwater Li content in the peat bog is higher by a factor
198 around 10.

199 Lithium-isotope compositions ($\delta^7\text{Li}$, ‰) are extremely variable in the site (Table 3), ranging
200 from +12‰ (R1, October 2007) up to +1226‰ (Q2, May 2007). The Li-isotope composition
201 at the peat bog outlet R1 fluctuated slightly during the survey period (+12.0 to +13.1‰).
202 Among the spring waters, S1 (+60.5‰) and S5 (+47.1‰) have a relatively high $\delta^7\text{Li}$ while on
203 the other hand, the S6 spring water has a slightly higher signature (+15.1‰) than that of the
204 peat outlet (+12 to +13.1‰) and a lower signature than that of the rest of the spring waters.
205 We suspect that the S6 spring may probably be connected to the surface water R1.
206 Wastewater (EU) has an enriched ^7Li value ($\delta^7\text{Li} = +80.9‰$). In contrast to spring water and
207 surface water, the groundwater in the peatland (Q1 and Q2) has singular $\delta^7\text{Li}$ values,
208 extremely enriched in ^7Li , ranging from +961 to +1111‰ for Q1 and from +1189 to +1236‰,
209 for Q2. Such high isotopic values occurred for high Li contents during the survey, around

210 $4.26 \pm 1.96 \mu\text{mol L}^{-1}$ (mean value and standard deviation) for Q1 and an even higher mean
211 value in Q2 ($17.69 \pm 7.58 \mu\text{mol L}^{-1}$).

212 The time variation of Li content from May 2007 to April 2008 is shown on Figure 2a. Both
213 Q1 and -Q2 show a significant decrease in Li content, though, where for Q2 the decrease is
214 continuous, for Q1 the Li contents showed an increase/steady-state/decrease pattern.
215 Conversely, there is no evidence of time variation in the Li content of the R1 surface water.
216 Figure 2b illustrates the $\delta^7\text{Li}$ variation during the same period and for the same sample set. Q2
217 varied little during the collection period with only 4% variation (between $\delta^7\text{Li} = +1189$ to
218 $+1236\text{‰}$), but the $\delta^7\text{Li}$ for Q1 had a larger range, with a 14% variation (between $\delta^7\text{Li} = +961$
219 to $+1111\text{‰}$). The time variation in the Li isotope of the R1 surface water is low with only 8%
220 variation (between $\delta^7\text{Li} = +12.0$ to 13.1‰).

221 **4.2. The peat**

222 Six brown and black solid peat samples collected in the central part of the maar were analysed
223 for Li content and Li isotopes (Table 1). Near piezometer Q1 (Fig. 1), the Li contents of the
224 solid phase are low in the first two samples, at $0.8 \mu\text{g. g}^{-1}$ at 0-0.6 m and $1.9 \mu\text{g. g}^{-1}$ at 1 m
225 depth, reaching $14.4 \mu\text{g. g}^{-1}$ at 2 m depth. Near piezometer Q2, the Li contents are higher and
226 range from $9.8 \mu\text{g. g}^{-1}$ on surface up to $15.5 \mu\text{g. g}^{-1}$ at 0.3 m depth, showing a slight decrease
227 at 1 m depth to $12.1 \mu\text{g. g}^{-1}$. Such Li contents in the peat are higher than those reported by
228 Kamenov et al. (2009). The $\delta^7\text{Li}$ values are close to -1.1‰ near piezometer Q1 and show
229 lower values near piezometer Q2, in the range of -0.4 to $+0.2\text{‰}$.

230 **4.3. Bedrock, rainwater and carbonaceous additives in fertilizers**

231
232 The lava is nepheline-normative basanite with 5–6 wt% $\text{Na}_2\text{O} + \text{K}_2\text{O}$, to basalt (Villemant et
233 al., 1981; Liotard et al., 1988). Recent Li-isotope data on volcanic rocks from the Massif
234 Central (Hamelin, 2008; Hamelin et al., 2009) reveal values from high $\delta^7\text{Li}$ in basalt ($+7\text{‰}$) to

235 lower values in more evolved lava, with a $\delta^7\text{Li}$ around 0‰ in trachyte with Li contents in the
236 range of 6-20 $\mu\text{g. g}^{-1}$.

237 For characterizing rainwater, we will consider the 15-month rainwater survey carried out in
238 the Massif Central (Négrel and Roy, 1998; Roy and Négrel, 2001) giving mean weighted Li
239 contents of around 0.05 $\mu\text{mol L}^{-1}$ and a mean weighted $\delta^7\text{Li}$ of around +25.4‰, (n=13, Millot
240 et al., 2010c, d). It is worth noting that the mean weighted Cl and Ca contents of the rainwater
241 are respectively close to 19 $\mu\text{mol L}^{-1}$ and 16 $\mu\text{mol L}^{-1}$ (Négrel and Roy, 1998).

242 Several additives used as fertilizers, such as carbonaceous additives or NPK, were analysed
243 during this study (Table 2). Carbonate amendment mainly consists of crushed carbonate and
244 carbonate-base (chalk or Mäerl), generally enriched in trace elements (mainly Zn and B). Soil
245 deficiency, because of the unavailability or exhaustion of metal ions, is very often the cause
246 of poor plant growth. In order to overcome these deficiencies, fertilizers with specific
247 chemical constituents in specific amounts are commonly added to soil, thus enriching the
248 growth medium. The fertilizers may be supplemented with certain trace elements, such as
249 copper, iron, manganese, zinc, cobalt, molybdenum and boron (Chen et al., 2010). Salts used
250 for B enrichment of carbonate amendments may also contain large amounts of Li. Many
251 enriched B-fertilizers use boron minerals, e.g. borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), octoborate
252 ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$), or colemanite ($\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$) that are expected to contain some trace
253 elements such as lithium in the order of several tens to hundreds of $\mu\text{g. g}^{-1}$. However, there is
254 no evidence as yet that lithium is essential for plants. Both stimulating and toxic effects of
255 lithium have been noted in various crops (Bingham et al., 1964; McStay et al., 1980), and
256 some investigators have found that lithium in sprays and nutrient solutions produced
257 beneficial effects on certain plant diseases (Allender et al., 1997). For crushed carbonate, the
258 Li content ranges from 0.71 to 2.16 $\mu\text{g. g}^{-1}$ (dry matter) and the $\delta^7\text{Li}$ fluctuates between +2.10
259 and +10.5‰. These $\delta^7\text{Li}$ values fully agree with the ranges given by Coplen et al. (2002) for

260 carbonates (0–12‰). For carbonate-base amendment, only one sample could be analysed
261 whose Li content was 0.17 $\mu\text{g. g}^{-1}$ (dry matter), the $\delta^7\text{Li}$ being significantly higher in ^7Li with
262 a value high $\delta^7\text{Li}$ of 215‰. In order to investigate this possibly enriched value for Ca-
263 amendment, we first analysed a carbonate base, Mäerl, which is marine biological carbonate,
264 and different additives (borax, Li-Cl, Li-B). The Mäerl sample has a marine signature of
265 +31‰ and only one additive was found to have an extremely ^7Li -rich signature (hydroxide
266 ^7Li monohydrate, $\delta^7\text{Li} = +344000\text{‰}$). Other additives, Li- and B-rich, have $\delta^7\text{Li}$ values
267 ranging between -16 and +8‰. With only five tested additives, these results confirm high
268 isotopic values as those over +2000 for Li-B reagents given by Qi et al. (1997).

269 **5 – Discussion**

270

271 **5.1. Origin of lithium in groundwaters**

272

273 The aim of the present discussion is to identify the different sources that can control lithium
274 concentrations in groundwaters. Chloride is classically used as an atmospheric-input reference
275 in many unpolluted hydrosystems (Meybeck, 1983; Sarin et al., 1989; Négrel, 1999), but Cl
276 can also result from human activities such as domestic sewage, fertilizers, de-icing salts, etc.
277 (Sherwood, 1989). Generally, a high Cl content in surface- and ground-waters reflects human
278 influence. Cl concentrations in the different waters from the Sauvetat site ranged between 100
279 and 2000 $\mu\text{mol L}^{-1}$. The highest Cl content is found in spring waters (2000 $\mu\text{mol L}^{-1}$), the
280 lowest in groundwater in the peatland (100 $\mu\text{mol L}^{-1}$), but all are higher than the Cl content of
281 the rainwater that ranges between 20 and 40 $\mu\text{mol L}^{-1}$ (Négrel and Roy, 1998).

282 Li shows a wide range of contents when plotted *versus* Cl (Fig. 3), all samples plotting with
283 Cl and Li contents clearly higher than those of rainwater, with the exception of the surface
284 water and groundwater from the springs in the peatland that have Li contents similar to that of
285 rainwater. Compared to rainwater, there is evidence of Cl input without Li input for these

286 samples, and it is very likely that this input may be related to fertilizers. For the groundwater
287 in the peat bog (Q1 and Q2), the R1 surface water and the S6 spring water, there is another
288 source of Li than rainwater without a large Cl input, as illustrated by the lack of a direct
289 relationship between Cl and Li contents.

290 In addition, we can compare the Li with elements resulting from water-rock interaction such
291 as Na, a very soluble element in this process (Chetelat et al., 2005; Zakharova et al., 2007).
292 There is no relation between Li and Na contents (not shown), suggesting that Li enrichment
293 does not originate from the weathering of bedrock in this context. When plotted *versus* Ca
294 (Fig. 4) and HCO₃ (not shown), all water samples plot with Ca contents clearly different from
295 rainwater (Ca range 1-80 μmol: Négrel and Roy, 1998). Low Ca and Li contents are observed
296 for surface sample R1 that plots close to the S6 spring waters. On the contrary, higher Li-Ca-
297 HCO₃ contents are observed for groundwater in the peatland, with a significant relationship
298 for Q2 between Li and Ca, and between HCO₃ and Li for Q1 and Q2. Additionally, the
299 relationship in Q2 groundwater shows the lowest contents for the winter and spring samples,
300 while the highest ones are for the summer samples. This indicates the existence of a common
301 source for Li-Ca-HCO₃ in the Q1 and Q2 groundwaters, this source being more marked
302 during the summer season. The other spring- and waste-waters have low Li contents with
303 similar Ca contents, but lower HCO₃ contents.

304 To conclude, we found an input into the peat system of Ca, HCO₃ and, noteworthy, Mg, (not
305 shown) and an even larger one for Li. It is very likely that this input is related to the
306 application of carbonate amendments used for supplying Ca and Mg as the soils are too poor
307 for normal plant growth. More constraints will be added by the use of Li isotopes discussed
308 below.

309 **5.2. The enriched ⁷Li signature in groundwater**

310

311 It is obvious that the Li-isotope signatures of the dissolved load in surface- and ground-waters
312 are not simply inherited from water/rock interactions and rainwater input, as suggested by the
313 graph showing $\delta^7\text{Li}$ versus Li contents (Fig. 5). All surface- and ground-waters have $\delta^7\text{Li}$
314 values higher than that of the bedrock, in agreement with the preferential incorporation of ^6Li
315 in secondary minerals during basalt weathering as demonstrated by Pistiner and Henderson
316 (2003). The difference is generally between 5 and 15‰ and was corroborated by experimental
317 and field studies (Vigier et al., 2008, 2009, Millot et al. 2010a, b). The Li-isotope composition
318 in R1 surface water is quasi constant over time, which fully agrees with data for surface
319 waters as given by Huh et al. (1998) and Millot et al. (2010a) and references therein, but is
320 slightly higher than the signature of other rivers in the Massif Central (+3.3 to +6.3‰,
321 Table 4). This constant signature is marked by a very low fluctuation of the Li content (mean
322 value and standard deviation of 0.39 and 0.04 $\mu\text{mol L}^{-1}$, respectively). The S6 spring water
323 has a slightly higher signature than that of the R1 surface water (+15.1‰) and a lower
324 signature than that of the rest of the spring waters. It is hydraulically not connected to the
325 peatland (same elevation as shown in Fig. 1) and its $\delta^7\text{Li}$ is very close to that of the surface
326 water in the outlet, suggesting that groundwater like S6 may represent the largest input of
327 water to the river.

328 The rainwater was analysed for Li near Clermont-Ferrand, a few kilometers distant from this
329 peat maar (Millot et al., 2010c), its range for $\delta^7\text{Li}$ (+3 to +95‰) and Li content (0.004 – 0.029
330 $\mu\text{mol L}^{-1}$) shown in Figure 5. Its contribution to the dissolved Li may be coherent with some
331 spring waters, even if the Cl content indicates a Cl-poor rain input (Fig. 3). The rainwater
332 contribution is negligible for the peat-groundwater system and seems minor for the S6 spring
333 water and the R1 surface water, agreeing with other surface waters collected in the Massif
334 Central (Table 4).

335 The large increase in Li content and $\delta^7\text{Li}$ in the peat groundwater can be *a priori* related to
336 two main different mechanisms. The first could be related to fractionation processes by
337 organic matter in the system, though biological uptake and vegetation recycling do not
338 significantly affect Li isotopes in the soil. The non-influence of litter degradation on Li-
339 isotope composition in soil is not surprising, as the Li concentration is a thousand times lower
340 in vegetation than in soil. Lemarchand et al. (2010) discussed a fractionation process by
341 organic matter that led to only a few tens ‰ of fractionation for Li isotopes. It is thus unlikely
342 that the ^7Li -rich values of groundwater could result from biological fractionation processes in
343 the system.

344 The second mechanism could be linked to a source effect with lithium enriched in ^7Li .
345 Lithium-6 is valued as a source material for tritium production and as a neutron absorber in
346 nuclear fusion. Natural lithium contains about 7.5 percent lithium-6 and large amounts of
347 lithium have been isotopically fractionated for use in nuclear weapons and thermonuclear fuel
348 stocks. Some of the material remaining from the production of lithium-6, which is depleted in
349 lithium-6 and enriched in lithium-7, is made commercially available, and some has been
350 released into the environment (Coplen et al., 2002). Depleted lithium-6 materials are
351 commonly available and the most enriched $\delta^7\text{Li}$ values reported by Qi et al. (1997) are
352 +3013‰ for a Li-OH reagent and +2333‰ for a $\text{Li}_2\text{B}_4\text{O}_7$ salt. We therefore propose that this
353 source effect may be related to the application of a carbonate amendment. This source is
354 represented in Figure 5 by the end-member EM1. We assume this end-member to represent
355 the required lithium content-Li isotope ratios to take all data into account (Négrel et al.,
356 2010). When consisting of crushed carbonate this may impact the Ca and HCO_3 budget of the
357 groundwater as well as the pH, , but also the Li budget as these amendments are artificially
358 enriched in trace elements. Soils contain trace elements (e.g. metal ions) in addition to other
359 macro- and micro-nutrients that are needed for plant growth.

360 Analysis of chemical reagents and additives (Qi et al., 1997; Table 2) can show enriched $\delta^7\text{Li}$
361 values, but among the analysed fertilizers in this study only one carbonate amendment has a
362 real enriched lithium value ($\delta^7\text{Li}$ over +200‰), reflecting the addition of 7-enriched Li in the
363 fertilizer manufacturing process, whose application may have an impact on the $\delta^7\text{Li}$ signature
364 of the groundwater.

365 First evidence of the impact of the carbonate amendment application is given by major ions.
366 Reporting data using Li-normalized ratios (in order to avoid concentration effects in Fig. 6 for
367 Ca/Li vs. HCO_3/Li) reveals trends between the peatland groundwater, the surface water and
368 the spring water that can be considered as mixing lines. Mixing of two solutions (a, b) with
369 different lithium-normalized ratios X/Li (X being Ca and HCO_3 in this case) will lead to a
370 mixed solution (i.e. “mix”) that will have a X/Li ratio of:

$$371 \quad \text{X/Li}_{\text{mix}} = m \text{X/Li}_a + (1 - m) \text{X/Li}_b \quad (\text{Eq. 1})$$

372 where X/Li_a , X/Li_b and X/Li_{mix} are the lithium-normalized ratios for the solution mix from
373 two end-members a and b, and m is the mixing proportion.

374 Two different mixing lines can then be calculated between the end-member EM1,
375 representing the application of carbonate amendment, the S6 spring water and other spring
376 waters. All groundwater samples from the peatland fall within these mixing lines, but EM1
377 has little impact on the surface waters as the samples deviate little from the S6 spring water.
378 The groundwater samples from the peatland clearly result from input of water from the spring
379 on the hill slope (“springs” in Fig. 6) inducing a dilution, the EM1 values reflecting
380 anthropogenic impact. However, the role of groundwater from the peatland on surface water
381 is not obvious when looking at the X/Li ratios, and constraints on Li isotopes will help
382 deciphering the functioning of the area.

383 To summarize, we explain the extremely enriched ^7Li signature of the groundwaters in the
384 peat land by an external input due to Ca-amendment used in local agriculture.

385 **5.3. Groundwater circulation**

386

387 Application of $\delta^7\text{Li}$ ratios to peatland waters provides a unique perspective on the
388 hydrogeochemical dynamics at the scale of this site. The groundwater from the peat (Q1 and
389 Q2), being Li-rich and with extremely enriched $\delta^7\text{Li}$ values, seems to have no impact on the
390 hydrologic budget from peat to the outlet (e.g. the Fouragettes stream). The $\delta^7\text{Li}$ values of
391 surface water (R1) are quasi constant throughout the survey, ranging between +12.0 and
392 +13.1‰, and moreover present non-enriched $\delta^7\text{Li}$ values. Li-isotope contents in the peat
393 system seem to vary due to a source effect and the groundwater in the peatland can be
394 considered as a “spiked solution” that may, or may not, mix with the rest of the input (i.e. the
395 spring waters) for which the river can be considered as the output.

396 The isotope systematics of two-component mixtures, described in detail by Faure (1986) and
397 used for Sr isotopes by Hogan et al. (2000) for tracing peatland groundwater circulation, can
398 be expressed as follows for Li isotopes and X/Li ratios (Eq. 3). The mixed solution will have
399 a $\delta^7\text{Li}$ of:

$$400 \quad \delta^7\text{Li}_{\text{mix}} = \{(X/\text{Li}_a \times \delta^7\text{Li}_a \times m)/(X/\text{Li}_{\text{mix}})\} + \{(X/\text{Li}_b \times \delta^7\text{Li}_b \times (1-m))/X/\text{Li}_{\text{mix}}\} \quad (\text{Eq. 2})$$

401 where X/Li_a , X/Li_b and X/Li_{mix} are the lithium normalized ratios for the solution mix from
402 two end-members a and b, $\delta^7\text{Li}_a$, $\delta^7\text{Li}_b$ and $\delta^7\text{Li}_{\text{mix}}$ are the lithium isotope compositions, and
403 m is the mixing proportion.

404 In Figure 7, the $\delta^7\text{Li}$ versus Ca/Li ratios are plotted together with two mixing lines calculated
405 between the $\delta^7\text{Li}$ -enriched/Li-concentrated end-member (EM1) with a low Ca/Li ratio and S6,
406 and the S1 and S5. It can be seen that the mixing line between EM1 and S6 could not be
407 invoked for explaining the range observed for Li isotopes of the peat groundwaters, as they
408 fall within the EM1-S1 and S5 mixing line. However, the surface waters are not included in
409 any mixing line as there is only weak variation in both the Ca/Li ratio and $\delta^7\text{Li}$ values. This
410 result agrees with the functioning of the peatland, with water input from the hill area

411 represented by S1 and S5 in addition to the impact of the amendment application. This
412 scheme induces dilution with a lower Ca/Li ratio and $\delta^7\text{Li}$ values during spring and winter
413 (Figs. 2, 4 and 5) in the peatland groundwater. There is no evidence of different pathways
414 using Li-isotope mixing plots and the peat system seems to be well mixed with regards to the
415 Li isotopes. In addition to showing mixing between EM1 and S1 and S5 waters, the mixing
416 plots also show that surface water at the outlet seems to be only controlled by the input of
417 groundwater like S6. The groundwater beneath the peatland has distinct ratios from that
418 which discharges into the stream; this strongly suggests that groundwater in the peatland does
419 not play any role in supplying surface-water runoff and may evolve as a stagnant system,
420 being only diluted as the contents (particularly Li) show.

421

422 **6 – Conclusions**

423

424 The results are described for lithium-isotope compositions of spring-, surface- and ground-
425 water samples collected in a peat bog located in the French Massif Central in a maar
426 depression.

427 Variations in $\delta^7\text{Li}$ values can be used for distinguishing between precipitation, groundwater
428 and anthropogenic inputs in peatlands, providing a unique perspective on the hydrologic
429 dynamics of the system. The primary finding of this work concerns the existence of hugely
430 enriched values for $\delta^7\text{Li}$ in groundwater from the peatland. Mixing relationships indicate that
431 most of the water in the peatland site derives from groundwater from the hill slope. Mixing
432 plots also show that the surface water at the outlet seems to be only controlled by input from
433 other groundwater bodies, and that groundwater in the peatland does not play any role in
434 supplying the surface water runoff and may evolve as a stagnant system.

435 This study highlights the possible role of Li isotopes as tracers of the surface- and ground-
436 water circulation in a wetland. When evaluating the transfer of water and/or solutes in a

437 wetland, such complementary tracers of basic hydrogeology are highly important for
438 constraining the system.

439 To conclude, the water within in the peatland exhibits very high $\delta^7\text{Li}$ values consistent with
440 artificially enriched ^7Li associated with Ca amendments. This study opens a new field for Li
441 isotope investigations in hydro-systems and potential utility of Li isotopes as environmental
442 tracers.

443

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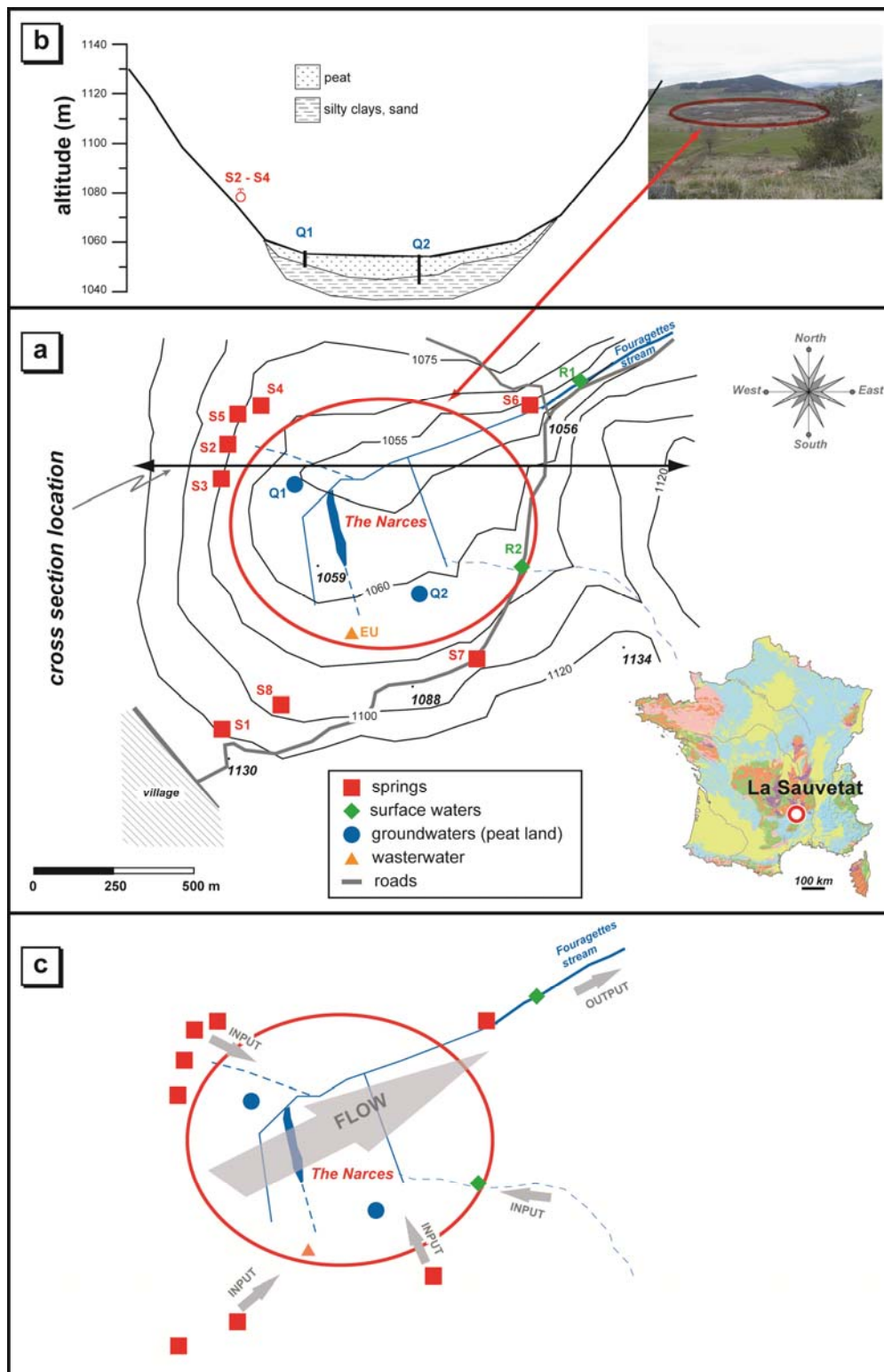
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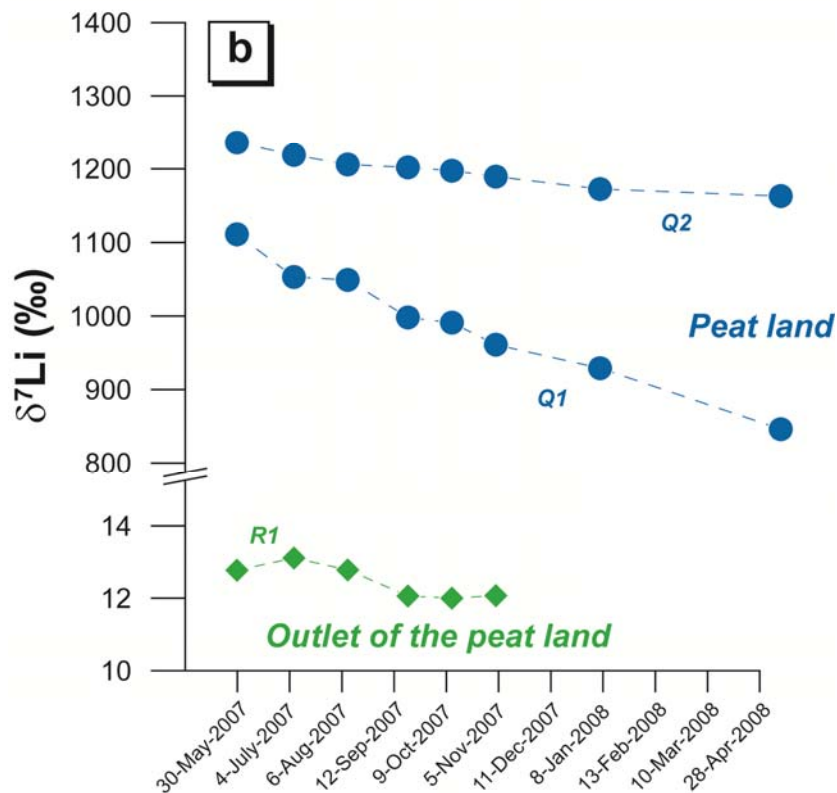
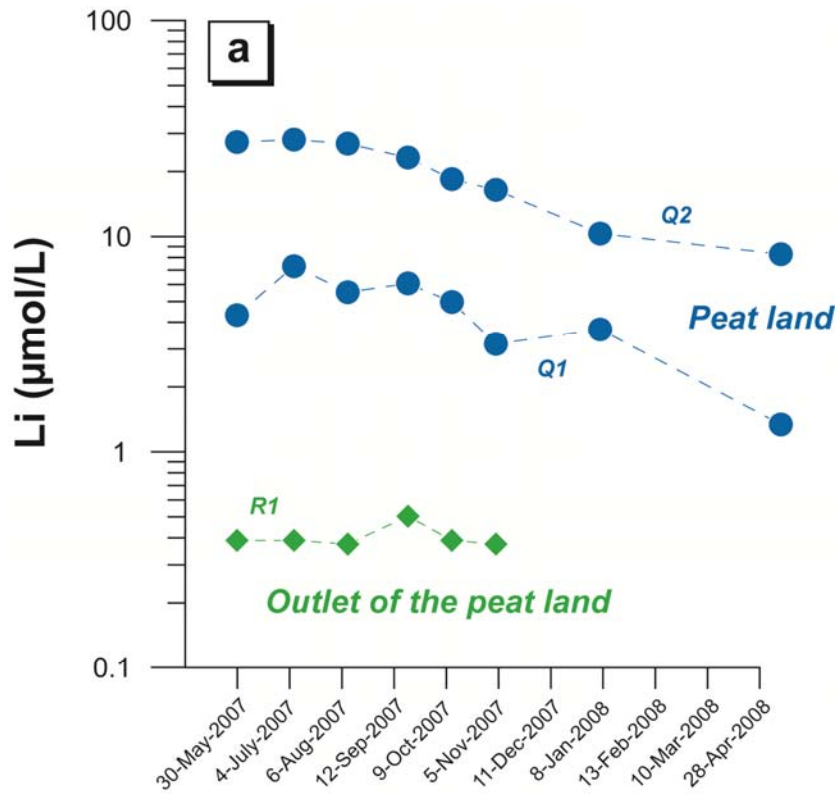
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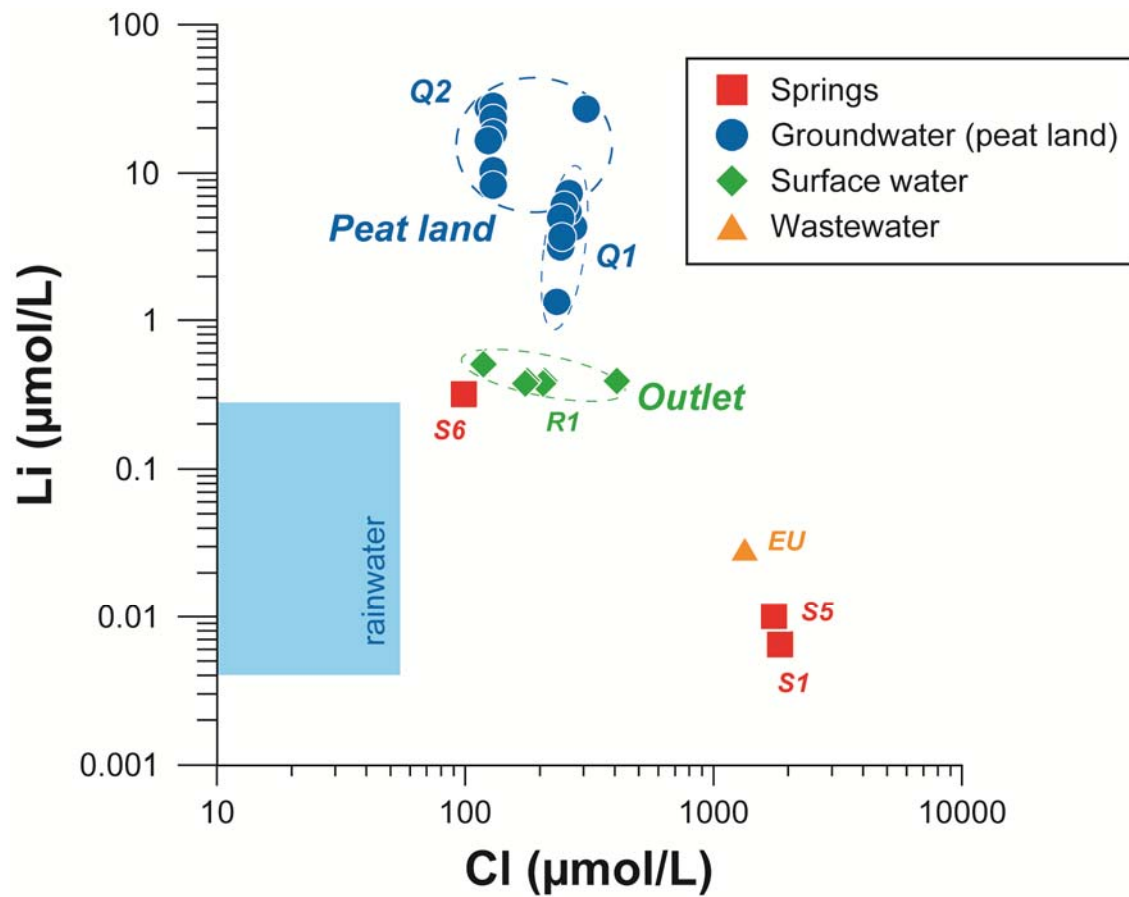
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610
 611 Figure 1. Location of the Narces de la Sauvetat peatland in the Massif Central (France).
 612 Simplified topographic map of the peatland with location of boreholes, springs and surface
 613 water identified on the site.

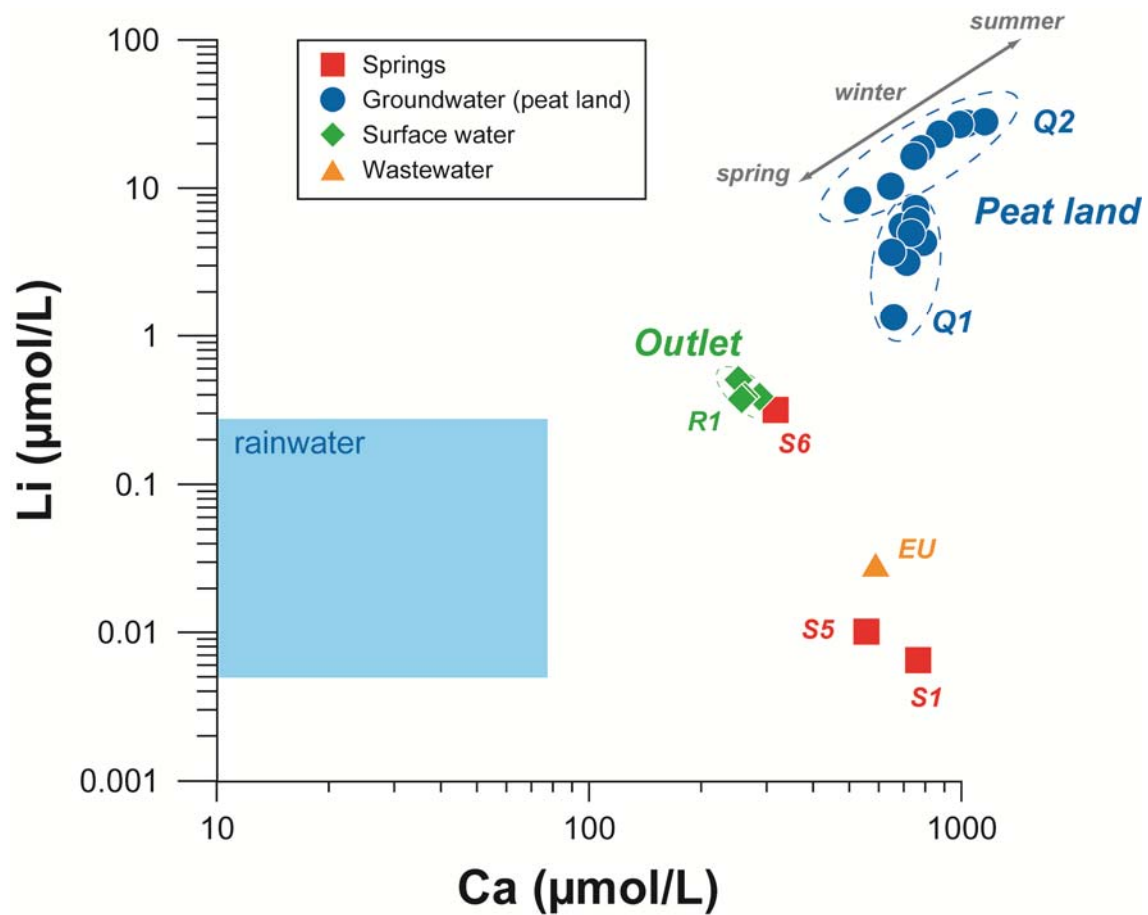


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 615 Figure 2. Time evolution between May 2007 and April 2008 of the Li concentration ($\mu\text{mol. L}^{-1}$) and $\delta^7\text{Li}$ in groundwater from the peatland (Q1 and -Q2) and surface water (R1) of the
 616
 617 Fouragettes stream, the outlet of the Narces de la Sauvetat peatland.



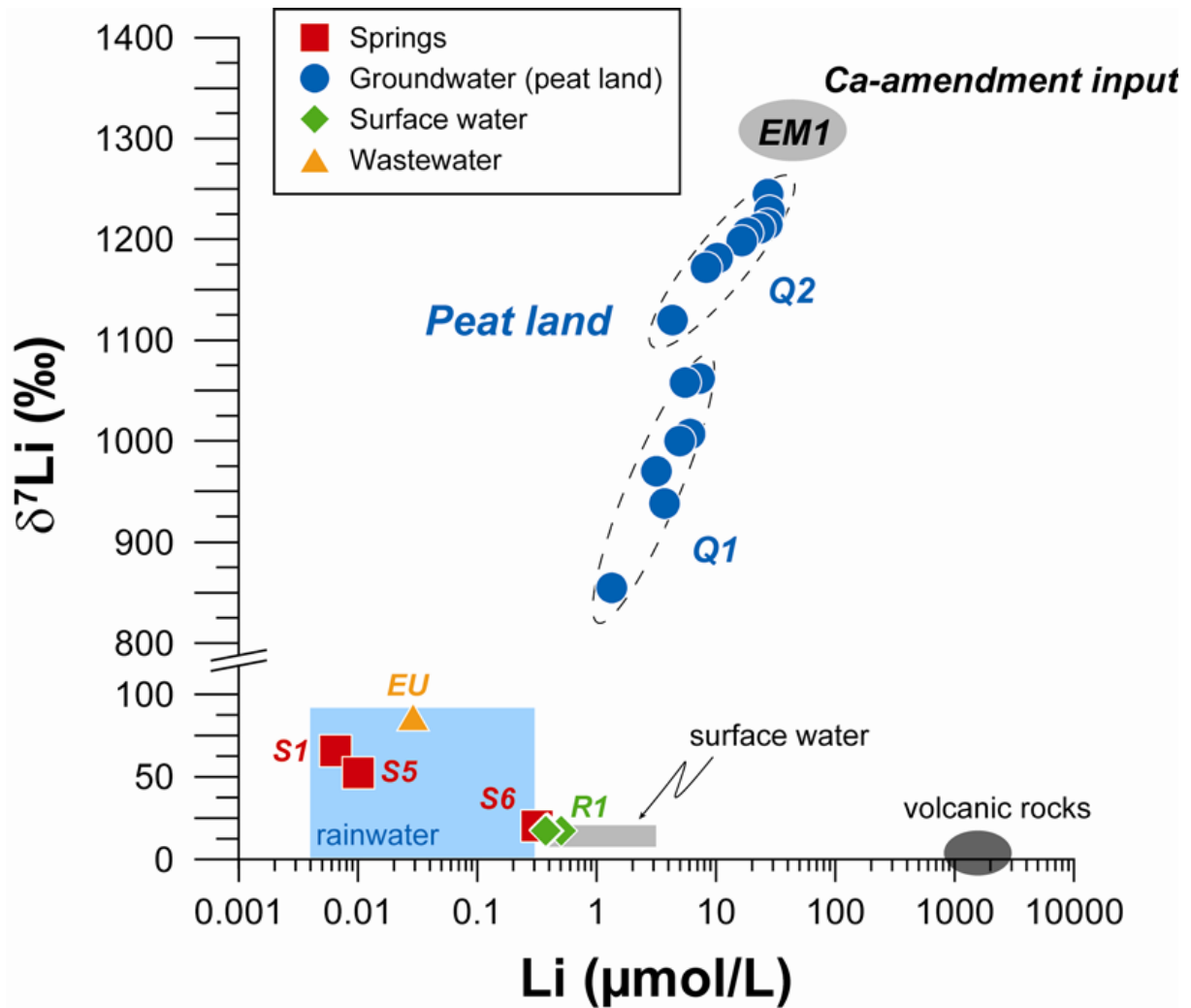
618

619 Figure 3. Li ($\mu\text{mol. L}^{-1}$) vs. Cl ($\mu\text{mol. L}^{-1}$) diagram for groundwater from the peatland (Q1 and
 620 -Q2), spring water S1 and S5 located on the hillslope on the western side and S6 (emerging
 621 close to the outlet of the area), wastewater EU and surface water R1 in the Narces de la
 622 Sauvetat peatland. Rainwater field from the Massif Central is also indicated (Milot et al.,
 623 2010c, d, see text).

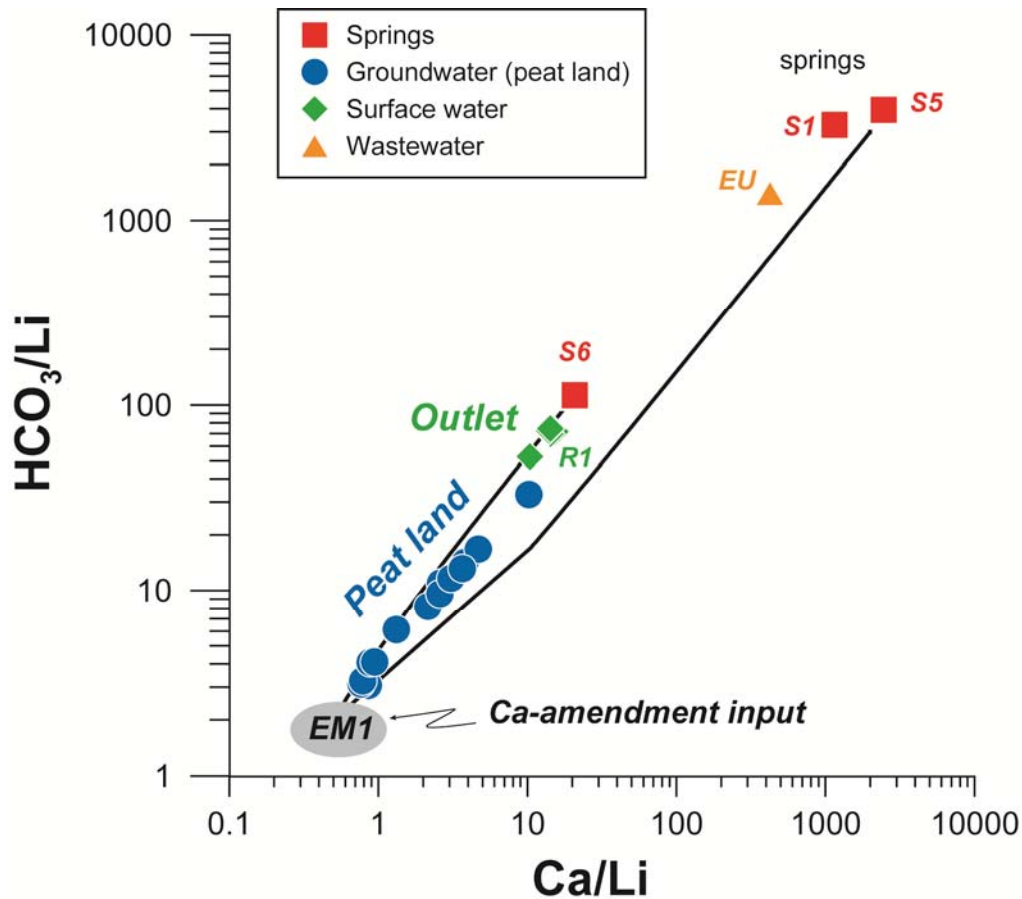


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625 Figure 4. Li ($\mu\text{mol. L}^{-1}$) vs. Ca ($\mu\text{mol. L}^{-1}$) diagram for groundwater from the peatland (Q1
 626 and Q2), spring waters S1 and S5 located on the hillslope on the western side and S6
 627 (emerging close to the outlet of the area), wastewater EU and surface water R1 in the
 628 Narces de la Sauvetat peatland. Arrow shows the evolution of Q2 groundwater in the
 629 peatland as a function of the season. Rainwater field from the Massif Central are also
 630 indicated (Millot et al., 2010c, d, see text).

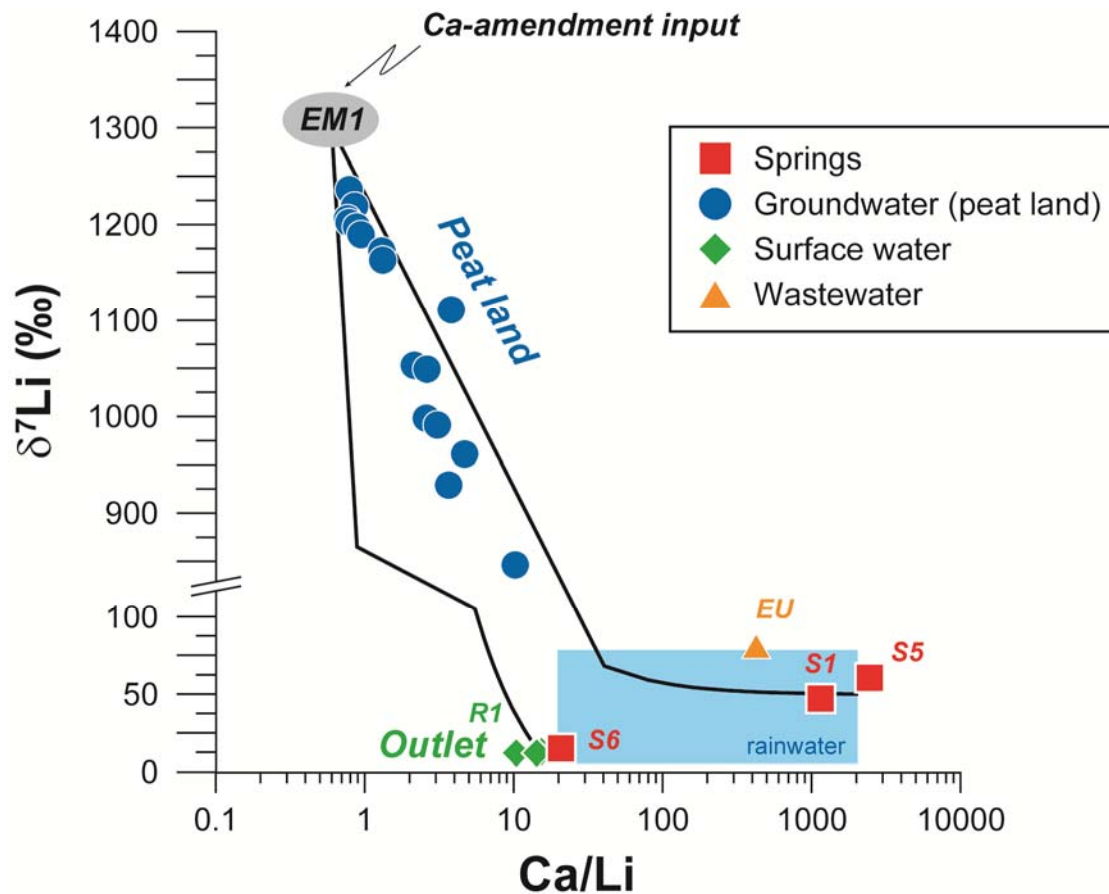


631
 632 Figure 5. Plot of $\delta^7\text{Li}$ vs. Li concentration ($\mu\text{mol. L}^{-1}$) for groundwater from the peatland (Q1
 633 and -Q2), spring water S1 and S5 located on the hillslope on the western side and S6
 634 (emerging close to the outlet of the area), wastewater EU and surface water R1 in the
 635 Narces de la Sauvetat peatland. Rainwater, volcanic rocks and surface water from the
 636 Massif Central are also indicated (see text). The end-member EM1 corresponds to the
 637 carbonate amendment input. Its location on the graph is assumed to represent the required
 638 lithium content-Li isotope ratios to take all data into account.



639

640 Figure 6. Plot of HCO_3/Li vs. Ca/Li ratios for groundwater from the peatland (Q1 and -Q2),
 641 spring water S1 and S5 located on the hillslope on the western side and S6 (emerging close
 642 to the outlet of the area), wastewater EU and surface water R1 in the Narces de la Sauvetat
 643 peatland. The end-member EM1 corresponds to the carbonate amendment input. Its
 644 location on the graph is assumed to represent the required Ca/Li and HCO_3/Li ratios to take
 645 all data into account. Two different mixing lines can then be calculated between the end-
 646 member EM1, representing the application of carbonate amendment, the S6 spring water
 647 and other spring waters (see text).



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Figure 7. Plot of $\delta^7\text{Li}$ vs. Ca/Li ratios for groundwater from the peatland (Q1 and -Q2), spring water S1 and S5 located on the hillslope on the western side and S6 (emerging close to the outlet of the area), wastewater EU and surface water R1 in the Narces de la Sauvetat peatland. The end-member EM1 corresponds to the carbonate amendment input. Its location on the graph is assumed to represent the required Ca/Li and Li isotope ratios to take all data into account. Two different mixing lines can then be calculated between the end-member EM1, representing the application of carbonate amendment, the S6 spring water and other spring waters (see text).

Sample	X	Y	Z	Li	$\delta^7\text{Li}$
			m	$\mu\text{g}\cdot\text{g}^{-1}$	‰
Q1 0-60	720157	1985198	0	0.84	-0.92
Q1 1	720157	1985198	1	1.9	-10.97
Q1 2	720157	1985198	2	14.36	-0.74
Q2surf	720542	1984852	0	9.83	-0.16
Q2 30	720542	1984852	0.3	15.51	0.29
Q2 1	720542	1984852	1	12.05	0.04

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668 Table 1. Results of Li concentration ($\mu\text{g}\cdot\text{g}^{-1}$) and $\delta^7\text{Li}$ in the peat samples collected at
669 different depths (Z in m) in the Narces de la Sauvetat peatland.

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Sample	Composition	Li	$\delta^7\text{Li}$
		$\mu\text{g}\cdot\text{g}^{-1}$	‰
<i>Fertilizers</i>			
MEAC	crushed carbonate	1.14	2.85
Jardidol	enriched carbonate	0.17	215
AMD	crushed carbonate	2.16	2.10
Carbocentre	crushed carbonate	0.71	10.50
BB600	NPK	1.08	23.10
MEAC2	NPK	1.75	12.90
<i>Additives</i>			
MAËRL	Marine carbonate	2.68	31.03
BORAX pentahydrate NEOBOR	Borax	13.16	4.96
BORAX decahydrate GRANULE	Borax	7.43	-16.05
Lithium Chloride	Li-Cl	115.26	0.05
$\text{Li}_2\text{B}_4\text{O}_7$	Li-B	19.97	8.18
Hydroxyde ^7Li monohydrate	Li	138.47	344000

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673 Table 2. Results of Li concentration ($\mu\text{g}\cdot\text{g}^{-1}$) and $\delta^7\text{Li}$ in various fertilizers and additives.

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Sample	Date	X	Y	Cl	Ca	Na	Mg	HCO ₃	Li	$\delta^7\text{Li}$
				$\mu\text{mol.L}^{-1}$	$\mu\text{mol.L}^{-1}$	$\mu\text{mol.L}^{-1}$	$\mu\text{mol.L}^{-1}$	$\mu\text{mol.L}^{-1}$	$\mu\text{mol.L}^{-1}$	‰
Groundwater										
Q1	30-mai-07	720157	1985198	273	791	200	852	2951	4.322	1111.0
Q1	04-juil-07	720157	1985198	262	753	200	840	2869	7.290	1053.0
Q1	06-août-07	720157	1985198	259	693	222	852	2918	5.518	1049.0
Q1	12-sept-07	720157	1985198	251	756	200	831	2803	6.065	998.0
Q1	09-oct-07	720157	1985198	242	733	200	790	2787	4.970	991.0
Q1	05-nov-07	720157	1985198	242	713	196	815	2557	3.170	961.0
Q1	08-janv-08	720157	1985198	245	651	178	737	2344	3.703	929.0
Q1	28-avr-08	720157	1985198	234	658	196	794	2131	1.340	846.1
Q2	30-mai-07	720542	1984852	124	1035	378	1181	4164	27.374	1236.0
Q2	04-juil-07	720542	1984852	130	1155	313	1267	4147	28.094	1219.0
Q2	06-août-07	720542	1984852	307	990	296	1082	4049	26.913	1206.0
Q2	12-sept-07	720542	1984852	130	875	265	909	3623	23.196	1202.0
Q2	09-oct-07	720542	1984852	130	781	256	811	3606	18.441	1197.5
Q2	05-nov-07	720542	1984852	124	746	248	786	3246	16.453	1189.4
Q2	08-janv-08	720542	1984852	130	646	248	733	3033	10.316	1172.5
Q2	28-avr-08	720542	1984852	130	526	226	597	2443	8.284	1163.0
Surface water										
R1	30-mai-07	721052	1985500	208	259	374	366	1361	0.389	12.8
R1	04-juil-07	721052	1985500	408	287	422	395	1344	0.389	13.1
R1	06-août-07	721052	1985500	206	257	330	346	1262	0.375	12.8
R1	12-sept-07	721052	1985500	118	252	348	309	1279	0.504	12.1
R1	09-oct-07	721052	1985500	177	262	357	329	1361	0.389	12.0
R1	05-nov-07	721052	1985500	175	257	352	342	1344	0.375	12.1
Spring water										
S1	06-août-07	719929	1984414	1854	766	426	728	1230	0.014	60.5
S5	07-août-07	719986	1985413	1752	556	270	823	1590	0.015	47.1
S6	30-mai-07	720878	1985444	99	317	443	387	1721	0.317	15.1
Wastewater										
EU	30-mai-07	720328	1984707	1335	589	1165	527	1951	0.029	80.9

690

691 Table 3. Results of Cl, Ca, Na, Mg, HCO₃ and Li concentration ($\mu\text{mol L}^{-1}$) and $\delta^7\text{Li}$ in
692 groundwater from the peatland (Q1 and -Q2), spring water S1 and S5 located on the
693 hillslope on the western side and S6 (emerging close to the outlet of the area), wastewater
694 EU and surface water R1 in the Narces de la Sauvetat peatland.

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River	X	Y	Li $\mu\text{mol.L}^{-1}$	$\delta^7\text{Li}$ ‰	$2\sigma_m$
Couze Groire	648 269	2 063 602	2.35	5.8	0.1
Couze Chaudefour	643 296	2 062 409	0.55	3.3	0.2
Couze Pavin	667 041	2 060 952	1.75	6.3	0.1

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702 Table 4. Results of Li concentration ($\mu\text{mol L}^{-1}$) and $\delta^7\text{Li}$ in several surface-water samples
703 from the Massif Central.

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