Lithium isotopes as tracers of groundwater circulation in a peat land

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Abstract

Water circulation in the peat bog of a maar depression in the Massif Central (France) was traced with lithium isotopes on water samples collected in the area from springs, surface- and groundwaters, as well as on solid samples taken from peat bogs. Lithium contents fluctuate significantly in the groundwaters, ranging from 0.01 µmol. L⁻¹ in springs feeding the peat bog, up to 28 µmol. L⁻¹ in the groundwater collected in the peat bog. Lithium-isotope compositions (δ⁷Li, ‰) are extremely variable within the site, ranging from +12‰ in the stream draining the area up to a ⁷Li-rich value of +1226‰ in groundwater from the peat bog. The δ⁷Li values in the streams agree with those reported in the literature for surface waters, while those of groundwater are far beyond the range of values measured in nature. In the present study, we explain the extremely enriched ⁷Li signature of the groundwaters by an external input due to Ca-amendment, used in local agriculture. The relationships between Li content and Ca, Mg and HCO₃ as well as the lack of a relationship between Li and Na plead in favour of ⁷Li-enriched carbonate amendments. This hypothesis was tested by Li-isotope analyses on the peat and on several amendment samples (carbonates and NPK fertilizers), confirming the potential role of amendments in the control of Li isotopes in peatland groundwater and showing high δ⁷Li values in fertilizers. Application of δ⁷Li ratios to peatland waters provides a unique perspective on the hydrogeochemical dynamics at the scale of this site, as the δ⁷Li values for the surface water were quasi constant throughout the survey period, and the peatland groundwater does not supply the surface-water runoff and may evolve as a stagnant system. To conclude, the water within the peatland exhibits very high δ⁷Li values consistent with artificially enriched ⁷Li associated with Ca amendments. This study open a new field for Li isotope investigations in hydro-systems and potential utility of Li isotopes as environmental tracers.

Keywords: peatland, groundwater, Li isotopes, Massif Central

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1 – Introduction

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

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

Lithium has two stable isotopes of mass 6 and 7, with natural abundances of 7.5% and 92.5% respectively. Lithium is a mobile element that tends preferentially to go into the fluid phase during water/rock interactions. The relative mass difference between the two isotopes is considerable at 17%, generating significant mass-dependant fractionation during geochemical processes. The range of variation in lithium-isotope compositions is more than 50‰ in geological materials (see Coplen et al., 2002; Tomascak, 2004 for data compilation). As Li is
a recently developed isotopic tracer, not all the processes that could induce and control isotopic fractionation are as yet well constrained. However, in the context of water/rock interactions, numerous studies (Huh et al., 1998, 2001; Pistiner et al., 2003; Kisakurek et al., 2004, 2005; Pogge von Strandmann et al., 2006; Millot et al., 2007, 2010a, 2010b) have clearly shown that isotopic fractionation supports the enrichment of the heavy isotope ($^7$Li) in solution, the light isotope ($^6$Li) being preferentially retained in secondary weathering minerals. Silicate rocks display Li isotope compositions ranging from –2 to +10‰ (Coplen et al., 2002; Teng et al. 2004), that of seawater is ~ +31‰ (Millot et al., 2004), river water has intermediate isotopic compositions (+6 to +23‰, Huh et al., 1998), and saline (thermo-mineral) water generally has isotopic compositions in the range of 0 to +15‰ (Millot and Négrel, 2007, Millot et al., 2010b) although Falkner et al. (1997) found Li isotopic compositions in the range of +17 to +35‰ in hot spring water from Lake Baikal.

Here, we present the first results of Li and its isotopes in all reservoirs of a peatland (groundwater, surface water, rainwater, wastewater, and solid peat samples) in order to evaluate the potential of Li isotopes as effective tracers of the connections between ground- and surface waters in a wetland. We also explore the role of groundwater in supplying surface-water output from a peatland, using Li isotopes as a new probe for such characterization.

2 - General setting

The Narces de la Sauvetat peatland is located in the French Massif Central, which is the main volcanic province in France (Brousse and Lefevre, 1990) and the largest magmatic province of the West-European Rift system (Michon and Merle, 2001). Alkali basaltic volcanism is widespread in the Massif Central, occurring as numerous small centres clustered into several fields (Fig. 1). The Narces de la Sauvetat peatland occupies a maar depression with lapilli tuff deposited on the flanks (Boivin and Gourgaud, 1978), one of the biggest maars in the Velay in
view of its 1.5-km diameter and 90-m depth (Fig. 1) (Cubizolle et al., 2007; Tourman, 2007).

A 37-m drill-hole on the edge of the peatland revealed 2 m of black peat with increasing clay content at depth. Below this lie sandy clay with peat debris from 2 to 3 m, sandy gravel with variable clay content, and basalt debris from scoria and lava from 3 to 6.4 m, and finally alternating sandy silt, sandy gravel and some clay layers from 6.4 to 37 m.

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

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

3 – Material and methods

3.1. Material
The site survey was carried out during one year, with a complete sampling of all selected points once a month (Fig. 1). The piezometer wells were pumped before sampling when approximately twice the well volume was removed before water sampling, the key parameter being the stability of electrical conductivity. Surface- and ground-water samples were collected in polyethylene bottles and separated into aliquots. Two of these were filtered through pre-cleaned 0.45 µm acetate filters using a pre-cleaned Nalgene filter apparatus; the filtrate of one of the aliquots was further separated into two additional aliquots (100 and 1000 ml). The latter was acidified with Suprapur HNO₃ (pH ~ 2) and stored in pre-cleaned polyethylene bottles for major-cation analysis and lithium-isotope and Li-content determinations.

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

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

In addition, several samples of fertilizers (carbonaceous additives and NPK), carbonate matrix (Mäerl) and agricultural additives (borax, Li-Cl, Li-OH) were collected and analysed for Li contents and Li isotopes (Table 2). Carbonaceous additives consist either of fine white powder or small grains (3-5 mm in size), while NPK consists only of small grains. The white
powder was directly dissolved in an HCl-HNO₃ mixture, but the small grains were first
crushed and then dissolved in HCL-HNO₃ at ambient temperature in the laboratory.

3.2. Methods

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

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

\[
\delta^{7}\text{Li} (\text{‰}) = \left( \frac{^{7}\text{Li} / ^{6}\text{Li}}{^{7}\text{Li} / ^{6}\text{Li}}_{\text{sample}} - 1 \right) \times 10^3
\]

The \(^{7}\text{Li} / ^{6}\text{Li}\) ratios were normalized to the L-SVEC standard solution (NIST SRM 8545)
following the standard-sample bracketing method. Typical in-run precision on the
determination of \(\delta^{7}\text{Li}\) is about 0.1-0.3‰ (2\(\sigma_{in}\), Millot et al., 2004; 2010a), but can be higher
(up to 1‰ for one analysis due to the low signal for this sample, Table 3). Chemical
separation of lithium from the matrix was achieved before mass analysis using 3 mL of
cationic resin (BioRad AG® 50W-X12, 200-400 mesh) and HCl acid media (0.2N) for 30 ng
of lithium. Blanks for the total chemical extraction were less than 20-30 pg of Li, which is
negligible since it represents a 10⁻³ blank/sample ratio. The accuracy and reproducibility of
the total method (purification procedure + mass analysis) were tested by repeated
measurement of a seawater sample (IRMM BCR-403) after separation of lithium from the
matrix, for which we obtained a mean value of \(\delta^{7}\text{Li} = +30.8\text{‰ ± 0.4 (2}\sigma, n = 15\) over the
duration of the analyses. This mean value is in good agreement with our long-term
measurement (\(\delta^{7}\text{Li} = +31.0\text{‰ ± 0.5, 2}\sigma, n=30, \text{Millot et al. 2004})).
The δ^7Li ratios and Li contents were measured on the solid peat samples and on the different fertilizers and additives, using standard acid-dissolution procedures and chemical separation of lithium from the matrix. For solid peat samples, a total digestion of the sample is necessary before separation of Li from the matrix. About 50 mg of crushed sample was dissolved in a closed beaker with an ultrapure mixture of three acids - 4 ml HF (23N), 1 ml HNO_3 (14N) and 0.1 ml HClO_4 (12N) - for 4 days at 100 °C. After evaporation of the acid mixture, 4 ml HCl acid (6N) was added for 4 days at 100 °C. Once this had evaporated, the residue of the acid dissolution was dissolved in 0.5 ml HCl (0.2N) and a sample aliquot (30ng of Li) was placed in a column containing cationic resin for Li separation. Blanks for the total digestion of the solid samples by acids (HF, HNO_3, HClO_4 and HCl) were less than 300 pg of Li. Considering a lithium concentration in the solid samples from 5 to 50 µg. g^-1 and the sample quantity taken for acid digestion (50 mg), it appears that the quantity of lithium ranges from 250 to 2500 ng. Consequently, the blanks account for only 0.01 to 0.1% of the sample, which is negligible.

The accuracy and the reproducibility of the procedure for solid samples (dissolution + purification procedure + mass analysis) were tested by repeated measurement of the JB-2 basalt standard (Geological Survey of Japan), giving a mean value of δ^7Li = +4.9‰ ± 0.6 (2σ, n=17) which is in good agreement with published values (see Carignan et al., 2007, and Tomascak, 2004, for data compilation). Consequently, based on long-term measurements of both seawater and JB-2 basalt standards, we estimate the external reproducibility of our method to be around ± 0.5‰ (2σ).

4 – Results and comments

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

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

Lithium-isotope compositions (\(\delta^{7}\text{Li}, \%\)) are extremely variable in the site (Table 3), ranging from +12‰ (R1, October 2007) up to +1226‰ (Q2, May 2007). The Li-isotope composition at the peat bog outlet R1 fluctuated slightly during the survey period (+12.0 to +13.1‰). Among the spring waters, S1 (+60.5‰) and S5 (+47.1‰) have a relatively high \(\delta^{7}\text{Li}\) while on the other hand, the S6 spring water has a slightly higher signature (+15.1‰) than that of the peat outlet (+12 to +13.1‰) and a lower signature than that of the rest of the spring waters. We suspect that the S6 spring may probably be connected to the surface water R1.

Wastewater (EU) has an enriched \(^{7}\text{Li}\) value (\(\delta^{7}\text{Li} = +80.9\%\)). In contrast to spring water and surface water, the groundwater in the peatland (Q1 and Q2) has singular \(\delta^{7}\text{Li}\) values, extremely enriched in \(^{7}\text{Li}\), ranging from +961 to +1111‰ for Q1 and from +1189 to +1236‰, for Q2. Such high isotopic values occurred for high Li contents during the survey, around
4.26 ± 1.96 µmol L⁻¹ (mean value and standard deviation) for Q1 and an even higher mean value in Q2 (17.69 ± 7.58 µmol L⁻¹).

The time variation of Li content from May 2007 to April 2008 is shown on Figure 2a. Both Q1 and -Q2 show a significant decrease in Li content, though, where for Q2 the decrease is continuous, for Q1 the Li contents showed an increase/steady-state/decrease pattern. Conversely, there is no evidence of time variation in the Li content of the R1 surface water.

Figure 2b illustrates the δ⁷Li variation during the same period and for the same sample set. Q2 varied little during the collection period with only 4% variation (between δ⁷Li = +1189 to +1236‰), but the δ⁷Li for Q1 had a larger range, with a 14% variation (between δ⁷Li = +961 to +1111‰). The time variation in the Li isotope of the R1 surface water is low with only 8% variation (between δ⁷Li = +12.0 to 13.1‰).

4.2. The peat

Six brown and black solid peat samples collected in the central part of the maar were analysed for Li content and Li isotopes (Table 1). Near piezometer Q1 (Fig. 1), the Li contents of the solid phase are low in the first two samples, at 0.8 µg. g⁻¹ at 0-0.6 m and 1.9 µg. g⁻¹ at 1 m depth, reaching 14.4 µg. g⁻¹ at 2 m depth. Near piezometer Q2, the Li contents are higher and range from 9.8 µg. g⁻¹ on surface up to 15.5 µg. g⁻¹ at 0.3 m depth, showing a slight decrease at 1 m depth to 12.1 µg. g⁻¹. Such Li contents in the peat are higher than those reported by Kamenov et al. (2009). The δ⁷Li values are close to -1.1‰ near piezometer Q1 and show lower values near piezometer Q2, in the range of -0.4 to +0.2‰.

4.3. Bedrock, rainwater and carbonaceous additives in fertilizers

The lava is nepheline-normative basanite with 5–6 wt% Na₂O + K₂O, to basalt (Villemant et al., 1981; Liotard et al., 1988). Recent Li-isotope data on volcanic rocks from the Massif Central (Hamelin, 2008; Hamelin et al., 2009) reveal values from high δ⁷Li in basalt (+7‰) to
lower values in more evolved lava, with a $\delta^7$Li around 0‰ in trachyte with Li contents in the range of 6-20 µg. g$^{-1}$.

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

Several additives used as fertilizers, such as carbonaceous additives or NPK, were analysed during this study (Table 2). Carbonate amendment mainly consists of crushed carbonate and carbonate-base (chalk or Mäerl), generally enriched in trace elements (mainly Zn and B). Soil deficiency, because of the unavailability or exhaustion of metal ions, is very often the cause of poor plant growth. In order to overcome these deficiencies, fertilizers with specific chemical constituents in specific amounts are commonly added to soil, thus enriching the growth medium. The fertilizers may be supplemented with certain trace elements, such as copper, iron, manganese, zinc, cobalt, molybdenum and boron (Chen et al., 2010). Salts used for B enrichment of carbonate amendments may also contain large amounts of Li. Many enriched B-fertilizers use boron minerals, e.g. borax (Na$_2$B$_4$O$_7$·10H$_2$O), octaborate (Na$_2$B$_8$O$_{13}$·4H$_2$O), or colemanite (CaB$_4$O$_7$·(OH)$_2$·H$_2$O)) that are expected to contain some trace elements such as lithium in the order of several tens to hundreds of µg. g$^{-1}$. However, there is no evidence as yet that lithium is essential for plants. Both stimulating and toxic effects of lithium have been noted in various crops (Bingham et al., 1964; McStay et al., 1980), and some investigators have found that lithium in sprays and nutrient solutions produced beneficial effects on certain plant diseases (Allender et al., 1997). For crushed carbonate, the Li content ranges from 0.71 to 2.16 µg. g$^{-1}$ (dry matter) and the $\delta^7$Li fluctuates between +2.10 and +10.5‰. These $\delta^7$Li values fully agree with the ranges given by Coplen et al. (2002) for
carbonates (0–12‰). For carbonate-base amendment, only one sample could be analysed whose Li content was 0.17 µg g⁻¹ (dry matter), the δ⁷Li being significantly higher in ⁷Li with a value high δ⁷Li of 215‰. In order to investigate this possibly enriched value for Ca-amendment, we first analysed a carbonate base, Mäerl, which is marine biological carbonate, and different additives (borax, Li-Cl, Li-B). The Mäerl sample has a marine signature of +31‰ and only one additive was found to have an extremely ⁷Li-rich signature (hydroxide ⁷Li monohydrate, δ⁷Li = +344000‰). Other additives, Li- and B-rich, have δ⁷Li values ranging between -16 and +8‰. With only five tested additives, these results confirm high isotopic values as those over +2000 for Li-B reagents given by Qi et al. (1997).

5 – Discussion

5.1. Origin of lithium in groundwaters

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

Li shows a wide range of contents when plotted versus Cl (Fig. 3), all samples plotting with Cl and Li contents clearly higher than those of rainwater, with the exception of the surface water and groundwater from the springs in the peatland that have Li contents similar to that of rainwater. Compared to rainwater, there is evidence of Cl input without Li input for these
samples, and it is very likely that this input may be related to fertilizers. For the groundwater
in the peat bog (Q1 and Q2), the R1 surface water and the S6 spring water, there is another
source of Li than rainwater without a large Cl input, as illustrated by the lack of a direct
relationship between Cl and Li contents.

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

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

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

The rainwater was analysed for Li near Clermont-Ferrand, a few kilometers distant from this peat maar (Millot et al., 2010c), its range for $\delta^7\text{Li}$ (+3 to +95‰) and Li content (0.004 – 0.029 µmol L$^{-1}$) shown in Figure 5. Its contribution to the dissolved Li may be coherent with some spring waters, even if the Cl content indicates a Cl-poor rain input (Fig. 3). The rainwater contribution is negligible for the peat-groundwater system and seems minor for the S6 spring water and the R1 surface water, agreeing with other surface waters collected in the Massif Central (Table 4).
The large increase in Li content and δ⁷Li in the peat groundwater can be *a priori* related to two main different mechanisms. The first could be related to fractionation processes by organic matter in the system, though biological uptake and vegetation recycling do not significantly affect Li isotopes in the soil. The non-influence of litter degradation on Li-isotope composition in soil is not surprising, as the Li concentration is a thousand times lower in vegetation than in soil. Lemarchand et al. (2010) discussed a fractionation process by organic matter that led to only a few tens ‰ of fractionation for Li isotopes. It is thus unlikely that the ⁷Li-rich values of groundwater could result from biological fractionation processes in the system.

The second mechanism could be linked to a source effect with lithium enriched in ⁷Li. Lithium-6 is valued as a source material for tritium production and as a neutron absorber in nuclear fusion. Natural lithium contains about 7.5 percent lithium-6 and large amounts of lithium have been isotopically fractionated for use in nuclear weapons and thermonuclear fuel stocks. Some of the material remaining from the production of lithium-6, which is depleted in lithium-6 and enriched in lithium-7, is made commercially available, and some has been released into the environment (Coplen et al., 2002). Depleted lithium-6 materials are commonly available and the most enriched δ⁷Li values reported by Qi et al. (1997) are +3013‰ for a Li-OH reagent and +2333‰ for a Li₂B₄O₇ salt. We therefore propose that this source effect may be related to the application of a carbonate amendment. This source is represented in Figure 5 by the end-member EM1. We assume this end-member to represent the required lithium content-Li isotope ratios to take all data into account (Nègrel et al., 2010). When consisting of crushed carbonate this may impact the Ca and HCO₃ budget of the groundwater as well as the pH, but also the Li budget as these amendments are artificially enriched in trace elements. Soils contain trace elements (e.g. metal ions) in addition to other macro- and micro-nutrients that are needed for plant growth.
Analysis of chemical reagents and additives (Qi et al., 1997; Table 2) can show enriched δ⁷Li values, but among the analysed fertilizers in this study only one carbonate amendment has a real enriched lithium value (δ⁷Li over +200‰), reflecting the addition of 7-enriched Li in the fertilizer manufacturing process, whose application may have an impact on the δ⁷Li signature of the groundwater.

First evidence of the impact of the carbonate amendment application is given by major ions. Reporting data using Li-normalized ratios (in order to avoid concentration effects in Fig. 6 for Ca/Li vs. HCO₃/Li) reveals trends between the peatland groundwater, the surface water and the spring water that can be considered as mixing lines. Mixing of two solutions (a, b) with different lithium-normalized ratios X/Li (X being Ca and HCO₃ in this case) will lead to a mixed solution (i.e. “mix”) that will have a X/Li ratio of:

\[ \frac{X}{Li_{mix}} = m \times \frac{X}{Li_a} + (1-m) \times \frac{X}{Li_b} \quad \text{(Eq. 1)} \]

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

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. All groundwater samples from the peatland fall within these mixing lines, but EM1 has little impact on the surface waters as the samples deviate little from the S6 spring water. The groundwater samples from the peatland clearly result from input of water from the spring on the hill slope (“springs” in Fig. 6) inducing a dilution, the EM1 values reflecting anthropogenic impact. However, the role of groundwater from the peatland on surface water is not obvious when looking at the X/Li ratios, and constraints on Li isotopes will help deciphering the functioning of the area.

To summarize, we explain the extremely enriched ⁷Li signature of the groundwaters in the peatland by an external input due to Ca-amendment used in local agriculture.
5.3. Groundwater circulation

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

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

$$
\delta^7\text{Li}_{\text{mix}} = \{(X/Li_a \times \delta^7\text{Li}_a \times m)/(X/Li_{\text{mix}})\} + \{(X/Li_b \times \delta^7\text{Li}_b \times (1- m))/X/Li_{\text{mix}}\} \tag{2}
$$

where $X/Li_a$, $X/Li_b$ and $X/Li_{\text{mix}}$ are the lithium normalized ratios for the solution mix from 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 $m$ is the mixing proportion.

In Figure 7, the $\delta^7\text{Li}$ versus Ca/Li ratios are plotted together with two mixing lines calculated between the $\delta^7\text{Li}$-enriched/Li-concentrated end-member (EM1) with a low Ca/Li ratio and S6, and the S1 and S5. It can be seen that the mixing line between EM1 and S6 could not be invoked for explaining the range observed for Li isotopes of the peat groundwaters, as they fall within the EM1-S1 and S5 mixing line. However, the surface waters are not included in any mixing line as there is only weak variation in both the Ca/Li ratio and $\delta^7\text{Li}$ values. This result agrees with the functioning of the peatland, with water input from the hill area.
represented by S1 and S5 in addition to the impact of the amendment application. This scheme induces dilution with a lower Ca/Li ratio and $\delta^7$Li values during spring and winter (Figs. 2, 4 and 5) in the peatland groundwater. There is no evidence of different pathways using Li-isotope mixing plots and the peat system seems to be well mixed with regards to the Li isotopes. In addition to showing mixing between EM1 and S1 and S5 waters, the mixing plots also show that surface water at the outlet seems to be only controlled by the input of groundwater like S6. The groundwater beneath the peatland has distinct ratios from that which discharges into the stream; this strongly suggests that groundwater in the peatland does not play any role in supplying surface-water runoff and may evolve as a stagnant system, being only diluted as the contents (particularly Li) show.

6 – Conclusions

The results are described for lithium-isotope compositions of spring-, surface- and groundwater samples collected in a peat bog located in the French Massif Central in a maar depression. Variations in $\delta^7$Li values can be used for distinguishing between precipitation, groundwater and anthropogenic inputs in peatlands, providing a unique perspective on the hydrologic dynamics of the system. The primary finding of this work concerns the existence of hugely enriched values for $\delta^7$Li in groundwater from the peatland. Mixing relationships indicate that most of the water in the peatland site derives from groundwater from the hill slope. Mixing plots also show that the surface water at the outlet seems to be only controlled by input from other groundwater bodies, and that groundwater in the peatland does not play any role in supplying the surface water runoff and may evolve as a stagnant system.

This study highlights the possible role of Li isotopes as tracers of the surface- and groundwater circulation in a wetland. When evaluating the transfer of water and/or solutes in a
wetland, such complementary tracers of basic hydrogeology are highly important for constraining the system.

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

Acknowledgements

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Millot, R., Guerrot, C., Petelet-Giraud, E., Négrel, Ph., 2010c. Multi-isotopic composition ($\delta^7$Li-$\delta^{11}$B-$\delta$D-$\delta^{18}$O) of rainwaters in France: origin and spatio-temporal characterization. Appl. Geochem, in revision.


Figure 1. Location of the Narces de la Sauvetat peatland in the Massif Central (France). Simplified topographic map of the peatland with location of boreholes, springs and surface water identified on the site.
Figure 2. Time evolution between May 2007 and April 2008 of the Li concentration (µmol. L⁻¹) and δ⁷Li in groundwater from the peatland (Q1 and Q2) and surface water (R1) of the Fouragettes stream, the outlet of the Narces de la Sauvetat peatland.
Figure 3. Li (µmol. L⁻¹) vs. Cl (µmol. L⁻¹) diagram 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. Rainwater field from the Massif Central is also indicated (Millot et al., 2010c, d, see text).
Figure 4. Li (µmol. L⁻¹) vs. Ca (µmol. L⁻¹) diagram for groundwater from the peatland (Q1 and Q2), spring waters 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. Arrow shows the evolution of Q2 groundwater in the peatland as a function of the season. Rainwater field from the Massif Central are also indicated (Millot et al., 2010c, d, see text).
Figure 5. Plot of $\delta^7\text{Li}$ vs. Li concentration ($\mu\text{mol. L}^{-1}$) 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. Rainwater, volcanic rocks and surface water from the Massif Central are also indicated (see text). The end-member EM1 corresponds to the carbonate amendment input. Its location on the graph is assumed to represent the required lithium content-Li isotope ratios to take all data into account.
Figure 6. Plot of HCO₃/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 HCO₃/Li 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).
Figure 7. Plot of $\delta^{7}$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).
Table 1. Results of Li concentration (µg. g⁻¹) and δ⁷Li in the peat samples collected at different depths (Z in m) in the Narces de la Sauvetat peatland.

<table>
<thead>
<tr>
<th>Sample</th>
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Table 2. Results of Li concentration (µg. g⁻¹) and δ⁷Li in various fertilizers and additives.

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<td>µg. g⁻¹</td>
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**Fertilizers**
- 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

**Additives**
- 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
- Li₂B₄O₇ Li-B: 19.97, 8.18
- Hydroxyde ⁷Li monohydrate Li: 138.47, 344000
### Table 3. Results of Cl, Ca, Na, Mg, HCO$_3$ and Li concentration (µmol L$^{-1}$) and $\delta^{7}$Li in 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.

<table>
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<th>Ca  µmol.L$^{-1}$</th>
<th>Na  µmol.L$^{-1}$</th>
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Table 4. Results of Li concentration (µmol L⁻¹) and δ⁷Li in several surface-water samples from the Massif Central.