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► **To cite this version:**

Romain Millot, Philippe Négrel. Lithium isotopes in the Loire River Basin (France): hydrogeochemical characterizations at two complementary scales. *Applied Geochemistry*, 2021, 125 (104831), 10.1016/j.apgeochem.2020.104831 . hal-03113284

HAL Id: hal-03113284

<https://brgm.hal.science/hal-03113284>

Submitted on 18 Jan 2021

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Lithium isotopes in the Loire River Basin (France):

hydrogeochemical characterizations at two complementary scales

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Abstract

We illustrate two different, but complementary, applications of lithium (Li) isotope tracers for river-basin characterization at two different scales within the Loire River basin (LRB) in France. The first example deals with the behaviour of Li and the fractionation of its isotopes during river weathering at the basin scale of the LRB (117,800 km²). The wide $\delta^7\text{Li}$ range (+5.0 to +13.3‰) in Loire basin streams, spatialized between the headwaters and the lowlands, is consistent with distinct weathering conditions and the distribution of Li from bedrock in the basin between the rivers and secondary mineral phases during water/rock interaction. Additionally, suspended sediments in the LRB streams are significantly ⁶Li enriched ($\delta^7\text{Li}$ from -8.7 to -7.6‰) compared to average river waters that range from +5.0 to +13.3‰. The second example focuses on the smaller scale Egoutier watershed (13 km²), part of the LRB, which shows that Li isotopes can be useful for distinguishing between natural input and anthropogenic pollution, like effluents from a water treatment plant connected to a hospital. Overall, we confirm that Li isotopes cannot be used as lithological tracers for river waters. However, we did find that Li isotopes can be good tracers of weathering conditions and of anthropogenic sources in an urbanized watershed.

Keywords: lithium isotopes, river water, sediment, Loire River Basin, wastewater, anthropogenic input, natural spring

4872 words (without references or captions)

1- INTRODUCTION

27

28 In the Earth Sciences, the field of stable-isotope geochemistry of metals has greatly expanded over
29 the past 20 years ([Johnson et al., 2004](#); [Teng et al., 2017](#)), which is mainly due to the recent
30 introduction of a new generation of Multi Collector Inductively Coupled Plasma Mass Spectrometers
31 (MC-ICP-MS) with enhanced sensitivity and better precision. These instrumental innovations have
32 opened new fields of research in metal-isotopes geochemistry ([Albarède et al., 2004](#); [Wiederhold,](#)
33 [2015](#)).

34 Among the stable-isotope systematics of metals studied so far, the geochemistry of lithium
35 (Li) has an excellent potential as a tracer of water/rock interactions within low- and high-
36 temperature systems ([Tomascak 2004](#); [Burton and Vigier 2011](#); [Tomascak et al., 2016](#); [Penniston-](#)
37 [Dorland et al., 2017](#)), whether in the field of surface waters ([Huh et al., 1998](#); [2001](#); [Vigier et al.,](#)
38 [2009](#); [Wimpenny et al., 2010](#); [Millot et al., 2010a](#); [Dellinger et al., 2014](#); [2015](#)), groundwaters ([Hogan](#)
39 [and Blum 2003](#); [Négrelet et al., 2010](#); [2012](#); [Meredith et al., 2013](#); [Pogge von Strandmann et al., 2014](#);
40 [Bagard et al., 2015](#)), geothermal waters ([Millot and Négrelet, 2007](#); [Millot et al., 2007](#); [Millot et al.,](#)
41 [2010b](#); [Millot et al., 2011](#); [2012](#); [Bernal et al., 2014](#)), rainwaters ([Millot et al., 2010c](#)) or Li-rich brines
42 ([Godfrey et al., 2013](#); [Araoka et al., 2014](#)).

43 Li isotopes are good tracers in geochemistry due to their involvement in water/rock
44 interactions at the Earth's surface. More precisely, Li and its isotopes can provide key information on
45 continental silicate weathering, which is the primary natural drawdown process of atmospheric CO₂
46 and a major control on climate ([Pogge von Strandmann et al., 2020](#)). Li isotopes help our
47 understanding of weathering via globally important processes, such as clay formation and cation
48 retention. Both these processes occur as part of weathering in surface environments, including
49 rivers, soil pore waters, and groundwater, but Li isotopes can also be used for tracking weathering
50 changes across major climate-change events ([Misra and Froelich, 2012](#)).

51 Furthermore, Li has a strategic importance for numerous industrial applications, including the
52 production of Li-ion batteries for mobile devices and electric vehicles ([World Economic Forum](#)

53 [Report, 2019](#)), or in pharmaceuticals used in the treatment of some mental diseases ([Aral and](#)
54 [Vecchio-Sadus 2008; 2011](#)).

55 Assessing the behaviour of Li and its isotopes during chemical weathering is important for a
56 better definition of water/rock interactions at the Earth's surface and also for refining our
57 understanding of the global Li cycle. Lithium (${}^6\text{Li} \sim 7.5\%$ and ${}^7\text{Li} \sim 92.5\%$) is a fluid, mobile metallic
58 element and, due to the large relative mass difference between its two stable isotopes, it is subject
59 to significant low-temperature mass fractionation that provides key information on weathering
60 processes.

61 Additionally, the contribution of human activities (industry, agriculture, and domestic inputs)
62 becomes increasingly significant in the chemical composition of dissolved river load ([Aral and](#)
63 [Vecchio-Sadus 2008; 2011](#)) as well as in that of soil ([Négrel et al., 2019](#)). Human factors thus act as an
64 additional key process and, therefore, a mass-balance for the budget of catchments and river basins
65 must also consider anthropogenic disturbance of Li ([Choi et al., 2019](#); [Négrel et al., 2020](#)).

66 To date, both the magnitude of Li-isotopic fractionation associated with water/rock
67 interaction processes, and the factors controlling such fractionation, are not totally understood.
68 However, both field- and experimental studies have shown that ${}^6\text{Li}$ is preferentially retained by
69 secondary minerals during silicate weathering ([Pistiner and Henderson 2003](#), [Kisakürek et al. 2004](#),
70 [Pogge von Strandmann et al. 2006](#), [Vigier et al. 2009](#)). Accordingly, the fractionation of Li isotopes
71 depends upon the extent of chemical weathering: strong fractionation seems to occur during
72 incipient and early weathering stages, while little fractionation is observed during more intense or
73 prolonged weathering in a stable environment, such as a low plain with long residence times; [Huh et](#)
74 [al. 1998, 2001](#), [Pogge von Strandmann et al. 2006](#), [Millot et al., 2010a](#)).

75 Li-isotope fractionation has been documented in numerous natural environments with
76 experimental and natural data ([Tomascak 2004](#), [Burton and Vigier 2011](#); [Tomascak et al., 2016](#);
77 [Penniston-Dorland et al., 2017](#); [Pogge von Strandmann et al., 2020](#)). It was shown that partial
78 dissolution of basalt does not result in Li-isotope fractionation, but that granite dissolution can cause

79 such fractionation (Pistiner and Henderson 2003; Négrel and Millot, 2019). In addition, adsorption
80 onto mineral surfaces can be another major mechanism of Li-isotopic fractionation in the
81 hydrosphere (Wenshuai and Liu, 2020; Andrews et al., 2020). Moreover, Li is not a nutrient and does
82 not participate in biologically mediated reactions, so no evidence of biological Li-isotope
83 fractionation has been observed to date (Rudnick et al., 2004; Marriott et al., 2004).

84 Here, we illustrate two applications at complementary scales of Li isotopes used for river-
85 basin hydrogeochemical surveys. The first example deals with the behaviour of Li and its isotopes at
86 the Loire basin (LRB) scale (117,800 km², France) for river water and sediment transported during
87 river flow. The second example focuses on a smaller scale: the Egoutier watershed (13 km²), part of
88 the LRB. The main objective of our work was to evaluate Li isotopes as 1) tracers of weathering
89 conditions over a large river basin, and 2) tracers of anthropogenic input at the scale of a small
90 watershed.

91 2- ANALYTICAL METHODS

92 2.1. Sampling methods and element concentration measurements

93 In the LRB (Table 1), river waters were sampled twice, first during low flow and then during high flow
94 (August/September 2012 and April 2013, respectively). Suspended sediments in the Loire at
95 Montjean (the farthest downstream sampling station of this study, 955 km from the Loire spring)
96 were sampled monthly between July 2012 and June 2013. For the Egoutier watershed, we collected
97 river water in April 2015), corresponding to the high-flow stage of the watershed.

98 In the field, 5 litres of river water were collected in acid-washed containers for major- and
99 trace-element and isotopic measurements (for details of the protocol see Millot et al., 2003).
100 Samples were filtered in the field, using a Sartorius frontal filtration unit (0.2 µm cellulose acetate
101 filter, 142 mm diameter). After filtration, samples were stored in acid-washed polypropylene bottles.
102 The river sediments were collected after drying and centrifugation of the river-water filtration
103 retentate. The samples for Li-concentration and Li-isotope analyses were acidified to pH=2 with
104 ultrapure HNO₃. Lithium concentrations in river-water and suspended-sediment samples were

105 determined by Quadrupole ICP-MS (Thermo X Series II) with indium as an internal standard, with a
106 precision of $\pm 5\%$.

107 **2.2 Lithium isotope measurements**

108 Lithium-isotopic compositions were measured using a Neptune⁺ Multi-Collector ICP-MS at the BRGM
109 (French Geological Survey; [Millot et al., 2004](#)). $^7\text{Li}/^6\text{Li}$ ratios were normalized to the L-SVEC standard
110 solution (NIST SRM 8545, [Flesch et al., 1973](#)) following the standard-sample bracketing method.
111 Typical in-run precision on the determination of $\delta^7\text{Li}$ was about 0.1-0.2‰ ($2\sigma_m$, standard error of the
112 mean). Chemical separation of Li from the matrix before isotope analyses was done with a cationic
113 exchange resin (a single column filled with 3 mL of BioRad AG[®] 50W-X12 resin, 200-400 mesh) and
114 HCl acid (0.2N) rendering 30 ng Li. Blanks for the total chemical extraction were <30 pg Li, which is
115 negligible as this represents a blank/sample ratio of $<10^{-3}$.

116 Successful quantitative measurement of Li-isotopic compositions requires 100% Li recovery
117 during laboratory processing. Therefore, frequent column calibrations were performed and repeated
118 analysis of an L-SVEC standard processed through the columns showed that no isotope fractionation
119 occurred as a result of the purification process.

120 The accuracy and reproducibility of the entire method (purification procedure + mass
121 analysis) were also tested by repeated measurement of a seawater standard solution (IRMM BCR-
122 403) after separation of Li from the matrix, giving a mean value of $\delta^7\text{Li} +30.8 \pm 0.4\%$ (2σ , $n=15$) over
123 the duration of the analyses. This mean value agrees with our long-term measurements ($\delta^7\text{Li} +31.0$
124 $\pm 0.5\%$, 2σ , $n=30$, [Millot et al., 2004](#)) and with other values reported in the literature (see for
125 example [Carignan et al., 2004](#) and [Tomascak 2004](#) for a data compilation).

126 For suspended sediments, a total digestion of 50 mg of crushed sample took place over
127 4 days at 100 °C in a closed beaker with a mixture of three ultrapure acids: 4 mL HF (23N), 1 mL HNO₃
128 (14N) and 0.1 mL HClO₄ (12N). The solution obtained was evaporated to dryness and 4 mL HCl (6N)
129 was added and left for a further 4 days at 100 °C. Sample aliquots (30 ng Li) of the residue of the acid
130 dissolution were then dissolved in 0.5 mL HCl (0.2N), before being placed in cation exchange columns

131 for Li separation. Accuracy and reproducibility of the entire procedure for solid samples (dissolution +
132 purification + mass analysis) were tested by repeated measurements of the JB-2 basalt standard
133 (Geological Survey of Japan), which gave a mean value of $\delta^7\text{Li} = +4.9\text{‰} \pm 0.6\text{‰}$ (2σ , $n=17$), in good
134 agreement with published values (see [Jeffcoate et al. 2004](#), [Tomascak 2004](#) and [Carignan et al. 2007](#)
135 for data compilation).

136 3- FIELD SITE DESCRIPTION

137 3.1 The Loire River Basin

138 We undertook a systematic study of the weathering products (both dissolved load and suspended
139 sediments) of the LRB, one of the major river basins in Europe. This area is of particular interest as it
140 has been extensively studied and is scientifically well characterized ([Négrel and Grosbois 1999](#);
141 [Grosbois et al., 2001](#)).

142 The Loire River in central France ([Fig. 1](#)) is approximately 1010 km long and drains an area of
143 117,800 km². Initially, the Loire flows north to northwest, originating in the Massif Central and
144 continuing up to the city of Orléans, about 650 km from the source. Beyond Orléans, the river turns
145 west to WSW, being one of the main European riverine inputs into the Atlantic Ocean. In the upper
146 basin, the bedrock is Palaeozoic plutonic rock overlain by sub-Recent volcanic rocks. The
147 intermediate basin includes three major tributaries flowing into the Loire from the left bank: the
148 Cher, the Indre and the Vienne rivers. Here, the Loire drains sedimentary rocks of the Paris Basin,
149 mainly carbonate deposits. The lower Loire basin drains Palaeozoic basement rocks of the Armorican
150 Massif and its overlying Mesozoic to Cenozoic sedimentary deposits.

151 Its spring is located at an altitude of 1,404 m (Mont Gerbier de Jonc) and its course is
152 classically divided into three parts from upstream to downstream: (i) the Upper Loire, (ii) the Loire
153 Valley, and (iii) the Lower-Loire, to the estuary. River discharge of the Loire is very irregular: in the
154 Lower Loire it can exceed 7000 m³/s, but at Orléans it is around 350 m³/s and during summer the
155 river can literally dry up, with flows less than 25 m³/s.

156 BRGM's expert knowledge of the LRB is recognized by the numerous, particularly isotopic,
157 studies, that have been carried out over the past decades (Négrel, 1997; Négrel and Grosbois, 1999;
158 Négrel et al., 2000; Négrel and Petelet-Giraud, 2012; Petelet-Giraud et al., 2018). The Loire has been
159 regularly monitored at Orléans and Tours over several hydrological cycles (Grosbois et al., 2000;
160 2001). Its physico-chemical parameters, major- and trace elements, and strontium-isotope ratios
161 were determined on the dissolved fraction over time spans ranging from two days to one week,
162 depending on river flow.

163 The relationships between chemical elements and flow as well as between isotopic ratios and
164 flow have shown that the dissolved fraction of the Loire results from a mixture between rainfall
165 input, input from the weathering of silicate- and carbonate bedrocks, and anthropogenic input of
166 agricultural and urban origin. Total dissolved-solids flow during a hydrological cycle is estimated at
167 1300×10^3 t/year at Orléans and 1620×10^3 t/year at Tours (Grosbois et al., 2001). For the river
168 sediments, work by Négrel and Grosbois (1999) on $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios suggests the existence of
169 at least two reservoirs of suspended matter transported by the river. One is related to the detrital
170 fraction from silicate erosion, the other to carbonate erosion. The stable isotopes of carbon and
171 oxygen in the fraction extracted by acid leaching from Loire sediments during periods of low water
172 flow (Négrel et al., 2000), confirm the formation of antigenic calcites in isotopic equilibrium with
173 Loire water (Fontes et al., 1973; Dever et al., 1983).

174 **3.2 The Egoutier watershed**

175 We also investigated anthropogenic Li tracing of wastewater release, using Li isotopes in the small
176 Egoutier catchment near Orléans (13 km², Fig. 2; in French, 'Egout' means 'Sewer', Desaulty and
177 Millot 2017).

178 Located in the Paris Basin on the Beauce plateau just east of Orléans, the Egoutier is a small
179 stream with its spring near the village of Chanteau and a length of 5 km before being channelled and
180 flowing into the Loire at Saint-Jean-de-Braye. For this study, we worked in a small built-up area

181 between its spring in the forest and a point just downstream of the departmental road D2060
182 (Fig. 2).

183 The study area integrates two main potential sources of metals due to human activities: The
184 first one is a psychiatric hospital with about 300 beds and many outpatients. The hospital also houses
185 an active laundry. About a ton of linen from different community sources (fire brigade, schools, etc.)
186 is washed and ironed every day. The second one is an industrial area including a slaughterhouse,
187 factories for processing animal products, and the oil depot of Saint-Jean-de-Braye that supplies fuel
188 oil to the Centre-Val-de-Loire region. This second area is drained by a stream that flows into the
189 Egoutier.

190 4- RESULTS

191 4.1 The Loire River basin

192 In the LRB (Table 1), natural Li concentrations in river water are between 2.0 and 46.5 µg/L whereas
193 $\delta^7\text{Li}$ -isotopic compositions range from +5.0 to +13.3‰. In more detail, there are slight differences
194 depending upon whether the rivers were sampled during low- or high-flow stages.

195 During low flow, Li concentrations are higher (3.4 to 46.5 µg/L; mean 15.9 µg/L n=20, Table 1) than
196 during high flow (Li concentrations from 2.0 to 30.0 µg/L with a mean of 7.4 µg/L, n=20, Table 1). In
197 parallel, the Li-isotopic compositions are little different for low- and high-flow samples, with $\delta^7\text{Li}$
198 values ranging from +5.0 to +13.3‰ and +5.2 to +11.7‰ respectively. These concentrations are
199 higher than the worldwide riverine average of 1.9 µg/L (Huh et al., 1998; Gaillardet et al., 2014). In
200 addition, Loire basin rivers have lower isotopic compositions than the average $\delta^7\text{Li}$ value for modern
201 river water of about +23‰ (Huh et al., 1998; Misra and Froelich, 2012). Finally, $\delta^7\text{Li}$ values for the
202 Loire basin rivers agree with previous data reported by Rivé et al. (2013) for the upstream Loire ($\delta^7\text{Li}$
203 from 4.0 to 24.0‰). Loire river suspended sediments collected monthly at Montjean/Loire (Table 2)
204 from July 2012 to June 2013 have Li concentrations between 41.3 and 73.0 µg/g (mean 60.2 µg/g,
205 n=7), significantly higher than those of the average Upper Continental Crust (UCC) at Li 35 ± 11 µg/g
206 (2σ , Teng et al., 2004). In addition, these sediments have low $\delta^7\text{Li}$ with strongly negative values

207 ranging from -8.7 to -7.6‰ (mean 8.2‰, n=7) when compared to the UCC value of 0‰ ±2 (Teng et
208 al., 2004).

209 **4.2 The Egoutier watershed**

210 Lithium concentrations in the Egoutier watershed cover a narrow range from 5.3 to 12.7 µg/L (mean
211 7.3 µg/L, n=9, Table 3), whereas the isotopic compositions of Li are comprised between -3.1 and
212 +4.2‰ (mean +0.5‰, n=10, Table 3). The Li concentrations and the $\delta^7\text{Li}$ values in the Egoutier
213 watershed are very different from the ones observed at the larger scale of the LRB.

214 **5- DISCUSSION**

215 **5.1 The Loire River basin: controlling parameters for the distribution of Li and its isotopes**

216 Overall, Li concentrations in Loire River mainstream waters span a wide range from 2.0 to 22.5 µg/L,
217 whereas $\delta^7\text{Li}$ values are between +5.9 and +13.2‰ (Table 1). Figures 3a and 3b show a clear contrast
218 for the main course of the Loire River between headwaters and lowlands. This contrast shows a
219 significant increase in Li concentrations from upstream to downstream (Fig. 3a). This feature is also
220 associated with a strong decrease in the $\delta^7\text{Li}$ values as a function of distance from the spring. These
221 variations for Li concentration and $\delta^7\text{Li}$ are observed for both high and low flow stages.

222 In addition, when all $\delta^7\text{Li}$ values are plotted for both the Loire and its major tributaries (Cher,
223 Indre, Vienne, Maine, Furan, Arroux and Allier rivers, Fig. 1) in a $\delta^7\text{Li}$ vs. Na/Li diagram (Fig. 4), the
224 data plot in a triangle formed by three endmembers. The first (Na/Li ~8000 and $\delta^7\text{Li}$ ~+12‰) is the
225 upstream Loire at Villerest; the second endmember is close to the Allier river (Na/Li ~500 and $\delta^7\text{Li}$
226 ~+5‰); and the third could be represented by rainwater. This agrees with the conceptual scheme of
227 the Loire hydrosystem based on $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data, suggesting that the Loire River is related to a
228 Massif Central surface-water supply for the main Loire and Allier streams, and to water/groundwater
229 interactions in the alluvial plains (Négrel et al., 2003).

230 For the second endmember, the Allier constitutes a major tributary of the Loire that mostly
231 drains the French Massif Central. As a result, its chemical (Na/Li) and isotopic signatures are
232 influenced by input from thermo-mineralized waters resulting from hydrothermal activity, as

233 demonstrated by [Négrel et al. \(1997\)](#). These thermal springs are well described for the whole Massif
234 Central area and have low $\delta^7\text{Li}$ values ([Fig. 4](#), [Millot et al., 2007](#)). The third endmember,
235 corresponding to rainwater input, is in a good agreement with our long-term monitoring values of
236 rainwater at Orléans and also near Clermont-Ferrand within the Massif Central, corresponding to the
237 continental signature of rainwaters in France ([Millot et al., 2010c](#)).

238 It is well known that rainfall on watersheds can supply an important fraction of dissolved
239 elements in river water ([Meybeck, 1983](#)). Atmospheric correction requires knowledge of the
240 chemical composition of rainwater (*op. cit.*; [Négrel et al., 1993](#)). The correction of atmospheric
241 contribution to water, for a given element Z, is estimated by reference to the Cl concentration, called
242 Cl_{ref} , multiplied by the Z/Cl ratio of rainwater. For the LRB and according to [Grosbois et al. \(2000\)](#), we
243 considered the Cl_{ref} at 2.62 $\mu\text{g/L}$ (74 $\mu\text{mol/L}$). We applied the atmospheric correction to Na, Li and
244 $\delta^7\text{Li}$ values, as earlier done for other studies on Li isotopes ([Dellinger et al., 2015](#); [Négrel and Millot,](#)
245 [2019](#); [Négrel et al., 2020](#)). Here, we used the characterization of rainwater defined by [Négrel and Roy](#)
246 [\(1998\)](#), [Négrel et al. \(2007\)](#) and [Millot et al. \(2010c\)](#), who reported major ions, but also Li
247 concentrations and isotopes ([Millot et al., 2010c](#)). The different rainfall stations in France range from
248 near-ocean locations (Brest, Dax) to more continental ones (Orléans). The latter has the lowest Li
249 concentrations (0.37 $\mu\text{g/L}$) and $\delta^7\text{Li}$ values (+16.1‰). In view of its continental character, this station
250 is certainly the one that can best match the rain input over the LRB. [Table 1](#) shows that Li in waters
251 from atmospheric origin ranges from 1.2 to 16.8% and from 1.9 to 28.2%, respectively for low- and
252 high-flow stages.

253 Once atmospheric correction was applied to lithium and its isotopes ([Table 1](#); [Fig. 5](#)), the Li-
254 isotopic compositions of the Loire River were spatialized along the main course. [Figure 5](#) shows $\delta^7\text{Li}$
255 values plotted against Li concentrations: we see two parallel lines, one for high flow stages and the
256 second for low flow ones. The two lines are not interpreted as a mixing scheme for which the trends
257 may not be linear in such a representation. Nor could this feature be interpreted as a result of a
258 lithological contrast between the upstream and downstream Loire River (plutonic/volcanic rocks vs.

259 sedimentary deposits), in agreement with the results of [Kısakürek et al. \(2005\)](#), [Vigier et al \(2009\)](#) and
260 [Millot et al. \(2010a\)](#) that showed that Li isotopes cannot be used as lithological tracers in river basins.

261 This general picture might thus be better explained in terms of water/rock interaction: in the
262 upstream environments of the Loire basin, short water-residence times and rock weathering may
263 enhance processes that fractionate Li isotopes, such as adsorption and/or secondary-mineral-phase
264 formation, producing high $\delta^7\text{Li}$ in rivers ([Négrell and Millot, 2019](#)). By contrast, in the lowlands of the
265 Loire basin, longer water-residence time could enhance Li dissolution, with lower isotopic
266 fractionation (low $\delta^7\text{Li}$) approaching that of continental bedrock. Such a Li-isotope distribution has
267 already been reported for other large river basins, worldwide ([Lemarchand et al., 2010](#); [Millot et al.,](#)
268 [2010b](#); [Liu et al., 2013](#); [2015](#); [Dellinger et al., 2014](#); [2015](#); [Wang et al., 2015](#)).

269 More specifically, the Li-isotopic composition measured in the Loire basin rivers shows that
270 the dissolved load is significantly enriched in ^7Li when compared to suspended river load. Lithium
271 concentrations in suspended Loire sediment at Montjean ([Table 2](#)) contain 41 to 73 $\mu\text{g/g}$ and are
272 clearly ^6Li enriched; $\delta^7\text{Li}$ values being negative (-8.7 to -7.6‰), compared to dissolved loads (+5.0 and
273 +13.0‰). This result agrees with the fact that ^6Li is preferentially incorporated into suspended
274 sediment during weathering as also observed for other river basins worldwide ([Huh et al. 1998, 2001,](#)
275 [Pogge von Strandmann et al. 2006, Millot et al., 2010b](#)).

276 Finally, the relationship between $\delta^7\text{Li}$ and Al/Li in the suspended sediment ([Fig. 6](#)) could also
277 raise the question of the control by different mineral phases (clay minerals vs. oxy-hydroxide of Fe or
278 Mn, or carbonates) during Li-isotopic fractionation between water and solids. The variation of the
279 Al/Li ratio could reflect a compositional variation of clay minerals in suspended sediments. It is also
280 likely that the suspended sediments consist of both fine (clay rich) and coarse (carbonate rich)
281 factions.

282 Unfortunately, we do not dispose over specific mineral-characterization data on our samples
283 for further discussion of this point, but it is interesting to observe an inverse correlation between the
284 Li-isotope signatures of suspended sediments and the river discharge ([Fig. 7](#)). This trend could

285 possibly suggest at least two different sources for suspended sediments, one during high flow and
286 the other during low flow, agreeing with the results from Sr-isotopic ratios of the Loire sediments
287 (Négrel et al., 2000; Négrel and Roy, 2002).

288 A final point that might explain such a relationship could be that the $\delta^7\text{Li}$ content in solids
289 may reflect weathering intensity (i.e., soil formation/transformation, coarse/fine material), as argued
290 by Dellinger et al. (2014; 2015). Consequently, different pools of river sediments are likely to be
291 transported as a function of the river regime.

292 **5.2 Anthropogenic origin of Li in the Egoutier watershed**

293 Human activities such as industry, agriculture and domestic inputs, generally increase the quantity
294 and modify the quality of chemical compounds in the dissolved and suspended load of rivers (Viers et
295 al., 2009; Royer, 2016; Vanwallegem et al., 2017). Human factors can also act as another key
296 process for Li in rivers (Choi et al., 2019; Négrel et al., 2020). Therefore, the mass-balance for the
297 budget of catchments and river basins should include anthropogenic disturbance.

298 Here, we investigate the effect of wastewater release by tracing its impact through using Li
299 isotopes in the small Egoutier watershed (13 km², 5 km long). As a case study, we studied this small
300 watershed with a low housing density in the LRB (Ledieu et al., 2020). Its spring is located in a pristine
301 forested area, but some kilometres downstream it is affected by metal-rich effluents from a hospital
302 water-treatment plant as well as by input from an industrial area (Fig. 2, Desaulty and Millot, 2017).

303 Within the course of the Egoutier, we clearly see the impact of both human activities. When
304 Li concentrations are plotted as a function of distance from the spring (Fig. 8a), we see two different
305 inputs: one from the waste water treatment plant (WWTP) related to the psychiatric hospital and the
306 second from the stream draining the industrial area.

307 Whereas the natural background for Li in river waters is 5 to 6 $\mu\text{g/L}$, the values for the
308 Hospital WWTP release and the industrial area are 12.7 $\mu\text{g/L}$ and 9.4 $\mu\text{g/L}$, respectively. In addition,
309 Li-isotopic compositions are rather homogeneous in water of the Egoutier watershed, with $\delta^7\text{Li}$
310 values of around $+0.5\text{‰}\pm 1.2$ along the main course of the stream ($n=7$, grey arrow on Fig. 8b), but

311 the signatures of the hospital and industrial area releases are very different. The WWTP water has a
312 positive $\delta^7\text{Li}$ value of +4.2‰, whereas the stream draining the industrial area has a negative value at -
313 3.1‰. The two anthropogenic signatures are quite different for Li isotopes. As mentioned before, the
314 hospital is a psychiatric one and it is likely that the Li released by the WWTP mainly comes from
315 pharmaceutical products, such as Li carbonate used for bipolar disease treatment ([Machado-Vieira et](#)
316 [al., 2009](#)). The nearby industrial area is mostly impacted by effluents from a slaughterhouse and
317 animal-processing operations ([Desauty and Millot, 2017](#)).

318 These observations in the Egoutier watershed completely agree with recent work by [Choi et](#)
319 [al. \(2019\)](#), who investigated the impact of anthropogenic input on lithium content in river- and tap
320 waters within the metropolitan area of Seoul, South Korea. They showed that Li-enriched
321 wastewater can affect tap waters. They also report Li-isotopic signatures of both therapeutic drugs
322 (Li carbonate) and detergents that are compatible with our findings for the wastewater treatment
323 plant releases in the Egoutier, which combine waste from the laundry and the psychiatric hospital.

324 This example of the Egoutier watershed shows how Li isotopes can distinguish between
325 natural and anthropic origins at the scale of a small watershed. This ability was recently evoked for
326 Seoul (South Korea; [Choi et al. 2019](#)) as well as for the Dommel catchment (Belgium and
327 Netherlands; [Négrel et al., 2020](#)). In both cases, lithium and its isotopes are effective tracers of
328 wastewater releases in populated areas, as well as of industrial discharge (smelter effluents) into a
329 river, respectively.

330 Further investigations are now needed to more precisely determine the Li-isotopic
331 compositions of pharmaceutical formulations, but also the role of wastewater treatment processes
332 in the distribution of metals between liquid and solid phases within a treatment plant. The latter
333 point is particularly relevant, as [Choi and al. \(2019\)](#) showed that there is no significant difference
334 between influent and effluent waters for both Li concentrations and Li isotope compositions, thus
335 making this tracer a perfect conservative tool for tracing Li pollution in the environment.

336 This study can be considered as pioneering, since Li is found naturally in drinking water (Eyre-
337 Watt et al., 2020; Ewuzie et al., 2020) with various origins. In clinical practice, it is widely used in the
338 treatment of bipolar and of mood disorders. And, very importantly because of the increasing
339 production of lithium-ion batteries worldwide (Naish et al., 2008; Conolly 2010; Christmann et al.,
340 2015), Li pollution in surface- and groundwaters could become a major issue in coming years, as
341 recently suggested by Choi et al. (2019).

342 6- CONCLUDING REMARKS AND FUTURE DIRECTIONS

343 A large variability of Li-isotopic ratios exists within the Loire river basin (LRB) and $\delta^7\text{Li}$ is strongly
344 spatialized between the Loire headwaters and lowlands. In addition, the Allier river, a major tributary
345 in the French Massif Central, is clearly influenced by the contribution of thermo-mineral springs with
346 lower $\delta^7\text{Li}$. Suspended river sediments are ^6Li enriched ($\delta^7\text{Li}$ from -8.7 to -7.6‰) compared to river
347 waters (+5.0 to +13.3‰), agreeing with the fact that ^6Li is preferentially incorporated in suspended
348 sediments.

349 Overall, although the weathering mechanisms operating in the LRB must be defined in much
350 more detail, our work confirms that Li isotopes cannot be used as lithological tracers for river waters.
351 However, we also show that Li isotopes are good tracers of river weathering conditions, with an
352 innovative application for tracing anthropogenic Li sources in a small, urbanized watershed. Further
353 work is now required for better characterizing the chemical and isotopic signals of pharmaceutical
354 formulations containing Li as well as those of Li-ion batteries. More specifically, leaks from landfills
355 containing electronic products must be investigated for determining whether curative work is
356 needed to stop the spread of pollutants. To conclude, lithium and $\delta^7\text{Li}$ are good proxies for studying
357 weathering and anthropogenic activities.

358

359 **Acknowledgements:**

360 This work was supported by the Research Program ISOP2 (Origin and mobility of metals in water and
361 sediment of the Loire River Basin), cofounded by BRGM and the AELB Water Agency (Agence de l'Eau

362 Loire Bretagne). Special thanks are due to S. Perret for his help in sample preparation in the clean
363 laboratory and in the field. We acknowledge our fruitful discussions with A.M. Desaulty, X. Bourrain
364 and E. Petelet-Giraud. The BRGM Water, Environment, Process Development and Analysis Division is
365 acknowledged for funding. This study was part of the Service National d'Observation Environnements
366 Urbains: OBSERVIL (French Urban Observatory), accredited by the INSU/CNRS and on site certified by
367 the Zone Atelier Loire: OBSCURE [OBServatoire des Sédiments et de la Cascade sédimentaire en
368 milieu URbain : cas de l'Egoutier à Semoy (Loiret)] managed by A. Simonneau. We thank three
369 anonymous reviewers and the Associate Editor for their constructive comments and remarks.
370 H.M. Kluijver edited the final English version of the MS for language and content.
371 RM is particularly grateful to T.D. (Tom) Bullen for helping him in the first stages of Li-isotope
372 investigations at BRGM, more than 17 years ago; this work is dedicated to his memory.
373
374

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601 **Figure and Table Captions**

602 **Figure 1:** Map showing the Loire River Basin within France (right). The geological map shows the
603 different sampling points for the Loire River mainstream and the different tributaries.

604 **Figure 2:** Map of the Egoutier watershed. 2a: General location of the sampling points, 2b: Land cover
605 map, 2c: Geological map. Modified from [Desaulty and Millot \(2017\)](#). The locations of the hospital and
606 the industrial area are shown on 2b.

607 **Figure 3:** Li concentrations ($\mu\text{g/L}$, Fig. 3a) and Li isotopic compositions ($\delta^7\text{Li}$, ‰, Fig. 3b) in the Loire
608 mainstream for low- and high-flow stages plotted as a function of distance from the source (km).

609 **Figure 4:** $\delta^7\text{Li}$ (‰) plotted as a function of Na/Li mass ratio for the Loire River mainstream. Na
610 concentrations are from [Desaulty and Millot \(2017\)](#).

611 **Figure 5:** $\delta^7\text{Li}$ rainwater corrected (‰) plotted as a function of Li concentrations after rainwater
612 correction ($\mu\text{g/L}$) for both low- and high-flow water samples. See text for explanation.

613 **Figure 6:** $\delta^7\text{Li}$ (‰) plotted as a function of the Al/Li mass ratio for suspended Loire sediments of the
614 Loire at Montjean. Al data are from [Desaulty and Millot \(2017\)](#). (Determination coefficient $R^2 = 0.60$,
615 Correlation Coefficient $R = 0.78$).

616 **Figure 7:** Li isotopic compositions ($\delta^7\text{Li}$, ‰) in the Loire River sediments at Montjean as a function of
617 river discharge (m^3/s) (Coefficient of determination $R^2 = 0.48$, Correlation coefficient $R = 0.69$).

618 **Figure 8:** Li concentrations ($\mu\text{g/L}$, Fig. 8a) and Li isotopic compositions ($\delta^7\text{Li}$, ‰, Fig. 8b) in Egoutier
619 waters plotted as a function of distance from the source (km).

620

621 **Table 1:**

622 Major elements (Na, Cl), trace (Li) concentrations and Li-isotopic compositions ($\delta^7\text{Li}$, ‰) of Loire
623 waters and its main tributaries, at both high- and low-flow stages. The * means after atmospheric
624 correction (see text for explanations). River discharge data are also reported here.

625 **Table 2:**

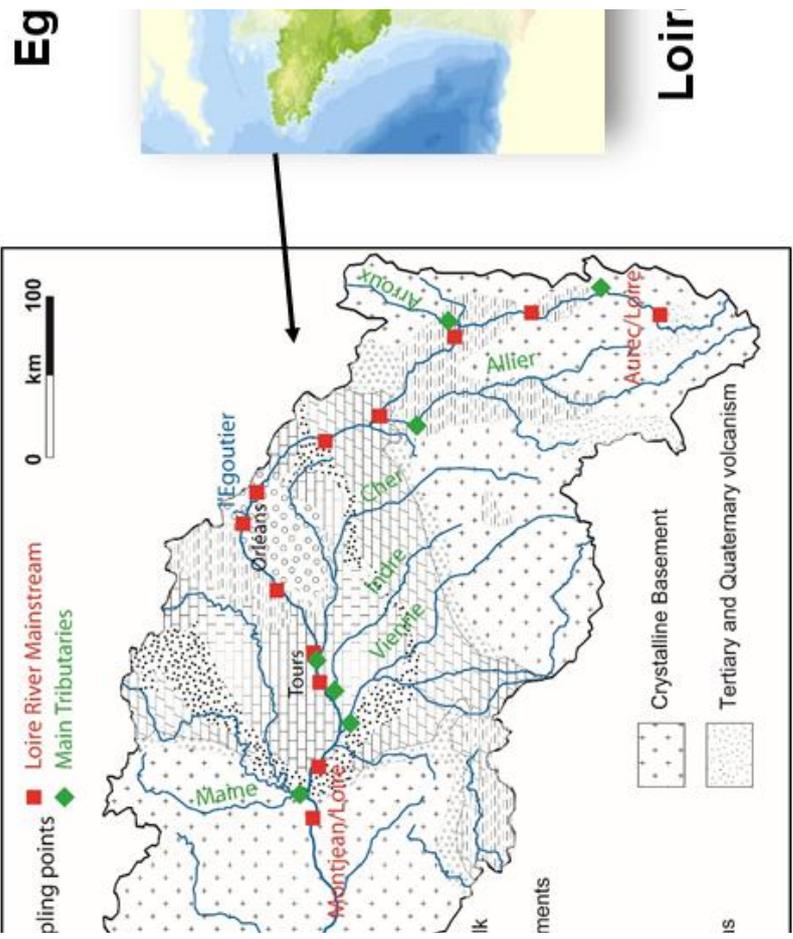
626 Aluminium and Lithium concentrations and Li-isotopic compositions ($\delta^7\text{Li}$, ‰) of suspended river
627 sediments sampled at Montjean/Loire. River discharge data are also reported here.

628 **Table 3:**

629 Li concentrations and Li isotopic compositions ($\delta^7\text{Li}$, ‰) of Egoutier catchment waters.

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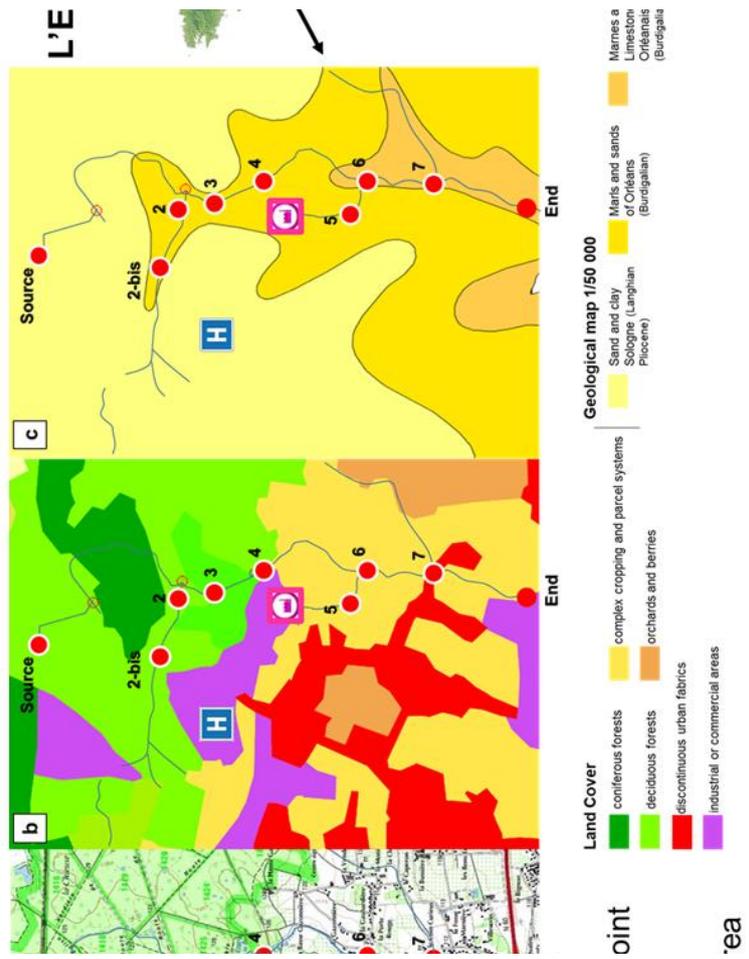
631 Figure 1



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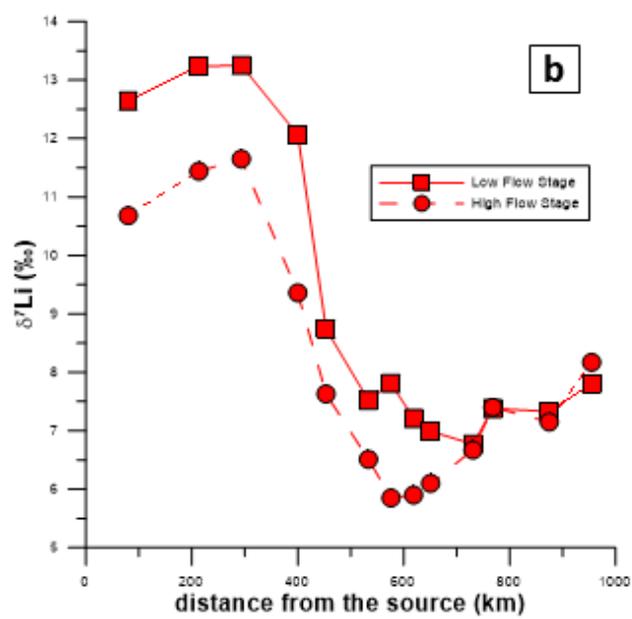
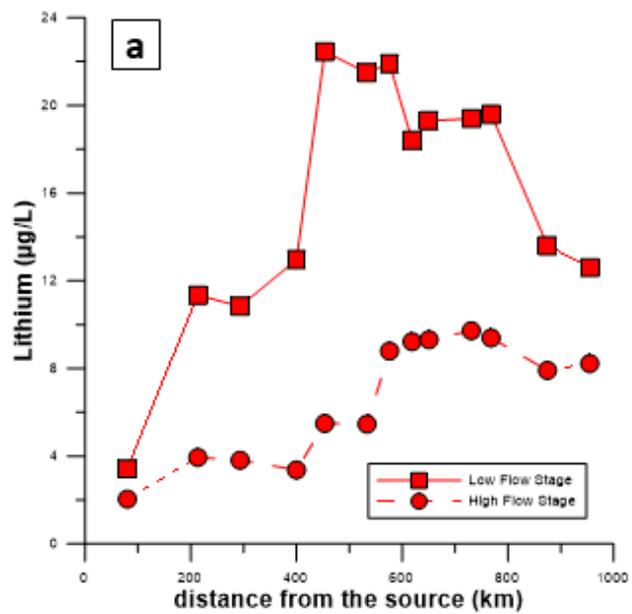
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634 Figure 2



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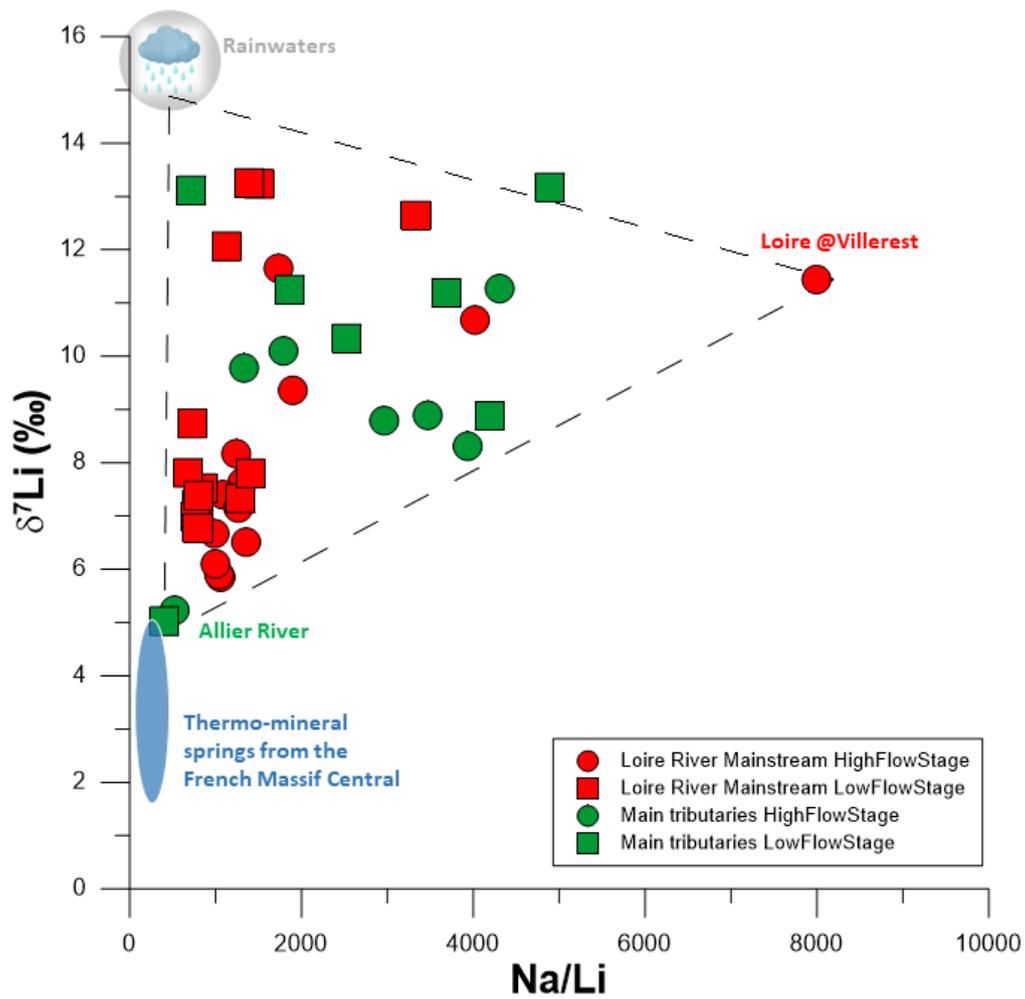
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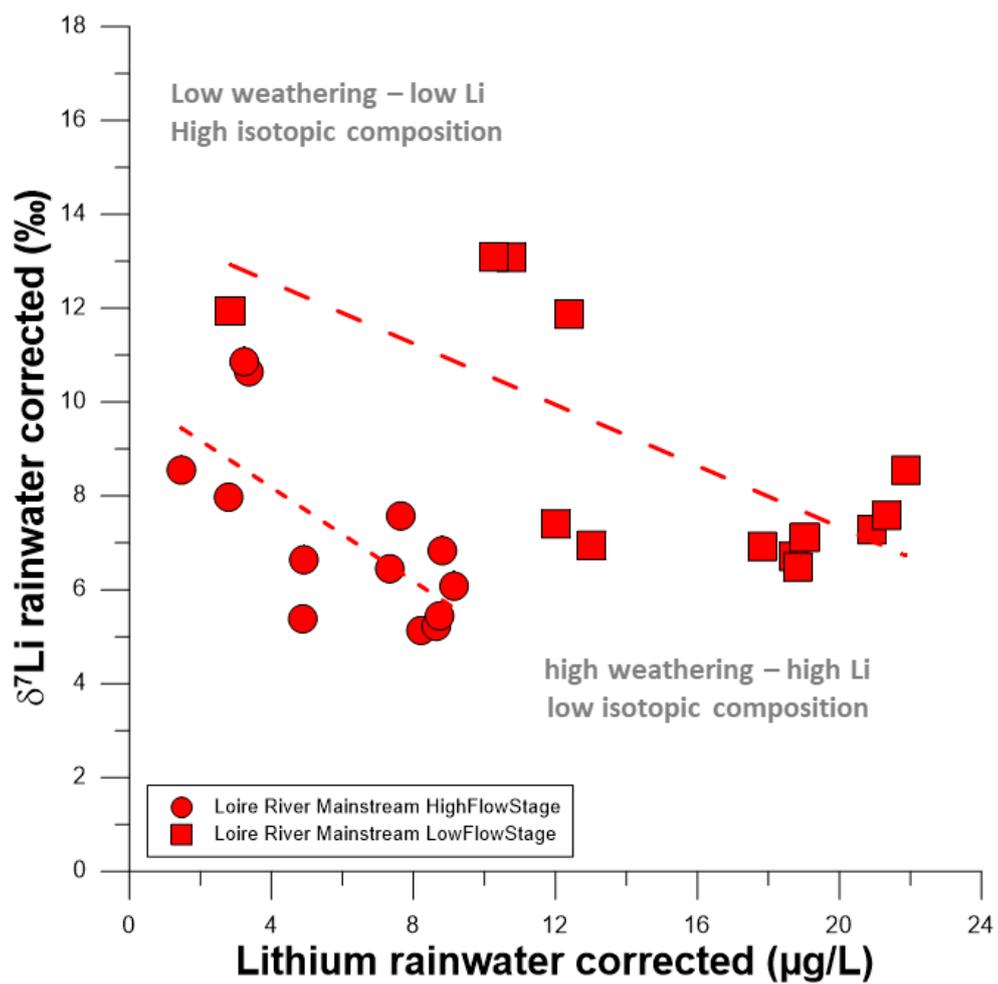
642 **Figure 04**



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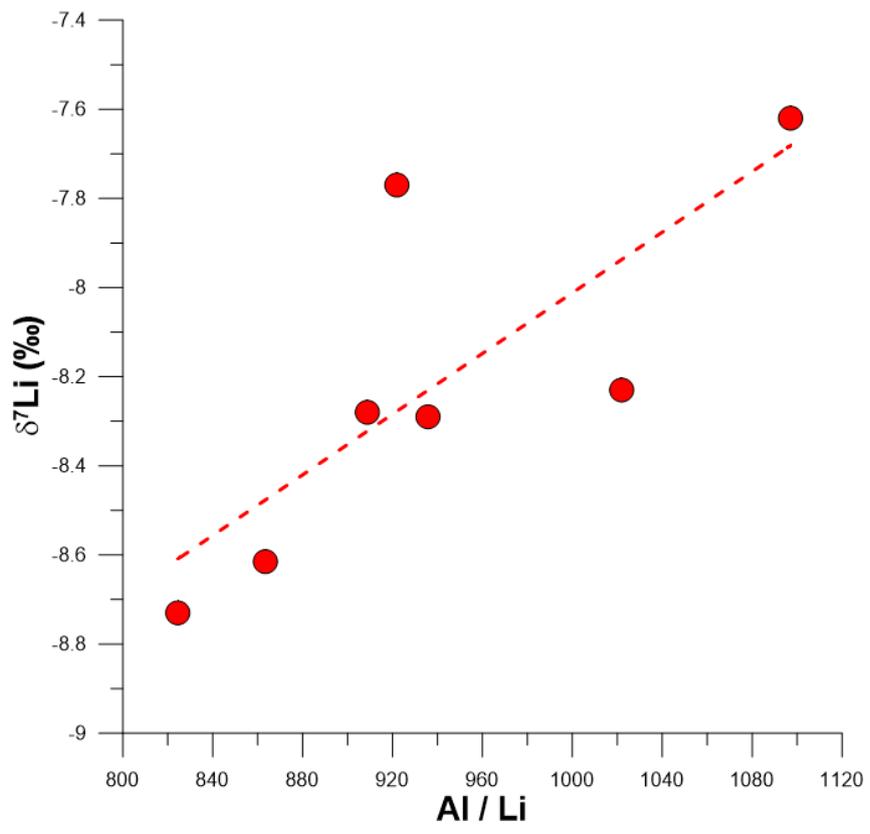
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651 **Figure 06**



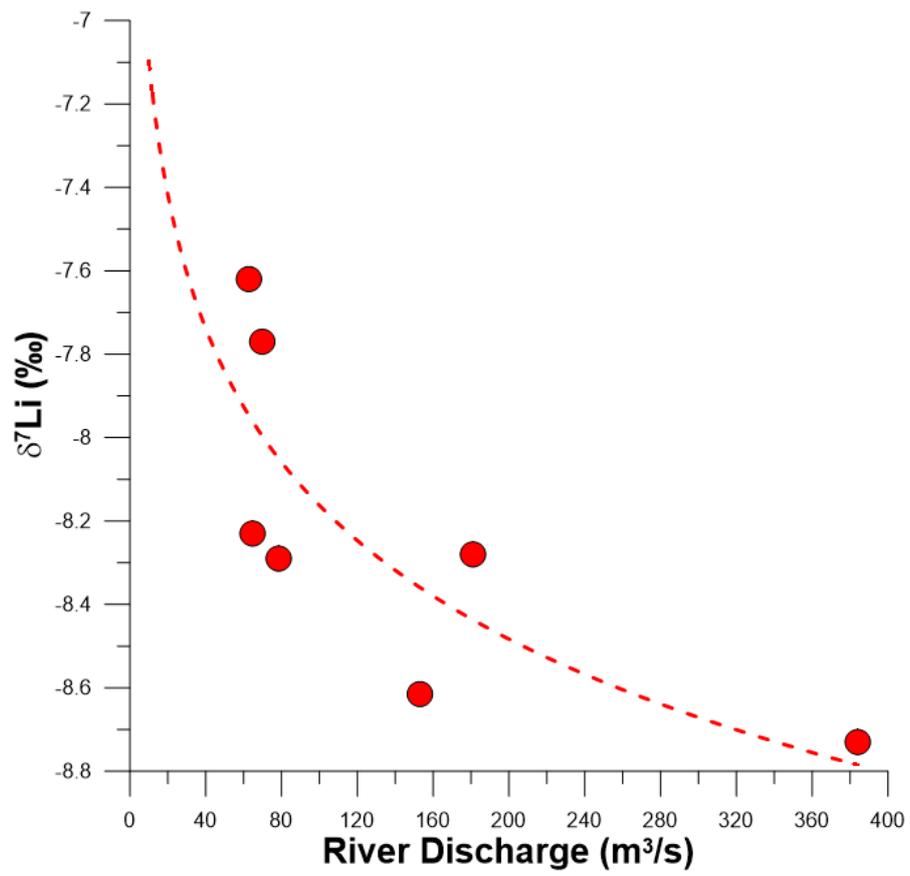
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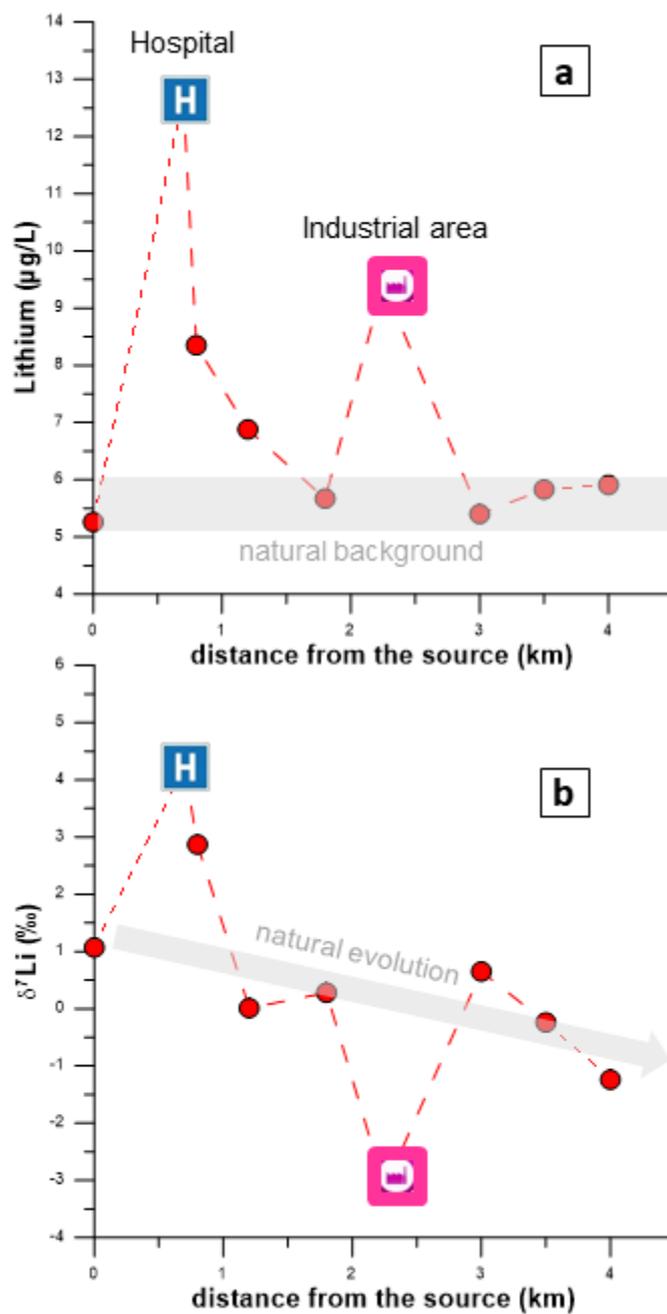
656 **Figure 07**



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	W) Cl (low)	Li (low)	Li* (low)	Li* (low)	δ ³⁴ Li (low)	δ ³⁴ Li* (low)	δ ³⁴ Li* (low)	δ ³⁴ Li* (low)	discharge (low)
	mg/L	μg/L	μg/L	μg/L	‰	‰	‰	‰	m ³ /s
1	16.1	3.4	2.8	12.6	11.9	11.9	10.7	10.7	41.6
1	22.7	11.3	10.8	13.2	13.1	13.1	27.6	27.6	67.0
1	21.8	10.8	10.3	13.3	13.1	13.1	67.0	67.0	89.9
1	20.9	13.0	12.4	12.1	11.9	11.9	68.6	68.6	60.4
1	22.2	22.5	21.9	8.7	8.5	8.5	60.4	60.4	78.7
1	23.2	21.5	20.9	7.5	7.3	7.3	127.0	127.0	144.0
1	19.3	21.9	21.3	7.8	7.6	7.6	9.7	9.7	3.3
1	20.2	18.4	17.8	7.2	6.9	6.9	31.4	31.4	8.0
1	21.4	19.3	18.7	7.0	6.7	6.7	11.2	11.2	1.7
1	21.1	19.4	18.8	6.8	6.5	6.5	7.7	7.7	7.7
1	21.9	19.6	19.0	7.4	7.1	7.1	127.0	127.0	144.0
1	22.9	13.6	13.0	7.3	6.9	6.9	127.0	127.0	144.0
1	25.7	12.6	12.0	7.8	7.4	7.4	144.0	144.0	37.1
1	24.4	5.7	5.1	10.3	9.7	9.7	9.7	9.7	3.3
1	30.3	4.8	4.2	11.2	10.5	10.5	3.3	3.3	3.3
1	22.5	4.3	3.7	13.2	12.7	12.7	31.4	31.4	-
1	38.4	5.1	4.5	8.9	8.0	8.0	-	-	-
1	73.3	29.9	29.3	11.3	11.2	11.2	1.7	1.7	1.7
1	20.7	14.3	13.7	13.1	13.0	13.0	7.7	7.7	7.7
1	25.1	46.5	45.9	5.0	4.9	4.9	37.1	37.1	37.1

667 **Table 2**

River	Sampling location	Sampling date	Al $\mu\text{g/g}$	Li $\mu\text{g/g}$	$\delta^7\text{Li}$ ‰	discharge m^3/s
Loire	Montjean/Loire	July 2012	45779	56	-8.7	384
Loire	Montjean/Loire	August 2012	46525	51	-8.3	181
Loire	Montjean/Loire	September 2012	50735	59	-8.6	153
Loire	Montjean/Loire	April 2013	75021	68	-7.6	62.75
Loire	Montjean/Loire	May 2013	74611	73	-8.2	64.69
Loire	Montjean/Loire	June 2013	67308	73	-7.8	69.78
Loire	Montjean/Loire	July 2013	38580	41	-8.3	78.47

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670 **Table 3**

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River	Sampling location	Li µg/L	δ⁷Li ‰
Egoutier	Source	5.3	1.1
Egoutier	point 2	8.4	2.9
Egoutier	point 2 bis	12.7	4.2
Egoutier	point 3	6.9	0.0
Egoutier	point 4	5.7	0.3
Egoutier	point 5	9.4	-3.1
Egoutier	point 6	5.4	0.7
Egoutier	point 7	5.8	-0.2
Egoutier	end	5.9	-1.2

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