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 δ^7Li 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 ^{6}Li enriched (δ^7Li 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

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

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

Li isotopes are good tracers in geochemistry due to their involvement in water/rock interactions at the Earth's surface. More precisely, Li and its isotopes can provide key information on continental silicate weathering, which is the primary natural drawdown process of atmospheric CO_2 and a major control on climate (Pogge von Strandmann et al., 2020). Li isotopes help our understanding of weathering via globally important processes, such as clay formation and cation retention. Both these processes occur as part of weathering in surface environments, including rivers, soil pore waters, and groundwater, but Li isotopes can also be used for tracking weathering changes across major climate-change events (Misra and Froelich, 2012).

Furthermore, Li has a strategic importance for numerous industrial applications, including the 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}Li ~ 7.5% and ^{7}Li ~ 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}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

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

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

2- ANALYTICAL METHODS

2.1. Sampling methods and element concentration measurements

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

In the field, 5 litres of river water were collected in acid-washed containers for major- and trace-element and isotopic measurements (for details of the protocol see Millot et al., 2003). Samples were filtered in the field, using a Sartorius frontal filtration unit (0.2 µm cellulose acetate filter, 142 mm diameter). After filtration, samples were stored in acid-washed polypropylene bottles. The river sediments were collected after drying and centrifugation of the river-water filtration retentate. The samples for Li-concentration and Li-isotope analyses were acidified to pH=2 with ultrapure HNO_3. 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 ±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). $^{7}Li/^{6}Li$ 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 $\delta^{7}Li$ 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 $\delta^{7}Li$ +30.8 ±0.4‰ (2σ, n=15) over
123 the duration of the analyses. This mean value agrees with our long-term measurements ($\delta^{7}Li$ +31.0
124 ±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 HNO_3
128 (14N) and 0.1 mL $HClO_4$ (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

for Li separation. Accuracy and reproducibility of the entire procedure for solid samples (dissolution + purification + mass analysis) were tested by repeated measurements of the JB-2 basalt standard (Geological Survey of Japan), which gave a mean value of δ^7Li = +4.9‰±0.6‰ (2σ, n=17), in good agreement with published values (see Jeffcoate et al. 2004, Tomascak 2004 and Carignan et al. 2007 for data compilation).

3- FIELD SITE DESCRIPTION

3.1 The Loire River Basin

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

The Loire River in central France (Fig. 1) is approximately 1010 km long and drains an area of 117,800 km^2. Initially, the Loire flows north to northwest, originating in the Massif Central and continuing up to the city of Orléans, about 650 km from the source. Beyond Orléans, the river turns west to WSW, being one of the main European riverine inputs into the Atlantic Ocean. In the upper basin, the bedrock is Palaeozoic plutonic rock overlain by sub-Recent volcanic rocks. The intermediate basin includes three major tributaries flowing into the Loire from the left bank: the Cher, the Indre and the Vienne rivers. Here, the Loire drains sedimentary rocks of the Paris Basin, mainly carbonate deposits. The lower Loire basin drains Palaeozoic basement rocks of the Armorican Massif and its overlying Mesozoic to Cenozoic sedimentary deposits.

Its spring is located at an altitude of 1,404 m (Mont Gerbier de Jonc) and its course is classically divided into three parts from upstream to downstream: (i) the Upper Loire, (ii) the Loire Valley, and (iii) the Lower-Loire, to the estuary. River discharge of the Loire is very irregular: in the Lower Loire it can exceed 7000 m^3/s, but at Orléans it is around 350 m^3/s and during summer the river can literally dry up, with flows less than 25 m^3/s.

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

The relationships between chemical elements and flow as well as between isotopic ratios and flow have shown that the dissolved fraction of the Loire results from a mixture between rainfall input, input from the weathering of silicate- and carbonate bedrocks, and anthropogenic input of agricultural and urban origin. Total dissolved-solids flow during a hydrological cycle is estimated at $1300x10^3$ t/year at Orléans and $1620x10^3$ t/year at Tours (Grosbois et al., 2001). For the river sediments, work by Négrel and Grosbois (1999) on $^{87}Sr/^{86}Sr$ isotope ratios suggests the existence of at least two reservoirs of suspended matter transported by the river. One is related to the detrital fraction from silicate erosion, the other to carbonate erosion. The stable isotopes of carbon and oxygen in the fraction extracted by acid leaching from Loire sediments during periods of low water flow (Négrel et al., 2000), confirm the formation of antigenic calcites in isotopic equilibrium with Loire water (Fontes et al., 1973; Dever et al., 1983).

3.2 The Egoutier watershed

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

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

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

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

4- RESULTS

4.1 The Loire River basin

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

During low flow, Li concentrations are higher (3.4 to 46.5 µg/L; mean 15.9 µg/L n=20, Table 1) than 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 parallel, the Li-isotopic compositions are little different for low- and high-flow samples, with δ^7Li values ranging from +5.0 to +13.3‰ and +5.2 to +11.7‰ respectively. These concentrations are higher than the worldwide riverine average of 1.9 µg/L (Huh et al., 1998; Gaillardet et al., 2014). In addition, Loire basin rivers have lower isotopic compositions than the average δ^7Li value for modern river water of about +23‰ (Huh et al., 1998; Misra and Froelich, 2012). Finally, δ^7Li values for the Loire basin rivers agree with previous data reported by Rivé et al. (2013) for the upstream Loire (δ^7Li from 4.0 to 24.0‰). Loire river suspended sediments collected monthly at Montjean/Loire (Table 2) from July 2012 to June 2013 have Li concentrations between 41.3 and 73.0 µg/g (mean 60.2 µg/g, n=7), significantly higher than those of the average Upper Continental Crust (UCC) at Li 35 ± 11 µg/g (2σ, Teng et al., 2004). In addition, these sediments have low δ^7Li 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 δ^7Li 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 δ^7Li 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 δ^7Li values as a function of distance from the spring. These
221 variations for Li concentration and δ^7Li are observed for both high and low flow stages.

222 In addition, when all δ^7Li 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 δ^7Li *vs.* Na/Li diagram (Fig. 4), the
224 data plot in a triangle formed by three endmembers. The first (Na/Li ~8000 and δ^7Li ~+12‰) is the
225 upstream Loire at Villerest; the second endmember is close to the Allier river (Na/Li ~500 and δ^7Li
226 ~+5‰); and the third could be represented by rainwater. This agrees with the conceptual scheme of
227 the Loire hydrosystem based on δ^{18}O and $^{87}Sr/^{86}Sr$ 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

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

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

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

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

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

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

Finally, the relationship between δ^7Li and Al/Li in the suspended sediment (Fig. 6) could also raise the question of the control by different mineral phases (clay minerals *vs.* oxy-hydroxide of Fe or Mn, or carbonates) during Li-isotopic fractionation between water and solids. The variation of the Al/Li ratio could reflect a compositional variation of clay minerals in suspended sediments. It is also likely that the suspended sediments consist of both fine (clay rich) and coarse (carbonate rich) factions.

Unfortunately, we do not dispose over specific mineral-characterization data on our samples for further discussion of this point, but it is interesting to observe an inverse correlation between the 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 δ^7Li 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; Vanwalleghem 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 µg/L, the values for the
308 Hospital WWTP release and the industrial area are 12.7 µg/L and 9.4 µg/L, respectively. In addition,
309 Li-isotopic compositions are rather homogeneous in water of the Egoutier watershed, with δ^7Li
310 values of around +0.5‰±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 δ^7Li 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 (Desaulty 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.

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

6- CONCLUDING REMARKS AND FUTURE DIRECTIONS

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

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

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600

Figure and Table Captions

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

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

Figure 3: : Li concentrations (µg/L, Fig. 3a) and Li isotopic compositions (δ^7Li, ‰, Fig. 3b) in the Loire mainstream for low- and high-flow stages plotted as a function of distance from the source (km).

Figure 4: δ^7Li (‰) plotted as a function of Na/Li mass ratio for the Loire River mainstream. Na concentrations are from Desaulty and Millot (2017).

Figure 5: δ^7Li rainwater corrected (‰) plotted as a function of Li concentrations after rainwater correction (µg/L) for both low- and high-flow water samples. See text for explanation.

Figure 6: δ^7Li (‰) plotted as a function of the Al/Li mass ratio for suspended Loire sediments of the Loire at Montjean. Al data are from Desaulty and Millot (2017). (Determination coefficient R^2 = 0.60, Correlation Coefficient R = 0.78).

Figure 7: Li isotopic compositions (δ^7Li, ‰) in the Loire River sediments at Montjean as a function of river discharge (m^3/s) (Coefficient of determination R^2 = 0.48, Correlation coefficient R = 0.69).

Figure 8: Li concentrations (µg/L, Fig. 8a) and Li isotopic compositions (δ^7Li, ‰, Fig. 8b) in Egoutier waters plotted as a function of distance from the source (km).

Table 1:

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

Table 2:

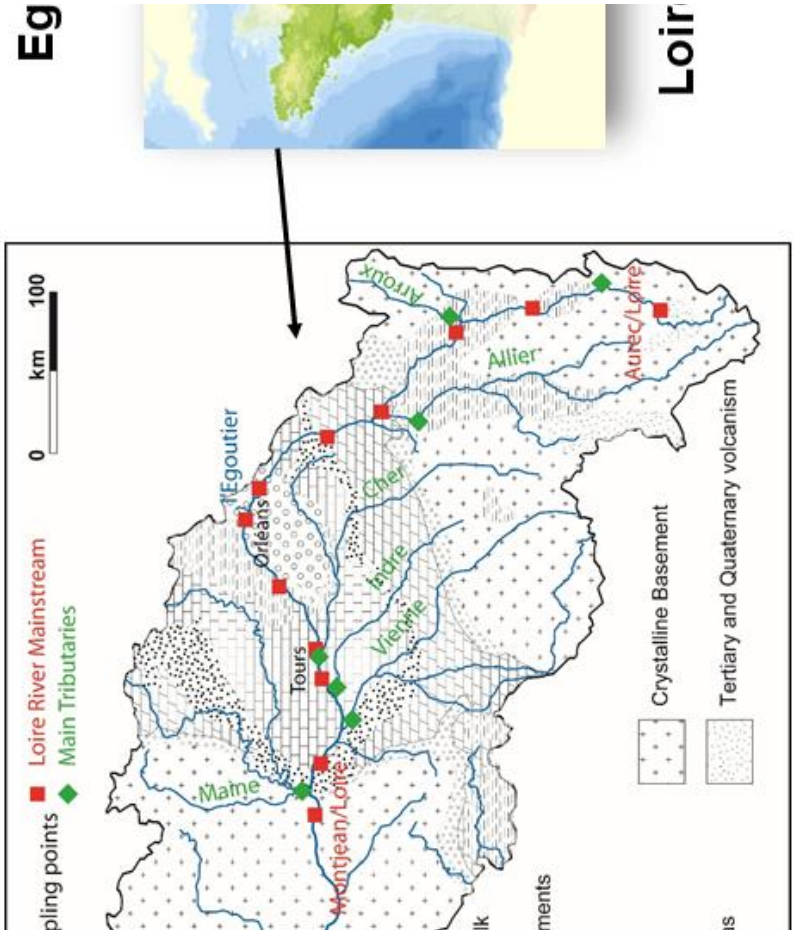
626 Aluminium and Lithium concentrations and Li-isotopic compositions (δ^7Li, ‰) of suspended river
627 sediments sampled at Montjean/Loire. River discharge data are also reported here.

628 **Table 3:**

629 Li concentrations and Li isotopic compositions (δ^7Li, ‰) of Egoutier catchment waters.

630

631 **Figure 1**



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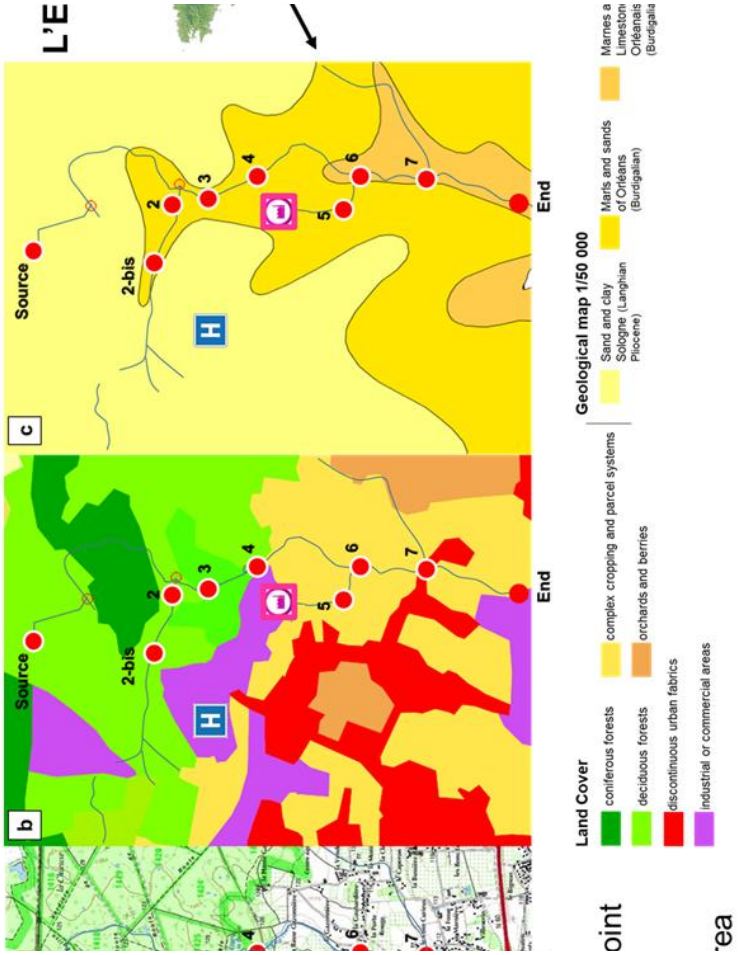
634 **Figure 2**



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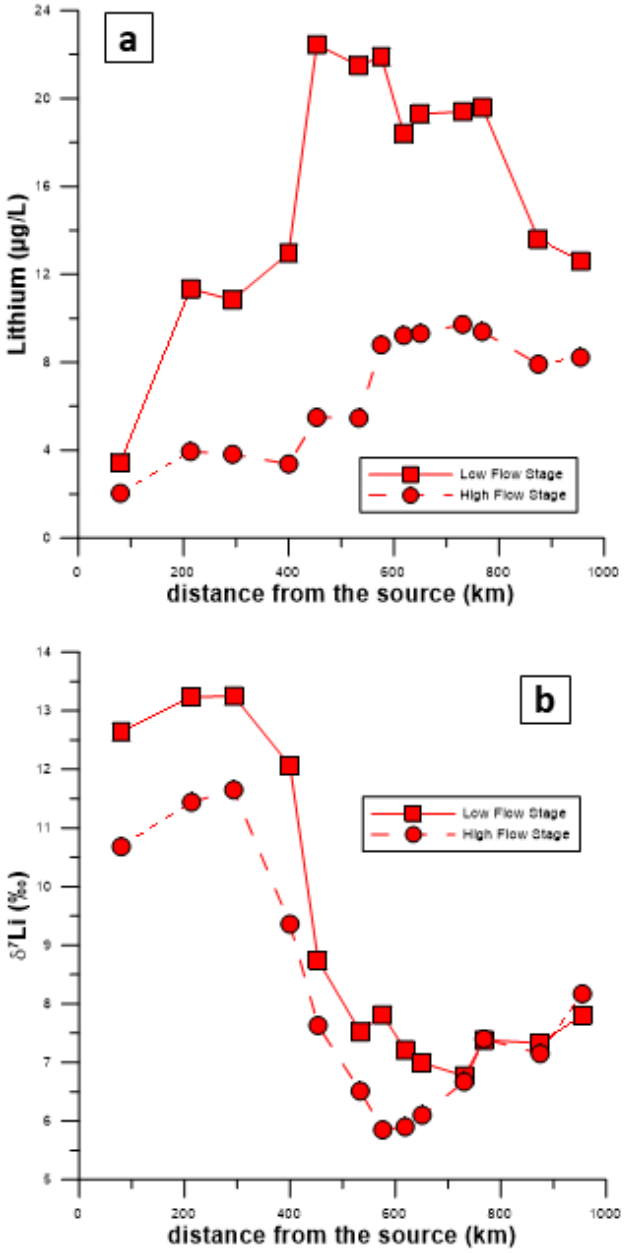
637 **Figure 3**



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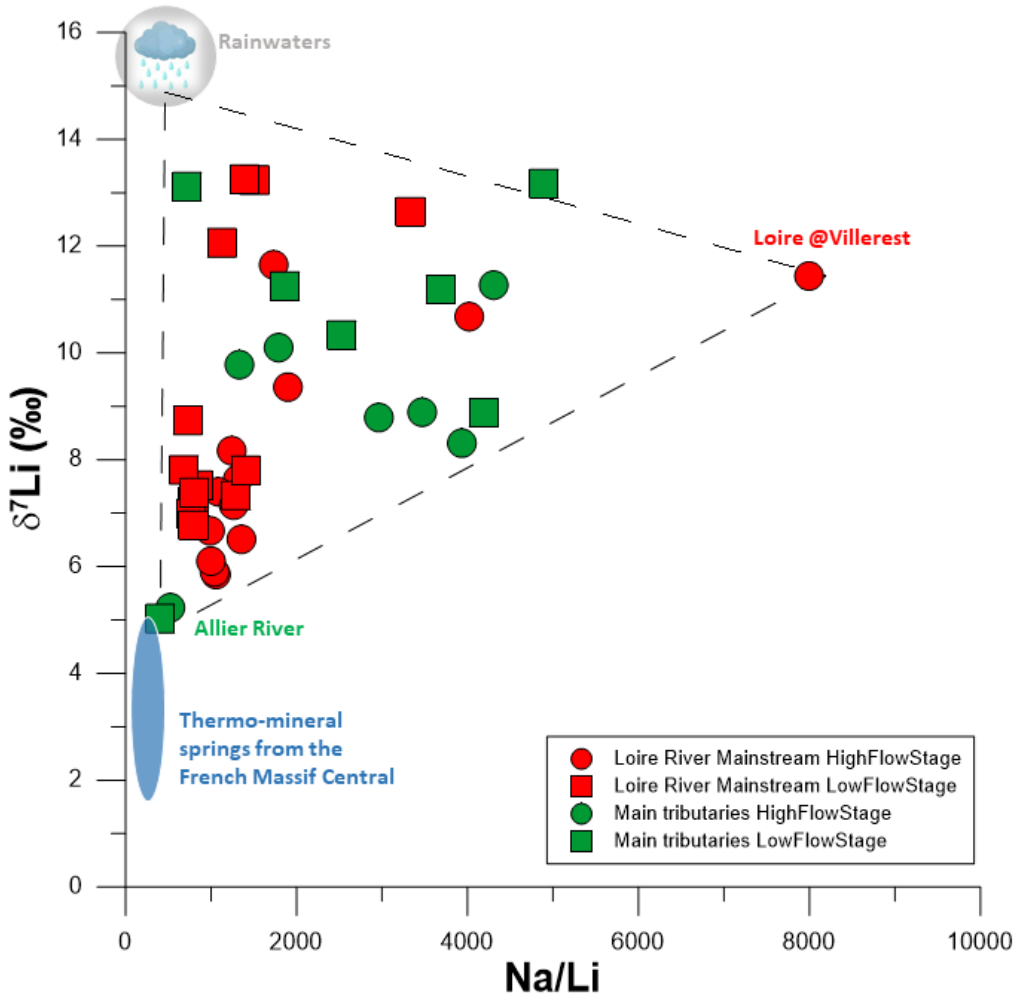
642 **Figure 04**



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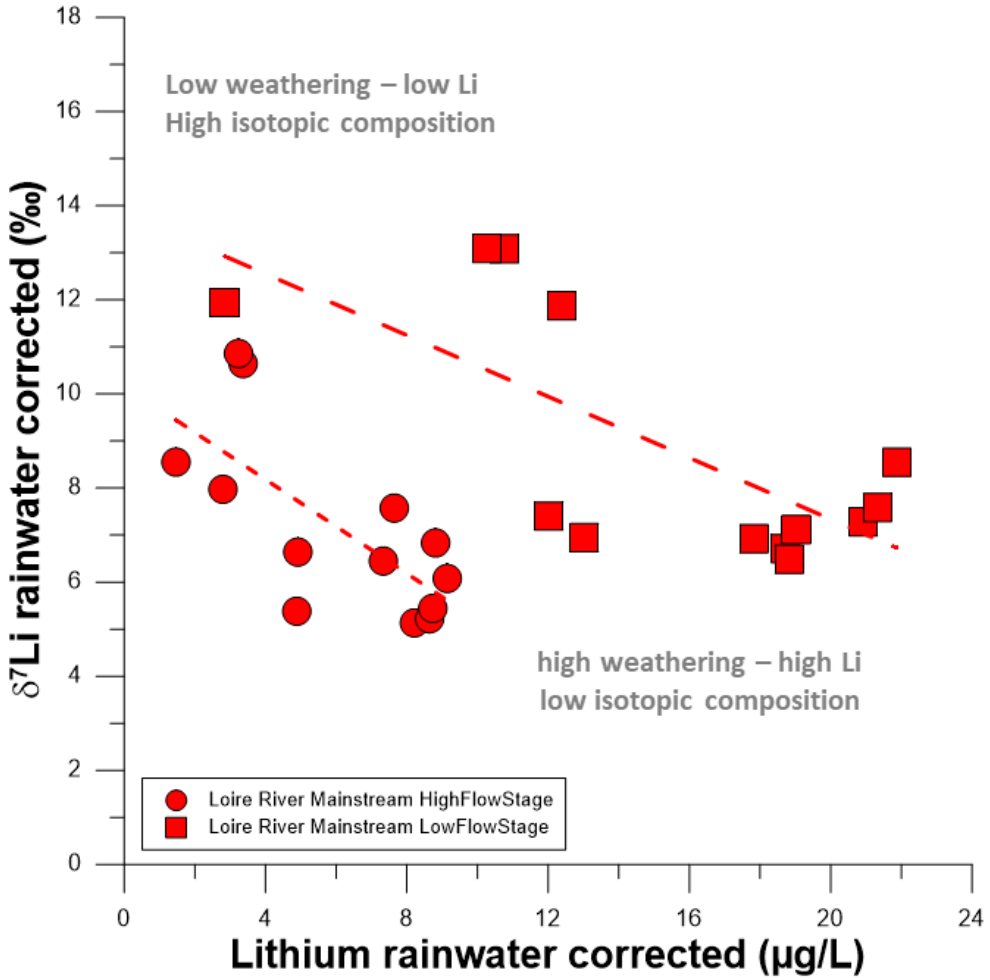
646 **Figure 05**



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651 **Figure 06**

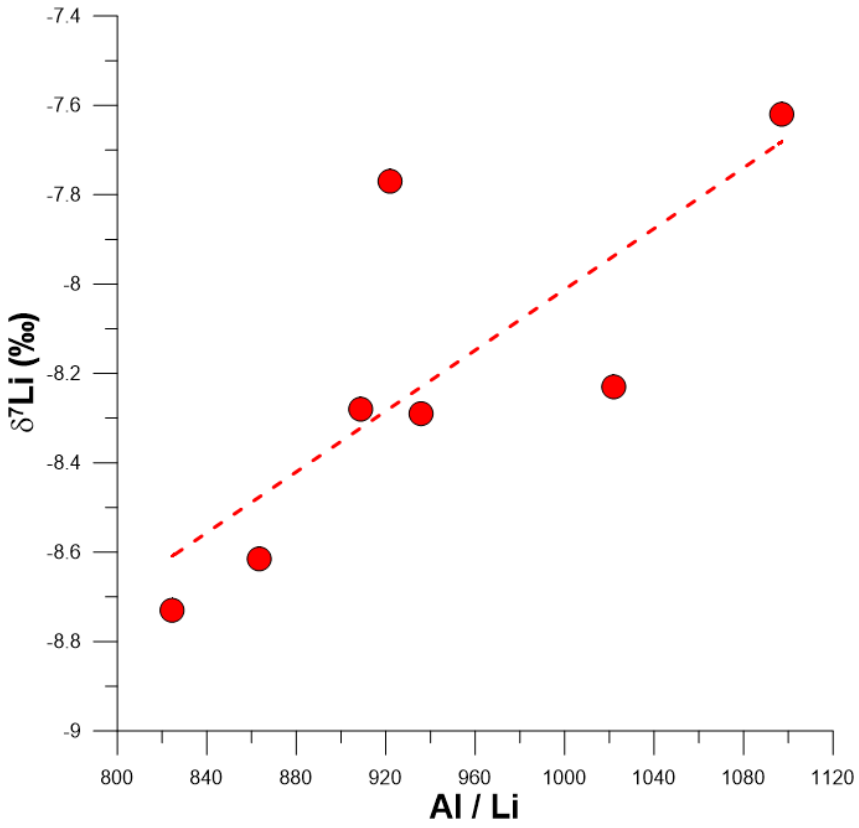

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Figure 07

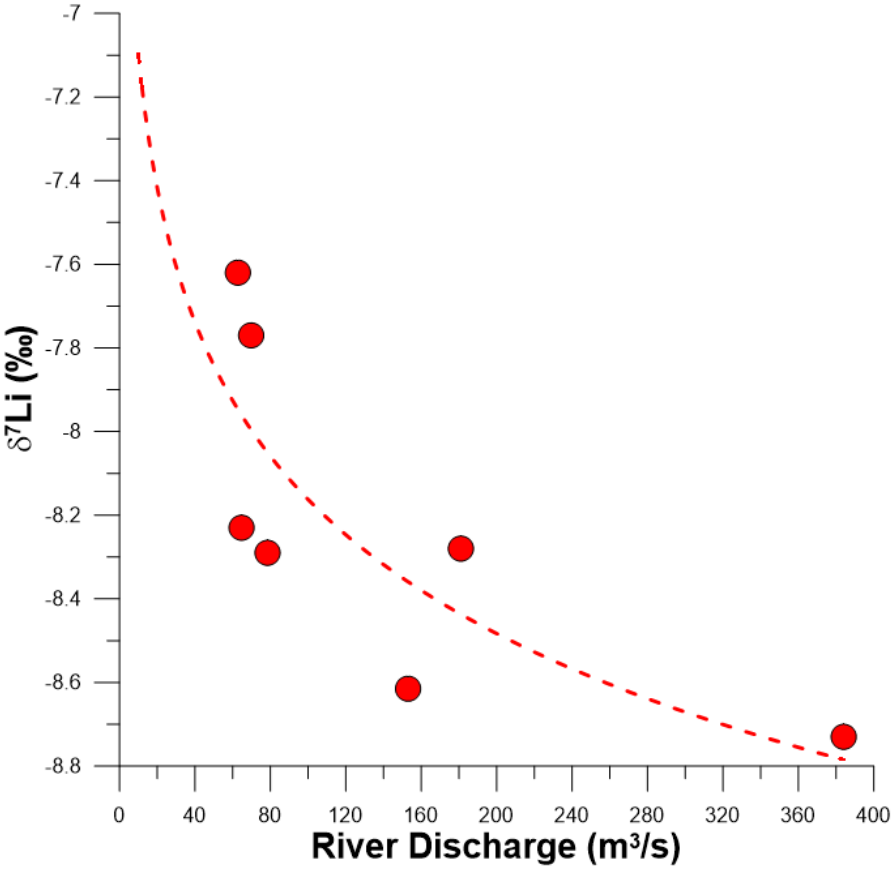
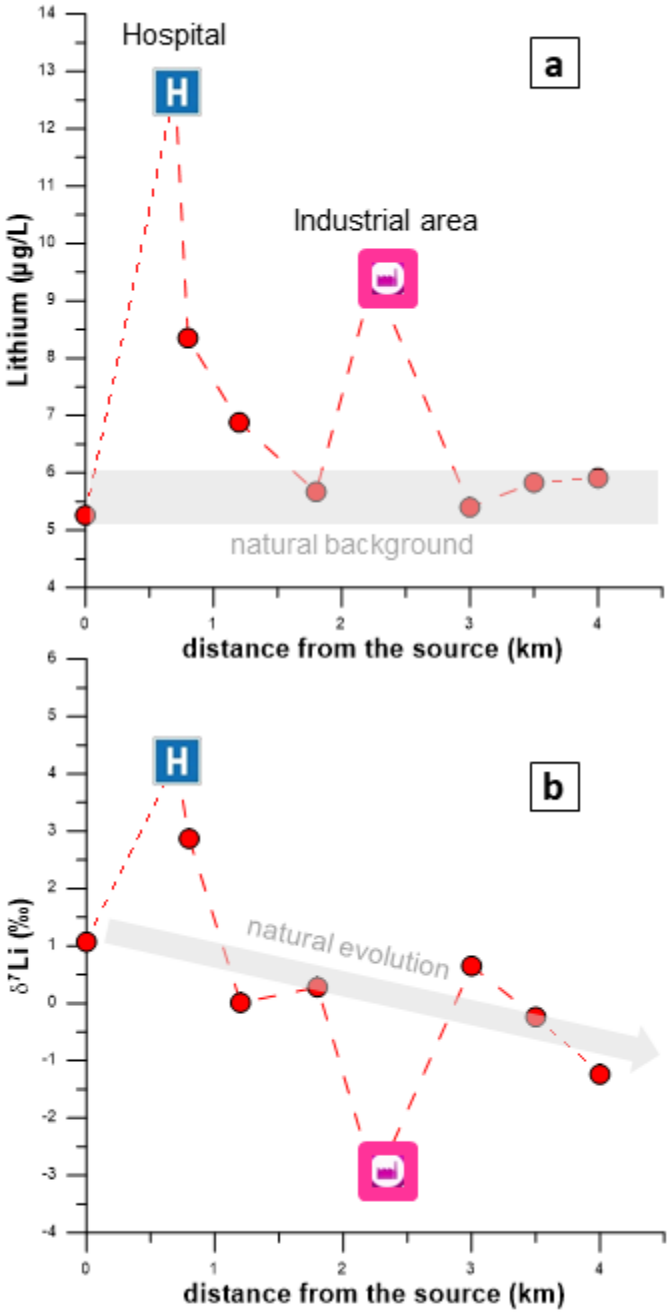

-7
-7.2
-7.4
-7.6
-7.8
-8
-8.2
-8.4
-8.6
-8.8
δ7Li (‰)
0
40
80
120
160
200
240
280
320
360
400
River Discharge (m3/s)

Figure 08


Hospital
a
Industrial area
Lithium (µg/L)
natural background
distance from the source (km)
b
natural evolution
δ7Li (‰)
distance from the source (km)

664 **Table 1**

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666

w) Cl (low)	Li (low)	Li* (low)	δ^7Li (low)	δ^7Li* (low)	discharge (low)
L mg/L	µg/L	µg/L	‰	‰	m^3/s
16.1	3.4	2.8	12.6	11.9	10.7
22.7	11.3	10.8	13.2	13.1	41.6
21.8	10.8	10.3	13.3	13.1	27.6
20.9	13.0	12.4	12.1	11.9	67.0
22.2	22.5	21.9	8.7	8.5	89.9
23.2	21.5	20.9	7.5	7.3	68.6
19.3	21.9	21.3	7.8	7.6	60.4
20.2	18.4	17.8	7.2	6.9	60.4
21.4	19.3	18.7	7.0	6.7	78.7
21.1	19.4	18.8	6.8	6.5	78.7
21.9	19.6	19.0	7.4	7.1	77.1
22.9	13.6	13.0	7.3	6.9	127.0
25.7	12.6	12.0	7.8	7.4	144.0
24.4	5.7	5.1	10.3	9.7	9.7
30.3	4.8	4.2	11.2	10.5	3.3
22.5	4.3	3.7	13.2	12.7	31.4
38.4	5.1	4.5	8.9	8.0	-
73.3	29.9	29.3	11.3	11.2	1.7
20.7	14.3	13.7	13.1	13.0	7.7
25.1	46.5	45.9	5.0	4.9	37.1

667 **Table 2**

River	Sampling location	Sampling date	Al µg/g	Li µg/g	δ^7Li ‰	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	δ^7Li ‰
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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