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Lithium isotopic fingerprints of sources and processes in surface waters of the Ebro River Basin (Spain).

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Abstract

The Ebro River in north-eastern Spain is among the largest contributors of freshwater to the Mediterranean Sea and ends in the Ebro delta, one of the major wetlands in Europe. The bedrock of the Ebro River basin mainly consists of carbonate rocks and evaporites of Paleozoic and Mesozoic age, and the river flows through several large cities, and agricultural and industrial areas. The Ebro River outlet at Amposta was sampled once a month for a year (2006), and a field campaign in April of the same year sampled the Ebro along its main course as well as its principal tributaries. In the present study, the behaviour of Li and its isotopes was investigated at basin scale, with the objective of elucidating the processes controlling the isotope signatures of a large river draining mostly sedimentary bedrock. $\delta^7\text{Li}$ values ranged from +17.1‰ to +18.3‰ along the Ebro main stream, and between +16.3 and +18.9‰ at the outlet. In the major tributaries, the $\delta^7\text{Li}$ values ranged from +12.9‰ to +20.9‰, with bedrock values ranging from +0.5 to +29.3‰. Comparing Li concentrations with Cl and SO_4 ones, it appears that evaporite weathering plays an important role in controlling Li, but no anthropogenic agricultural or industrial influence on Li concentrations was detected. The Na/Li, Cl/Li and SO_4/Li ratios clearly reflect the role of halite dissolution for some tributaries (Gallego, Ega and Aragon), gypsum dominating others (Guadalope, Matarrana, Huerva and Segre), and little influence of carbonate in all tributaries, the Ebro itself being a mixture of all tributaries. We tentatively applied the simple Rayleigh fractionation model, but most $\delta^7\text{Li}$ values of the Ebro water samples plotted away from the fractionation line, reinforcing the major role of mixing processes in the Ebro basin, rather than fractionation processes during water/rock interactions. A comparison of $\delta^7\text{Li}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios further demonstrates the role of gypsum/anhydrite and limestone in the Ebro and its tributaries. Sr-isotopes show a non-negligible role of carbonate dissolution, generally considered to be weak in the control of the lithium cycle in catchments.

Keywords: Ebro River, Li isotopes, dissolved load, evaporite, carbonate

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32 **1 – Introduction**

33 Lithium is one of the modern tools for studying water-rock interaction processes. This is done
34 by coupling geochemical processes during such processes, with the capability of lithium to go
35 into the fluid phase with significant mass-dependent fractionation between the two stable
36 isotopes ^6Li (natural abundance 7.5%) and ^7Li (natural abundance 92.5%) (Huh et al., 1998,
37 2001; Pistiner and Henderson, 2003; Rudnick et al., 2004; Kisakürek et al., 2004; Pogge von
38 Strandmann et al., 2006, 2014, 2021; Millot et al., 2007, 2010a, b; Négrel et al., 2012;
39 Dellinger et al., 2014; 2015; Henchiri et al., 2016; Négrel and Millot, 2019; Qi et al., 2019;
40 Martin et al., 2020; Steinhoefel et al., 2021; Millot and Négrel, 2021). Recently, the variation
41 in $\delta^7\text{Li}$ values of water was used for distinguishing between natural and anthropogenic inputs
42 because lithium isotopes have been shown to be a probe for tracing anthropogenic activity
43 (Choi et al., 2019; Négrel et al., 2010, 2019; Millot and Négrel, 2021).

44 Lithium and its isotopes are of increasing interest in weathering studies through rivers
45 dissolved and suspended loads and groundwaters because Li is solubilized from minerals and
46 rocks during water–rock interactions (e.g. a mobile element) and not constrained by biological
47 processes. Such chemical weathering induces isotopic fractionation resulting in an enrichment
48 of the heavy isotope (^7Li) in solution, the light isotope (^6Li) being preferentially retained in
49 secondary weathering mineral phases (see Négrel and Millot (2019) and references therein).
50 In systems where few secondary phases are formed, lithium can evolve in terms of a tool
51 tracing the mixtures between waters (see Négrel et al. (2010) and references therein).

52 The weathering of silicate rocks is a major process at the earth's surface and to better
53 understand this process, many studies have deployed the use lithium isotopes(e.g., Burton and
54 Vigier, 2011; Steinhoefel et al., 2021 and references therein). However, carbonate and
55 evaporite weathering processes have hardly been studied through Li-isotope variations (Gou
56 et al., 2019; Martin et al., 2020). This can be explained by two features: i) Li contents in

57 evaporite and carbonate are low ($<12 \mu\text{g g}^{-1}$) compared to silicate rocks ($20\text{-}40 \mu\text{g g}^{-1}$ in
58 granite and around $60 \mu\text{g g}^{-1}$ in shales); and ii) the most common rock types in Europe are
59 39% plutonic and metamorphic rocks, 37% shales, 14% carbonate rocks, 9.5% sand-
60 sandstones, and volcanic rocks and evaporites playing a subordinate role (Caritat and
61 Reimann, 2012).

62 Here, we focus on Li-isotope data from the dissolved load of 25 river-water samples
63 collected in the Ebro Basin and of 2 groundwater samples. Among the rivers providing
64 freshwater in the Mediterranean Sea, the 2017 Mediterranean Quality Status Report
65 (downloaded at <https://www.medqsr.org/fr/node/230> on February 2023, 14th) classified the
66 rivers having their outlet in the Mediterranean through their annual climatological discharge
67 of freshwater in cubic metres per second. The Rhone and Po rivers have the highest discharge
68 ($1500\text{-}1800\text{m}^3/\text{s}$), then the Nile ($1000\text{-}1500\text{m}^3/\text{s}$) followed by the Ebro and the Drin with 500-
69 $1000\text{m}^3/\text{s}$, reflecting the importance of the Ebro in the hydrologic cycle of the Mediterranean
70 Sea. The last rivers supplying the Mediterranean are the Ceyhan, the Evros and the Tiber
71 ($150\text{-}500\text{m}^3/\text{s}$) and the Moulouya and Shellif ($10\text{-}150\text{m}^3/\text{s}$). We measured lithium and its
72 isotope values in all reservoirs, in parts of the basin affected by salinization and secondary
73 processes (precipitation, re-dissolution, mixing of water and anthropization), as well as in the
74 main bedrocks. Studies on river drainage basin having evaporite-type bedrocks are scarce and
75 in these cases, the evaporitic deposits are often located in headwaters and are not very
76 important in terms of surface area compared to the general geology (mainly silicate rocks) and
77 to the size of these of large river basins. The $\delta^7\text{Li}$ values generally observed in rivers draining
78 evaporites are either around $+20 \text{‰}$ (Huh et al., 1998; 2001; Gou et al., 2019; Yoon, 2010) but
79 other rivers also influenced by evaporite dissolution have low $\delta^7\text{Li}$ values, around $+8\text{‰}$ (Chen
80 et al., 2002; Chetelat et al., 2008, 2009; Wang et al., 2015; Ma et al., 2020), whereas
81 carbonate-dominated rivers are characterized by high $\delta^7\text{Li}$ values ($> +20\text{‰}$). The objectives

82 of our study were to constrain the Li cycling in a major river basin underlain by sedimentary
83 rock and affected by climatic impact (drought and water deficit), and to examine Li in the
84 rock-soil cycle through weathering processes and water use (agriculture, water reservoirs and
85 industry), again within a climate-change context.

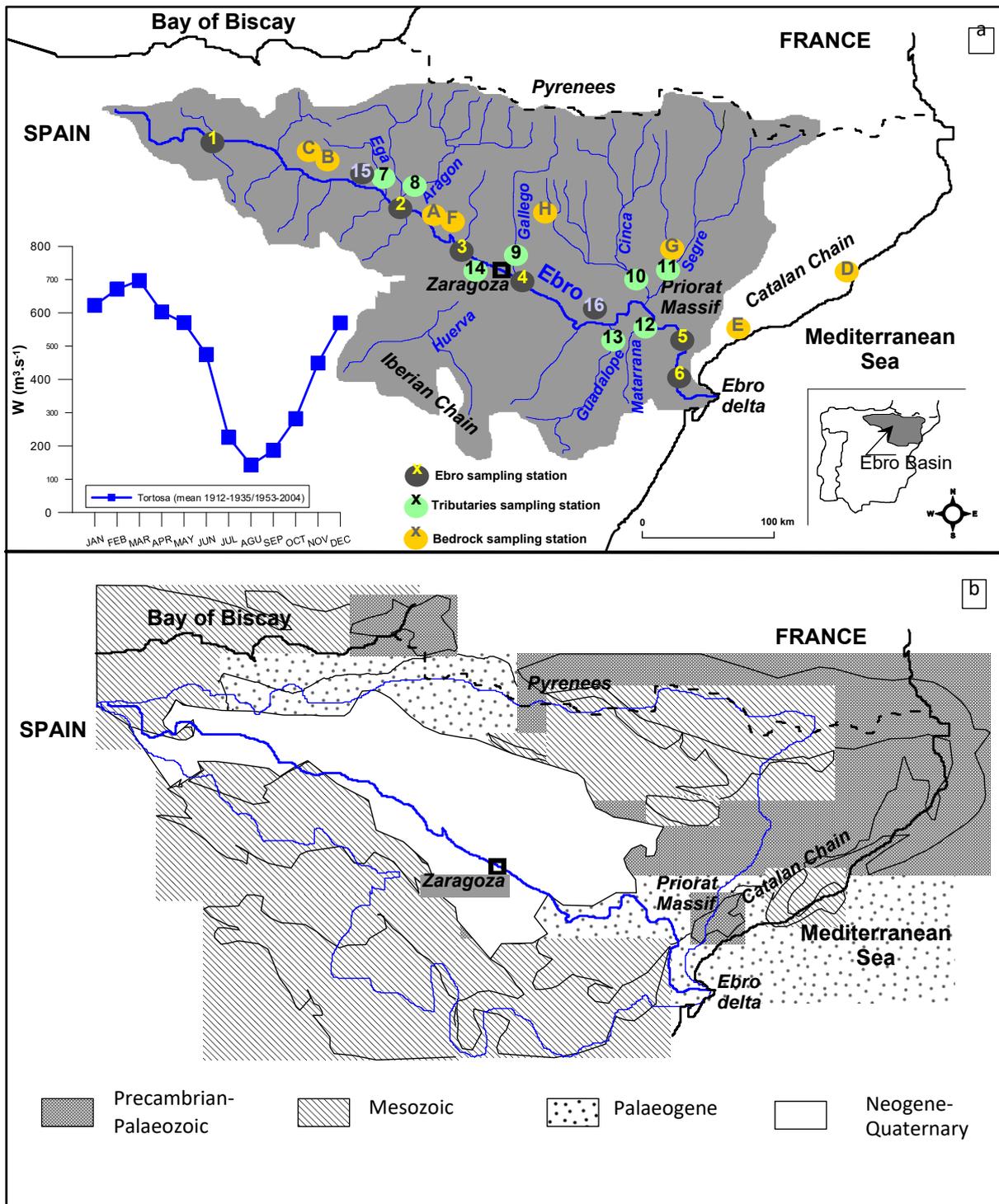
86 **2 - Characteristics of the Ebro Basin**

87 The Ebro River basin (Fig. 1) lies in north-eastern Spain, starting near the Atlantic coast in the
88 Cantabrian Mountains and flowing to the western Mediterranean Sea. Over its 85,530 km²
89 drainage basin and along its 928-km course, the Ebro River flows through several large cities
90 (Lleida, Logroño, Vitoria, Zaragoza, Huesca and Barcelona), and through agricultural, mining
91 and industrial areas. It is the largest Spanish river system and one of the largest contributors of
92 freshwater to the Mediterranean Sea (CHE, <http://www.chebro.es/>).

93 The geology of the Ebro Basin consists of (Guillén and Palanques, 1992; Luzón et al.,
94 2008; Mochales et al., 2007) sedimentary and metamorphic Palaeozoic rocks (Iberian and
95 Pyrenees mountains, Priorat Massif); Jurassic and Cretaceous carbonate rocks in the Iberian
96 Chain forming the southern margin of the Ebro Basin; sedimentary Tertiary rocks of the
97 Pyrenees foothills and the Ebro Valley; and Neogene and Recent delta-plain deposits near the
98 Mediterranean Sea (lower part of the Ebro River). The occurrence of evaporite deposits in the
99 Ebro River basin has been documented in detail (Castillo Herrador, 1974; Birnbaum, 1976;
100 Orti, 1990; Utrilla et al., 1992; Elorza and Santolalla, 1998).

101 The main tributaries of the Ebro are the Aragon, Gallego, Cinca and Segre rivers
102 (northern part of the basin, Fig. 1) flowing through silicate rocks of the Pyrenees Mountains in
103 their upper part, and through sedimentary rocks downstream. In the southern part of the basin,
104 the main tributaries are the Huerva, Guadalope and Matarrana (Fig. 1), flowing over
105 sedimentary rocks. The catchment of the Ega River, a tributary in the upper part of the basin,
106 consists of sedimentary and metamorphic Palaeozoic and Mesozoic rocks of the Iberian

107 Chain. The four described climatic areas in the Ebro Basin (Batalla et al., 2004) are the
108 Atlantic headwaters (annual average precipitation about 900 mm and contribution to runoff
109 23%), the west-central Pyrenees (950 mm, 31%), the eastern Pyrenees (800 mm, 41%) and
110 the southern Mediterranean zone (500 mm, 5%), with a mean annual runoff of approximately
111 6837.10^6 m^3 .



113

114 *Figure 1. a- General location of the Ebro basin in Spain, location of sampling points in the Ebro*
 115 *Basin. The main river was sampled upstream and downstream from the confluences of the main*
 116 *tributaries, numbers 1 to 5 (number 5 being Tortosa); the tributaries were sampled at numbers 7 to*
 117 *14. The Ebro outlet at Amposta (number 6; Cruzado et al., 2002) was sampled each month between*
 118 *June 2005 and May 2006. Groundwater was also sampled at two locations in the Ebro Basin (number*
 119 *15 Andosilla in Navarra; irrigation well at 6-m depth, and number 16 Lleida; irrigation well at 7-m*
 120 *depth). Long-term evolution of the mean monthly discharge of the Ebro river in Tortosa (number 5,*

121 *modified from Négrel et al., 2007). b- Geological sketch map of the Ebro Basin, modified from Luzón*
122 *et al., 2008 and Mochales et al., 2007).*
123

124 The discharge of the Ebro River decreased from around $590 \text{ m}^3 \text{ s}^{-1}$ in the “natural”
125 period 1914-1935, by 28% to $430 \text{ m}^3 \text{ s}^{-1}$ in the period 1960-1990 because of increased water
126 use for irrigation, reservoir storage and electricity production, and domestic consumption
127 (CHE, 1996; Ibáñez et al., 1996). The main water use is for irrigation with almost 700,000
128 irrigated hectares (total water demand of $6310 \text{ Hm}^3 \text{ y}^{-1}$, CHE, 1996; INE, 2003), causing a
129 huge hydraulic deficit. Nearly 60% of the surface area of the Ebro River Basin is covered by
130 agricultural land, and around 50% of Spain’s electricity is provided by hydroelectric power
131 plants along the Ebro system, causing another deficit. Around 14% of land use concerns urban
132 areas and industry, mainly located in the valleys.

133 More information on dissolved and suspended matter fluxes and weathering processes
134 can be found in the different investigations we have conducted in the Ebro River catchment
135 several, studying fluxes of (Négrel et al., 2007, 2016, 2021; Petelet-Giraud and Négrel, 2010).

136 **3 – Material and methods**

137 ***3.1. Water and rock sampling***

138 The Ebro River and its main tributaries were sampled in the centre of each river channel from
139 bridges (April 2006, Fig. 1). The main channel (samples 1 to 5, Fig. 1) was sampled upstream
140 and downstream from the confluences of the main tributaries (7 to 14, Fig. 1). In order to
141 monitor compositional variations over time in the river flow, the Ebro outlet at Amposta (6,
142 Fig. 1; Cruzado et al., 2002) was sampled each month between June 2005 and May 2006. To
143 provide an idea of the geochemical signature of potential groundwater input to surface water,
144 two groundwaters were also collected (15, Andosilla in Navarra; irrigation well G15 at 6-m
145 depth; and 16, Lleida; irrigation well GA-2 at 7-m depth). Representative gypsum, anhydrite

146 (4 samples) and carbonate (4 samples) bedrock samples were collected along the Ebro as well
 147 (Fig. 1, A to H; Table 1), halite is from University collection.

148

149 *Table 1: Rock type (gypsum, anhydrite and carbonate), sample ID, sampling station locations*
 150 *and deposit type, $\delta^7\text{Li}$ and Li content for the different bedrocks. Na and Sr contents, $^{87}\text{Sr}/^{86}\text{Sr}$*
 151 *ratios are from Négrel et al., 2021.*

152

Type	Reference	Samples	Deposits	$\delta^7\text{Li}$	Li	Na	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr
					mg g ⁻¹	mg g ⁻¹		μg g ⁻¹
gypsum	A	ABI-2	Miocene continental deposits	0.5	8.8	0.1	0.70818	2892
gypsum	B	MN14	Oligocene continental deposits	4.1	1.7	0.6	0.70830	2499
anhydrite	C	S3	Eocene marine deposits - Navarrese Potash Basin	13.6	9.2	2.7	0.70781	4590
anhydrite	D	TRIAS	Trias (Keuper) deposits	29.3	11.3	0.4	0.70766	2379
carbonate	E	S3 5.50m	Trias (Muschelkalk) limestone	12.6	3.4	0.7	0.70872	120
carbonate	F	ABC-4	Miocene continental deposits	17.7	7.7	1.2	0.70822	1035
carbonate	G	SA-40	Paleocene continental Garumnian facies	0.9	3.7	0.4	0.70779	511
carbonate	H	LFr2 14	Oligocene facies	15.3	1.4	0.8	0.70918	571
halite	Halites	HALITE	university collection	-	0.3	-	0.70864	2

153
 154

155 3.2 Methods

156 After collection, the water samples were filtered through pre-cleaned 0.45 μm acetate filters;
 157 100 mL was acidified with double-distilled nitric acid to pH around 2 and stored in pre-
 158 cleaned polyethylene bottles for major-cation analyses, and a further 100 mL was stored
 159 unacidified in polyethylene bottles for anion analysis. The water samples were analysed by
 160 ion chromatography for major ions, and by ICP-AES for Ca, Na, K, Mg and ICP-MS for trace
 161 elements (accuracy 5-10%) using protocols under accreditation. External and in-house
 162 standards as well as reference materials was used to calibrate and validate the values.
 163 Alkalinity was determined by the Gran titration method. We used HCl acid to titrate beyond
 164 the equivalence point. The quantity of acid added to the pH around 3 is used to determine this
 165 equivalence point with a mathematical method

166 Lithium-isotopic compositions (Millot et al., 2004) were measured with a Neptune
 167 Multi-Collector ICP-MS (Thermo Fisher Scientific). Chemical separation of lithium from the
 168 matrix before mass analysis used cationic resin (BioRad AG® 50 W-X12, 200–400 mesh)

169 and HCl acid (0.2 N) for 30 ng of lithium. Blanks for total chemical extraction were less than
170 20–30 pg Li, which is negligible as it represents a 10^{-3} blank/sample ratio. The $^7\text{Li}/^6\text{Li}$ ratios
171 were normalized to a $\delta^7\text{Li}$ determination of about 0.1–0.2‰ (2σ). Accuracy and
172 reproducibility of the total method (purification procedure + mass analysis) were tested by
173 repeated measurement of a seawater sample (IRMM BCR-403) after separation of lithium
174 from the matrix, for which we obtained a mean value of $\delta^7\text{Li}=+30.8\text{‰} \pm 0.4$ (2σ , $n=15$) over
175 the duration of the analyses. This mean value agrees with our long-term measurements
176 ($\delta^7\text{Li}=+31.0\text{‰} \pm 0.5$, 2σ , $n=30$).

177 **4 – Results**

178 Table 1 contains all analytical results for the different bedrocks and Table 2 contains data for
179 the river water and groundwater.

180

181 ***4.1. Bedrock***

182 The highest lithium content is observed in Trias-Keuper D anhydrite with a maximum around
183 $11.3 \mu\text{g g}^{-1}$, whereas the Oligocene B gypsum and Oligocene H carbonate have low lithium
184 contents (about 1.4 to $1.7 \mu\text{g g}^{-1}$). The $\delta^7\text{Li}$ ranges from +0.5 to +0.9‰ for the lowest values,
185 observed in Miocene A continental gypsum (Li content about $8.8 \mu\text{g g}^{-1}$) and in Paleocene G
186 continental carbonate (Li content about $3.7 \mu\text{g g}^{-1}$), up to +29.5‰ in Trias-Keuper D
187 anhydrite and a highest Li content of around $11.3 \mu\text{g g}^{-1}$.

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193 **4.2. Tributaries, Ebro main channel, and outlet survey**

194 The eight sampled tributaries of the Ebro River (Fig. 1) show a minimum Li content of around
 195 $12 \mu\text{g l}^{-1}$ in the Rio Aragon and a maximum value of $66.9 \mu\text{g l}^{-1}$ in the Rio Guadalope. The
 196 $\delta^7\text{Li}$ value ranges from $+12.9\text{‰}$ in Rio Matarrana to $+20.9\text{‰}$ in the Rio Cinca.

197 *Table 2: Sample ID, distance to Ebro source, river discharge ([CHE]), $\delta^7\text{Li}$ and Li content*
 198 *for surface water (Ebro survey at the Amposta station, Ebro main channel, tributaries, Fig. 1)*
 199 *and groundwater (Fig. 1) in the Ebro River Basin. Na and Sr contents, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios*
 200 *are from Négrel et al., 2021.*

Samples	Station	Sampling date	Distance to the source km	Discharge $\text{m}^3 \text{s}^{-1}$	$\delta^7\text{Li}$ ‰	Li $\mu\text{g L}^{-1}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr $\mu\text{g L}^{-1}$	Na $\mu\text{g L}^{-1}$
Ebro survey Amposta Station									
jun.	E6	6/15/2005	552	150.7	17.4	13.3	0.70847	1150	65
jul.	E6	7/15/2005	552	141.6	17.3	15.4	0.70848	1370	77
Aug.	E6	8/11/2005	552	119.0	17.7	16	0.70854	1759	141
Sep.	E6	9/20/2005	552	124.5	17.7	23.3	0.70859	2437	171
Oct.	E6	10/10/2005	552	118.3	18.9	28.3	0.70854	2488	239
Nov.	E6	11/14/2005	552	120.8	18.3	35.8	0.70857	2660	245
Dec.	E6	12/21/2005	552	300.0	17.6	32.8	0.70844	2490	142
Jan.	E6	1/17/2006	552	402.3	17.5	23.2	0.70841	1940	97
Feb.	E6	2/15/2006	552	173.0	17.6	17.9	0.70850	1540	84
Mar.	E6	3/14/2006	552	452.0	16.3	13.6	0.70842	1180	65
Apr.	E6	4/19/2006	552	202.1	17.9	15.2	0.70849	1250	69
May	E6	5/22/2006	552	225.3	17.3	12.5	0.70858	1120	55
Ebro main stream									
Miranda	E1	04/18-20-2006	104	-	17.1	5.3	0.70864	704	48
Lodosa	E2	04/18-20-2006	241	68.2	18.3	6.9	0.70856	855	42
Gallur	E3	04/18-20-2006	281	97.1	16.7	16.6	0.70837	1440	96
Presa de Pina	E4	04/18-20-2006	336	105.9	16.2	23.5	0.70842	1850	138
Tortosa	E5	04/18-20-2006	543	138.0	16.5	14.7	0.70849	1270	70
Tributaries									
Ega	E7	04/18-20-2006	216	7.8	15.4	16.3	0.70807	1210	128
Aragon	E8	04/18-20-2006	233	9.4	13.9	12	0.70814	973	88
Galliego	E9	04/18-20-2006	328	2.6	19.0	20.7	0.70861	1750	223
Huerva	E10	04/18-20-2006	324	-	20.2	40.9	0.70862	3200	101
Guadalope	E11	04/18-20-2006	397	80.9	17.1	66.9	0.70786	5090	68
Matarrana	E12	04/18-20-2006	457	3.8	12.9	14.8	0.70796	1280	21
Cinca	E13	04/18-20-2006	422	0.2	20.9	20.7	0.70877	1550	118
Segre	E14	04/18-20-2006	422	3.0	18.9	16.2	0.70897	1840	53
Groundwater									
G15	E15	04/18-20-2006	200	-	17.4	126	0.70840	7400	732
GA-2	E16	04/18-20-2006	370	-	18.1	21.1	0.70847	3020	262

201
 202
 203
 204 Similar to other studies of downstream and/or seasonal changes of lithium isotope
 205 ratios in river systems (Farber et al., 2004; Manaka et al. 2017; Pogge von Strandmann et al.,
 206 2017), we present their variation along the Ebro. Samples were collected from 100 km
 207 downstream of the river source to nearly the outlet, 450 km downstream.. The Li contents in
 208 tributaries, the main channel and the sampling-location distance from the source are plotted
 209 on Figure 2a, and the $\delta^7\text{Li}$ values on Figure 2b.

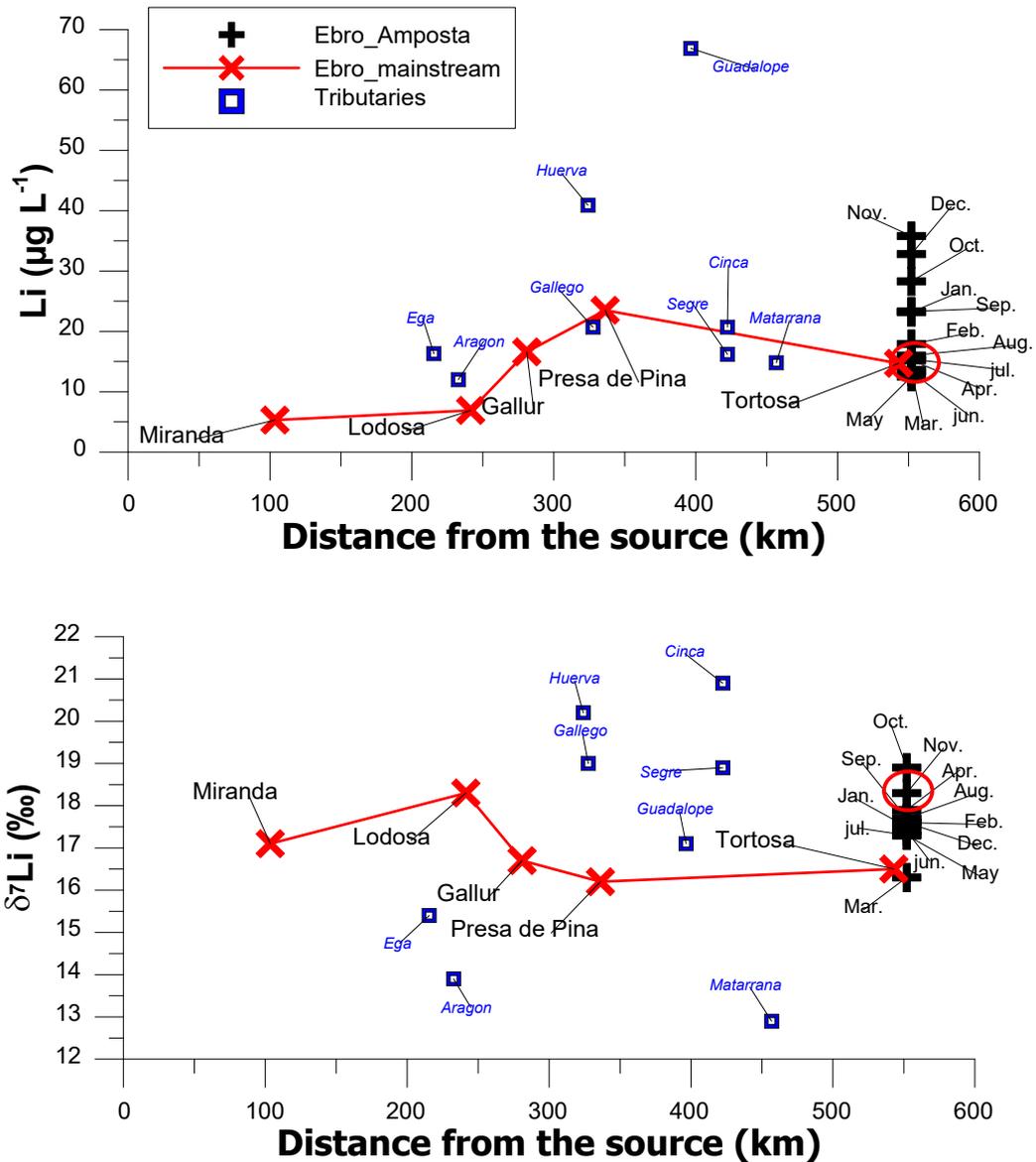


Figure 2a, b. (a) downstream variation of the Li concentrations ($\mu\text{g L}^{-1}$) and (b) $\delta^7\text{Li}$ (‰) values with distance from the source (0 km) to the outlet (500 km) for the Ebro main channel and tributaries. The variations at the outlet (Amposta, number 6 in Fig. 1a) are plotted with their sampling month; the red circle marks the Amposta sampling at the same time as the Ebro main-stream sampling.

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218 The Li content in samples collected along the Ebro increases from $5 \mu\text{g L}^{-1}$ farthest
219 upstream, to $23 \mu\text{g L}^{-1}$ 350 km downstream, and then decreases to $15 \mu\text{g L}^{-1}$ just before
220 Amposta. During the survey in Amposta, Li contents varied between $12 \mu\text{g L}^{-1}$ in May and
221 $36 \mu\text{g L}^{-1}$ in November. The $\delta^7\text{Li}$ values along the main channel increased slightly from
222 $+17.1\%$ in Miranda de Ebro up to $+18.3\%$ in Lodosa and then, until Tortosa, remained

223 invariant around +16.5‰ (Fig. 2b). At Amposta, the $\delta^7\text{Li}$ value ranged between +16.3 and
224 +18.9‰. Please note the difference between the $\delta^7\text{Li}$ values in Amposta and Tortosa (a few
225 km upstream), whereas Li contents remained similar. This agrees with the discrepancies noted
226 for the $\delta^{44}\text{Ca}_{\text{sw}}$ and Ca contents in the same sample set (Négrel et al., 2021). This difference
227 may be related to the fact that these isotopic systems are sensitive to fractionation processes
228 (Dellinger et al., 2015; Négrel et al., 2020; 2021), and to the presence of dams between
229 Tortosa and Amposta increasing fractionation (Gou et al., 2019), both factors influencing the
230 isotopic values. Concerning the dams, their physical role is the retention and release of water
231 stocks. Depending on the periods of filling and emptying, the water stocks have different ages
232 as shown by Négrel et al., (2016) using H-O isotopes of the water molecule. These filling -
233 emptying processes must affect the isotopic values of chemical elements like calcium and
234 lithium which are subject to fractionation processes.

235 The PHREEQ-C code (Parkhurst and Appelo, 1999) allows to calculate the
236 distribution of aqueous species in water samples and the saturation index for minerals based
237 on the water data (e.g. the temperature, pH, redox and the concentrations of chemical
238 elements) and using the database of the thermodynamic parameters of the minerals (e.g. the
239 most recent Lawrence Livermore National Laboratory LLNL database). None of the water
240 samples in the Ebro Basin were undersaturated with respect to gypsum and anhydrite when
241 calculated with PHREEQ-C.”Additionally, water samples of the tributaries and the Ebro were
242 systematically supersaturated for calcite, aragonite and dolomite. Samples from Amposta
243 showed various saturation degrees. Between December and May, the water samples were
244 undersaturated for calcite and dolomite (October to May for aragonite) and supersaturated
245 between June and November (or September for aragonite).

246

247 **5 – Discussion**

248 249 *5.1 Relative contribution to the dissolved Li load*

250 It is generally agreed that dissolved Li in most of the world's major rivers comes from silicate
251 weathering, and that the fraction derived from carbonate rocks or evaporite is negligible (e.g.,
252 Kisakürek et al., 2005; Gou et al., 2019; Murphy et al., 2019; Martin et al., 2020). In addition,
253 atmospheric deposition from cyclic salts plays a very minor role in the dissolved Li budget
254 (Dellinger et al., 2015; Song et al., 2021). To overcome this input on the Ebro Basin, we
255 corrected only for marine aerosols using the characteristics of modern seawater

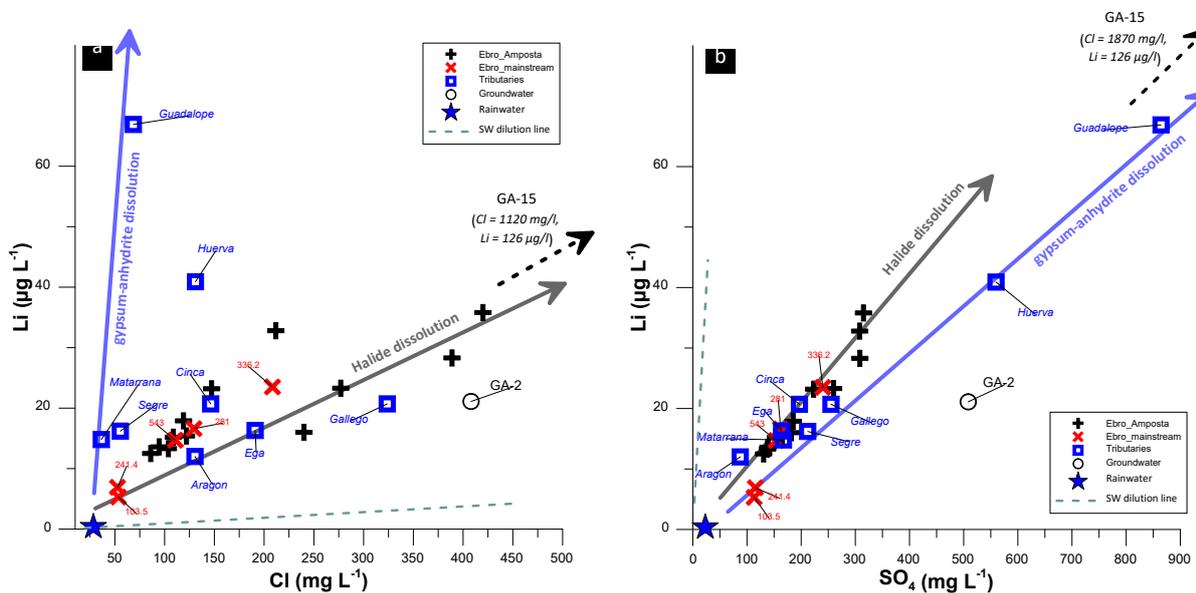
256 The Li concentration from atmospheric input is given by multiplying the Cl
257 concentration from rainwater by the Li/Cl ratio in seawater (Négrel et al., 1993; Dellinger et
258 al., 2015). With a maximum estimated chlorine concentration of 85 $\mu\text{mol L}^{-1}$ deriving from
259 marine input (Avilla and Alarcon, 1999), and a seawater Li/Cl ratio of 5×10^{-5} (Milot et al.,
260 2010a), the calculated Li input from rain is low, with a maximum estimated contribution of
261 rainwater-derived Li in the Ebro Basin of 0.04-0.20% for the main tributaries, 0.10-0.40% for
262 the Ebro, and 0.09–0.20% for the outlet. In the Ebro Basin, due to its geological framework,
263 the contribution of carbonate and evaporite dissolution to the dissolved load should be the
264 major input, while the one from silicate can be ignored (Négrel et al., 2007; 2021; Petelet-
265 Giraud and Négrel, 2010).

266 Figure 3 shows the binary plots between chemical elements in Ebro water, Li is
267 compared to Cl (Fig. 3a) and SO_4 (Fig. 3b). The dissolved load of the Ebro basin (tributaries,
268 main channel, outlet and groundwater) is clearly controlled by gypsum/anhydrite and halite
269 dissolution; few or none of the samples are close to the seawater dilution line regardless of the
270 concentrations (Ega and GA2 groundwater (16, Fig. 1). As can be seen in Figures 3, two main
271 evolution trends explaining most of the Ebro Basin samples, namely the halite-dissolution and

272 gypsum/anhydrite -evolution lines, respectively constrained by variations in Cl and in SO₄
 273 concentration.

274 In the Cl vs. Li plot (Fig. 3a), the gypsum/anhydrite -evolution line explains the
 275 sample values in the Matarrana, Segre and Guadalope tributaries. The halite-dissolution line
 276 explains the Aragon, Ega and Gallego tributaries, as well as the samples from the Ebro at
 277 103 km and 241 km from the river source, several outlet results, and groundwater GA15. The
 278 rest of the samples plot between these two trends. In the SO₄ vs. Li plot (Fig. 3b), the
 279 gypsum/anhydrite -evolution line explains the Gallego, Huerva, Segre and Guadalope
 280 tributaries, the Ebro sample at 103 km and 241 km from the river source, and groundwater
 281 GA15. The halite-dissolution line explains the Matarrana, Ega, Aragon and Cinca tributaries,
 282 the Ebro samples at 281 km, 336 km and 543 km from the source, and all samples from the
 283 outlet surveys.

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286 *Figure 3. Data from the Ebro Basin regarding tributaries, main channel, outlet and*
 287 *groundwater for concentrations of (a) Cl vs. Li, and (b) SO₄ vs. Li (all values in µg L⁻¹).*
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289 The distribution along the two main evolution lines confirms that evaporite weathering
 290 plays an important role in controlling Li concentrations, as shown for Cl–SO₄ (Négrelet et al.,

291 2007; Petelet-Giraud and Négrel, 2010). This is in agreement with Isidoro and Aragüés,
292 (2007) who argue that the salinity of water in the Ebro basin originates from three major
293 sources, associated with three minerals, namely gypsum/anhydrite, halite and calcite.
294 Regarding a possible anthropogenic control on Li concentrations, in addition to bedrock
295 sources of dissolved chloride-sulphate, the streams in the Ebro Basin are likely to integrate
296 input from farming and industrial activities. Pollutant investigations have revealed high
297 concentrations near industrial sites for persistent organic pollutants and heavy metal (Bovolo
298 et al., 2011). Among framing impacts, the main pressure on water quality in the Ebro basin is
299 from irrigated areas through the irrigation return flow. The different components of the
300 irrigation return flow are bypass waters, tail-waters and subsurface drainage waters that may
301 be enriched in phosphorous, pesticides, salts and agrochemicals (Aragüés and Tanji, 2003)
302 and constitute generally the primary source of pollution. Heavy metal, pesticide and nutrient
303 pollution are widespread in relation to farming activities (pesticides and fertilizers
304 uses). Nitrates fluctuate little, between 4 mg L⁻¹ (Gallego) and 19 mg L⁻¹ (Huerva) for the
305 maximum range observed in tributaries. Regarding the Ebro itself, the highest NO₃ value
306 (16 mg L⁻¹) is observed at 281 km from the river source, decreasing to 9 mg L⁻¹ at 543 km
307 from the source. All outlet survey samples agree with this range of values (6 to 14 mg L⁻¹).
308 No relation is observed between NO₃ and Li concentrations and NO₃ and Cl concentrations,
309 except that the highest NO₃ values correspond to the lowest Li ones. This shows the unrelated
310 behaviour of these elements and the fact that no anthropogenic agricultural or industrial
311 influence on Li can be detected in the Ebro Basin. Even in the two groundwater samples, the
312 high NO₃ concentrations (GA2 = 56 mg L⁻¹, GA15 = 88 mg L⁻¹) are not mirrored by high Li
313 contents, confirming the different origins of Li and NO₃, with a major lithological control for
314 Li.

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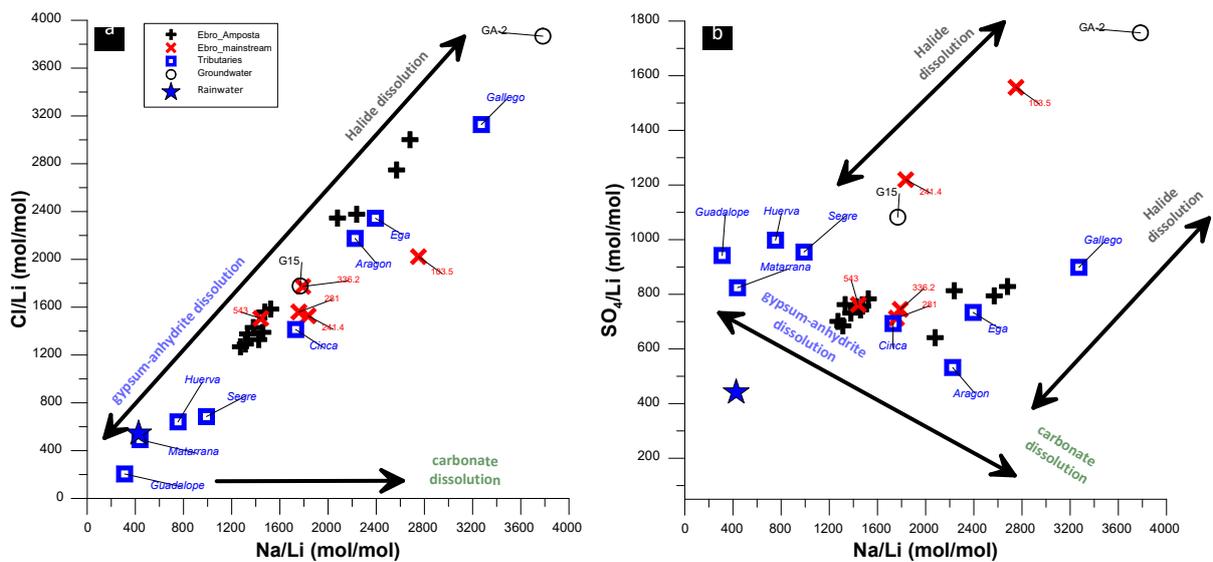
316 **5.2 Constraints added by Li isotopes: lithological control and fractionation processes**

317 It is now well agreed that $\delta^7\text{Li}$ values in river waters are higher than in the parent rocks, due to
 318 the strong fractionation between the ^7Li and ^6Li isotopes during weathering (e.g., Huh et al.,
 319 1998; 2001; Pistiner and Henderson, 2003; Kisakurek et al., 2005; Vigier et al., 2008; Millot
 320 et al., 2010a; Verney-Carron et al., 2011, Dellinger et al., 2015; Wang et al., 2015; Bagard et
 321 al., 2015; Négrel and Millot, 2019; Gou et al., 2019; Steinhöfel et al., 2021). While the ^6Li
 322 isotope is preferentially retained and incorporated into secondary weathering products such as
 323 clays and oxides, the ^7Li isotope is enriched in the dissolved load, leading to relatively high
 324 $\delta^7\text{Li}$ values in rivers.

325 The $\delta^7\text{Li}$ values are commonly correlated with the Na/Li ratio (Millot et al., 2010;
 326 Dellinger et al., 2015; Wang et al., 2015; Négrel et al., 2020) and less with the Cl/Li and
 327 SO_4/Li ratios (Liu et al., 2011). Figure 4 plots Na/Li ratios *versus* Cl/Li (4a) and SO_4/Li (4b)
 328 ones and, in addition to the halite and gypsum/anhydrite dissolution end-member, we consider
 329 here Parker's (1967) carbonate dissolution end-member.

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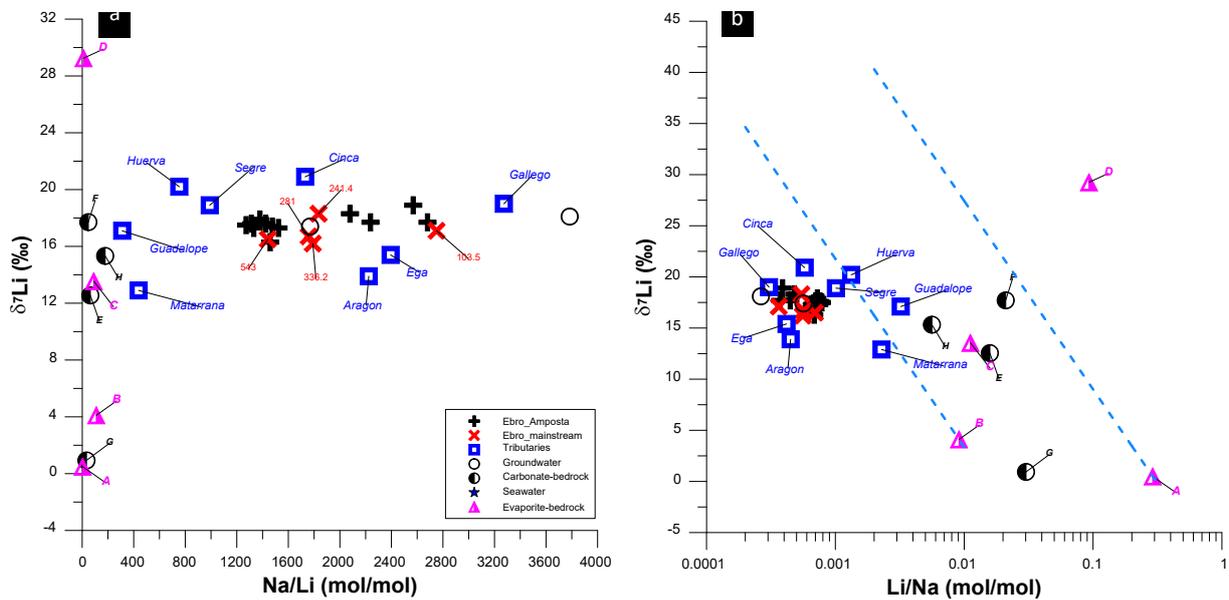


333 *Figure 4. Data from the Ebro Basin concerning tributaries, main channel,*
334 *outlet and groundwater for concentrations of: (a) Na/Li vs. Cl/Li ratios (in mol/mol), (b)*
335 *Na/Li vs. SO₄/Li ratios (in mol/mol).*

336
337 Na/Li *versus* Cl/Li ratios (Fig. 4a) show the role of halite and gypsum/anhydrite psum
338 dissolution, but less that of carbonate. All samples plot along a linear trend with increasing
339 Na/Li and Cl/Li ratios. More precisely than the relationships shown on Figure 3, because
340 concentration effects are reduced when using element ratios, it appears that the Guadalupe,
341 Matarrana, Huerva and Segre tributary samples agree with gypsum/anhydrite dissolution,
342 whereas the Gallego, Ega and Aragon ones and GA2 (groundwater) reflect the dissolution of
343 halites. The Ebro samples at 103.5 km from the source appear shifted to the right due to
344 carbonate dissolution, but some samples from the outlet surveys (August to November) are
345 more influenced by halite dissolution when compared to the rest of the survey. The Na/Li
346 *versus* SO₄/Li ratios (Fig. 4b) reflect a more complex behaviour. Guadalupe, Matarrana,
347 Huerva and Segre still agree with gypsum/anhydrite dissolution, but Aragon and Cinca for the
348 tributaries, and samples from the Ebro and the outlet show a lowering of SO₄/Li ratios
349 through carbonate dissolution. Gallego and Ega tributary samples and the August to
350 November ones for the outlet are also affected by halite dissolution. Na and Li thus seem to
351 be good indicators of rock-weathering processes in the Ebro Basin, combined as either Na/Li
352 or Li/Na ratios.

353 It is generally accepted that a positive relationship between the Na/Li molar ratio and
354 the $\delta^7\text{Li}$ value relates to silicate weathering (Millot et al., 2010; Liu et al., 2011; Dellinger et
355 al., 2015; Wang et al., 2015; Négrel et al., 2020; Steinhoefel et al., 2021), whereas no
356 relationship exists when water is strongly affected by evaporite dissolution (Liu et al., 2011;
357 Wang et al., 2015). In the case of water-evaporite interaction, the Na/Li molar ratio can
358 fluctuate strongly (200 to 550 on the Qinghai-Tibet Plateau; Liu et al., 2011), but less than the
359 variation observed in the Ebro Basin (400 to 3800; Fig. 5a).

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Figure 5. (a) Relationship between dissolved $\delta^7\text{Li}$ values and molar Na/Li ratios in samples from the Ebro Basin (tributaries, mainstream, outlet, groundwater) and from bedrock. (b) Relationship between dissolved $\delta^7\text{Li}$ values and molar Li/Na ratios with the simple Rayleigh fractionation model (dotted lines).

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Referring to Figure 5, the Segre, Huerva, Matarrana and Guadalupe samples are influenced by gypsum/anhydrite dissolution, whereas the Aragón, Gallego and Ega ones show halite-dissolution influence. Thus (Fig. 5a), as these two groups of rivers constitute the extremes of the Na/Li molar-ratio values, the main influence on this ratio is that of the nature of the weathered rocks rather than a fractionation effect (see below). The main feature of Figure 5a is the evidence of two end-members in the tributaries, one marked by gypsum/anhydrite dissolution with low Na/Li molar ratios and the other one marked by halite dissolution with a higher Na/Li molar ratio. Both end-members help explaining the variations observed in the Ebro itself and at the outlet, even if the variations are more marked for the Na/Li molar ratios rather than on the $\delta^7\text{Li}$ values (Fig. 2a). This scheme reflects a mixing for Li and its isotopes in water being mainly affected by evaporite dissolution, even if the role of carbonate dissolution (less marked in Na concentrations) and a possible influence of Li-

380 isotope fractionation cannot be precluded. The samples collected along the Ebro itself evolve
381 along this mixing scheme. The most upstream value corresponds to an end-member
382 characterized by halite dissolution, and farther downstream the samples are increasingly
383 marked by a component defined by gypsum/anhydrite dissolution. Most of the samples
384 collected at the Ebro outlet can be explained by a component characterized by
385 gypsum/anhydrite dissolution, except for the samples from August to December, with a
386 higher influence of the end-member defined by halite dissolution. Using O and H isotopes,
387 Négrel et al. (2016) showed that from September to November, the Ebro at the outlet is
388 mostly supplied by groundwater and some water retained by dams, as the main river discharge
389 is low. This causes a data shift towards the halite-dissolution end-member, which is well
390 reflected in the groundwater sample that exceeds the Na/Li molar ratio in the Gallego and
391 Cinca waters, reflecting a large influence of evaporite dissolution. This can be due to a double
392 influence of mainly halite dissolution and, secondarily, gypsum/anhydrite dissolution (Figs 2a
393 and 2b) for the E16 groundwater sample from a 7-m-deep irrigation well in Lleida (16,
394 Fig. 1).

395 In order to complete this interpretation, we tentatively applied the simple Rayleigh
396 fractionation model (Fig. 5b) that can describe Li removal from water to secondary phases,
397 using the Li/Na molar ratio and the $\delta^7\text{Li}$ values (Bagard et al., 2015; Manaka et al., 2017).
398 This model is described by the general equations:

$$399 \quad \delta^7\text{Li}_w = \delta^7\text{Li}_i + 1000(\alpha - 1) \ln(f_w^{\text{Li}}) \quad (\text{Eq. 1})$$

$$400 \quad f_w^{\text{Li}} = \text{Li}/\text{Na}_w / \text{Li}/\text{Na}_i \quad (\text{Eq. 2})$$

401 where $\delta^7\text{Li}_w$ and $\delta^7\text{Li}_i$ are the Li isotope composition of the dissolved phase w and its initial
402 value in the rocks i, α is the fractionation factor, and f_w^{Li} is the Li fraction remaining in the
403 dissolved phase.

404 However, such a model requires an initial value for calculating the fractionation effect
405 on the Li isotopes. Due to the congruent dissolution of evaporite deposits, we applied Eq. 1 on
406 two initial values representative of the extreme rock end-members, and then examined the
407 Rayleigh fractionation curves obtained by applying Eqs. 1 and 2. These end-members are the
408 two gypsum samples, one from Miocene continental deposits (A in Table 12) with a $\delta^7\text{Li}_i$ of
409 0.49 and Li/Na_i of 0.29, and the other from Oligocene continental deposits (B in Table 1) with
410 a $\delta^7\text{Li}_i$ of 4.11 and Li/Na_i of 0.0091. Values generally used for the fractionation factor α range
411 from 0.996 to 0.993 (Bagard et al., 2015; Manaka et al., 2017)—the latter being accepted for
412 the Ganges, and down to 0.991 for the Amazon River (Dellinger et al., 2015). This range of
413 the fractionation factor α is generally used for silicate weathering studies (Golla et al., 2021),
414 or for large watersheds of varied geology, such as the Ganges or Amazon Basins (Dellinger et
415 al., 2015; Pogge von Strandmann et al., 2021; Yoshimura et al., 2021).

416 Figure 5b illustrates the relationship between dissolved $\delta^7\text{Li}$ values and molar Li/Na
417 ratios, with the simple Rayleigh fractionation model from Eqs. 1 and 2. Guadalupe plots
418 within the fractionation lines, but Mattarana and Huerva (and Segre to a lesser extent) plot
419 along fractionation line starting from sample B (Oligocene continental deposits). However,
420 most of the $\delta^7\text{Li}$ values of the water samples in the Ebro plotted away from the fractionation
421 line for $\alpha=0.992$ chosen on Fig. 5b. This value of 0.992 is close to the α calcite-solution given
422 by Day et al. (2021). It therefore seems confirmed that the Rayleigh fractionation model, as
423 described in Equation 1 and shown on Figure 5b, is not valid in the case of the Ebro. This may
424 be explained by three points. The first concerns the non-removal of Li from water to
425 secondary phases caused by the presence of many dams on the river and its tributaries that
426 trap the suspended load, which is reduced to a few mg/L at Amposta (Négrelet et al., 2007)
427 precluding this process. The second explanation concerns the impossibility of applying a
428 fractionation model in this particular case, which may be due to the fact that i) the model was

429 generally applied in rivers draining silicates (Kisakurek et al., 2005; Millot et al., 2010a;
430 Dellinger et al., 2014; 2015), and that ii) the derived α values were defined under specific
431 weathering conditions or in laboratory experiments, but not under evaporite and carbonate
432 weathering (Song et al., 2021). The third explanation concerns another process that can
433 control Li at the Ebro Basin scale: in the limestone-evaporite dominated rivers from the Ebro
434 Basin, we have modelled the Sr isotopes as a mixture between carbonate and evaporite
435 endmembers that cover the variability of all samples from the Ebro Basin (Négrel et al.,
436 2021). This reinforces the major role of mixing processes in the Ebro Basin rather than
437 fractionation processes, previously reported and discussed for silicate rocks.

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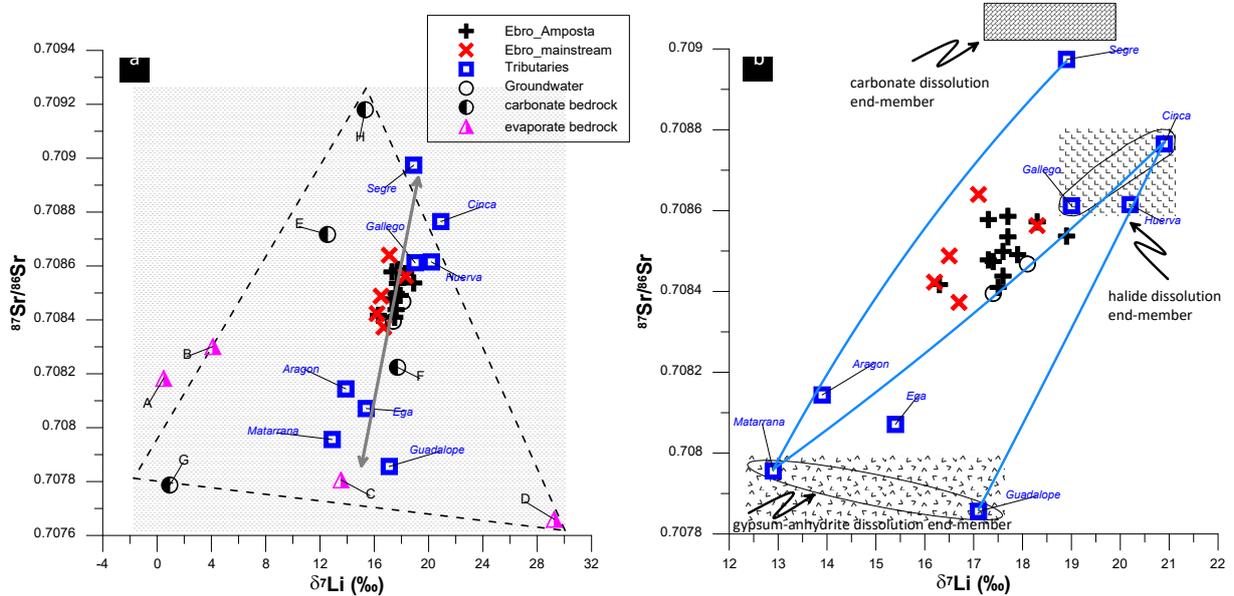
439 *5.3 Coupling Li and Sr isotopes: lithological control and mixing processes*

440 Several studies (Phan et al., 2016; Manaka et al., 2017) have shown that $\delta^7\text{Li}$ combined with
441 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes has the potential of distinguishing between the different rock types subject
442 to weathering, or of explaining mixing processes (Henrichi et al., 2016; Li et al., 2020). Sr
443 isotopes are a robust tracer of mixing because these isotopes do not fractionate (Millot et al.,
444 2011) and combine with Li when the effects of weathering (and/or mixing) supplant those of
445 the fractionation between water and secondary phases (Schmitt et al., 2012). Figure 6a
446 illustrates the relationship between $\delta^7\text{Li}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the dissolved load from
447 the Ebro Basin and the various carbonate and evaporite bedrocks. We first note that the Li and
448 Sr isotopes are scattered in the different bedrocks, whose three apexes are the carbonates G
449 (continental Paleocene) and H (Oligocene carbonate), and the evaporite D (Trias anhydrite).
450 Furthermore, all water samples collected in the Ebro Basin lie within the area defined by the
451 bedrocks and define a positive trend (grey arrow on Fig. 6a). Négrel et al. (2021) found that
452 the Sr-isotope levels in the Aragon, Ega, Matarrana and Guadalope samples are explained by
453 a mixing scheme that is mainly influenced by evaporite weathering (gypsum/anhydrite and

454 halite), whereas the Huerva, Gallego, Cinca and Segre samples show a shared role of
 455 evaporite (halites) and carbonate weathering.

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459 *Figure 6. a - Relationship between dissolved $\delta^7\text{Li}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the samples*
 460 *from the Ebro Basin (tributaries, mainstream, outlet, groundwater) and bedrock (A to H,*
 461 *Table 1).*

462 *b - Extended view of the relationship between the $\delta^7\text{Li}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Ebro*
 463 *basin samples. The carbonate end-member is from Négrel et al., 2021 and this study). Solid*
 464 *lines show theoretical mixtures between the different end-members.*
 465

466 The relationships between several end-members in Figure 6a are represented by
 467 hyperbolae (Langmuir et al., 1978; Négrel et al., 2010) and can be expressed as by equation 3,
 468 below, I_{mix} being the isotope composition of the mixed solution:

469
$$I_{\text{mix}} = \left\{ \frac{[]_a \times I_a \times m}{[]_{\text{mix}}} \right\} + \left\{ \frac{[]_b \times I_b \times (1 - m)}{[]_{\text{mix}}} \right\} \quad (\text{Eq. 3})$$

470 where $[]_a$, $[]_b$ and $[]_{\text{mix}}$ are the Li or Sr concentrations for the solution mix from two end-
 471 members a and b, I_a , I_b and I_{mix} are the Li or Sr isotope compositions or value for the solution
 472 mix from two end-members a and b, and m is the mixing proportion.

473 Figure 6b shows the relationships between the $\delta^7\text{Li}$ values and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and
 474 the mixtures between different end-members are represented by curves according to Eq. 3.

475 Considering only mixing processes, all samples are explained by mixing lines with different
476 end-members, here represented by the Matarrana and Guadalope samples for the
477 gypsum/anhydrite dissolution end-member, and by the Cinca and Gallego ones for the halite
478 dissolution end-member (Figs. 4 and 5). Négrel et al. (2021) found that the Segre water is
479 strongly influenced by carbonate dissolution, and was therefore selected to represent this end-
480 member. Mixtures between Matarrana-plus-Segre and Guadalope-plus-Cinca (and a mixture
481 between Matarrana and Cinca) explain all Li-Sr relationships in the Ebro Basin samples. This
482 mixing scheme again illustrates the major role of evaporite dissolution on Li isotopes, with a
483 non-negligible role of carbonate dissolution, generally considered to be weak in controlling
484 the lithium cycle in watersheds (Kisakurek et al., 2005; Wang et al., 2015).

485

486 **6 – Conclusions**

487

488 The Ebro River Basin is the largest catchment of the Iberian Peninsula and one of the largest
489 in the Mediterranean region. Investigations of surface waters and groundwaters defined a
490 detailed behaviour of Li isotopes in the weathering environment at catchment scale. In the
491 rivers dominated by limestone-evaporite bedrock, the waters are isotopically in accordance
492 with the bedrock for their $\delta^7\text{Li}$ signatures.

493 Li, Cl and SO_4 concentrations show that they are controlled by evaporite weathering,
494 and that a possible anthropogenic agricultural or industrial influence on Li concentrations can
495 be discarded. The Na/Li, $\delta^7\text{Li}$, Cl/Li and SO_4/Li ratios reflect the role of halite dissolution for
496 some tributaries, gypsum/anhydrite dissolution dominates others, but the role of carbonate
497 weathering is minor. Samples from the Ebro main channel and from the outlet logically
498 showed a mix of waters.

499 Application of the Rayleigh fractionation model cannot explain the observed data. This
500 fact reinforces the major role of mixing processes in the Ebro Basin as fractionation cannot
501 explain the mineral concentrations in most samples. The mixing model is further confirmed
502 by comparison of $\delta^7\text{Li}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

503 Compared with results from other large basins, such as the Amazon, Congo and
504 Ganges-Brahmaputra ones, as well as with data from much smaller catchments and even soil
505 profiles, our study confirms that lithium isotopes are a powerful tool for tracing basin
506 evolution, through different weathering regimes, relief and climate conditions observed in
507 various bedrock-types catchments, including carbonate-evaporite-dominated catchments.

508

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520

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