

This item is the archived peer-reviewed author-version of:

Sea spray influences water chemical composition of Mediterranean semi-natural springs

Reference:

Fernandez-Martinez Marcos, Margalef O., Sayol F., Asensio D., Bagaria G., Corbera J., Sabater F., Domene X., Preece Catherine.- Sea spray influences water chemical composition of Mediterranean semi-natural springs
Catena: an interdisciplinary journal of geomorphology, hydrology, pedology - ISSN 0341-8162 - 173(2019), p. 414-423
Full text (Publisher's DOI): <https://doi.org/10.1016/J.CATENA.2018.10.035>
To cite this reference: <https://hdl.handle.net/10067/1545950151162165141>

1 **Sea spray influences water chemical composition of**
2 **Mediterranean semi-natural springs**

3 **Authors:** M. Fernández-Martínez^{*1,2}, O. Margalef^{3,4}, F. Sayol³, D. Asensio^{3,4}, G. Bagaria³,
4 J. Corbera², F. Sabater^{2,4,5}, X. Domene^{3,6}, C. Preece^{3,4}.

5 **Affiliations:**

6 ¹ Centre of Excellence PLECO (Plant and Vegetation Ecology), Department of Biology,
7 University of Antwerp, Wilrijk, 2610, Belgium

8 ² ICHN, Delegació de la Serralada Litoral Central, Mataró, 08302, Catalonia, Spain

9 ³ CREAF, 08193 Bellaterra (Cerdanyola del Vallès), Catalonia, Spain

10 ⁴ CSIC, Global Ecology Unit, CREAF-CSIC-UAB, 08193 Bellaterra (Cerdanyola del
11 Vallès), Catalonia, Spain

12 ⁵ Department of Ecology, University of Barcelona, Barcelona, 08028, Catalonia, Spain

13 ⁶ Department of Animal Biology, Plant Biology and Ecology, Autonomous University of
14 Barcelona, Cerdanyola del Vallès, 08193, Barcelona, Catalonia, Spain

15 ***Corresponding author**

16 Marcos Fernández-Martínez

17 E-mail address: marcos.fernandez-martinez@uantwerpen.be

18

19 **Keywords:** Groundwater, ions, trace elements, sea aerosol

20 **Abstract**

21 Sea spray aerosol (SSA) is responsible for the large-scale transfer of particles from
22 the sea to the land, leading to significant deposition of a range of ions,
23 predominantly Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Cl^- . Up to now, there has been little
24 research into the effects of SSA on spring water chemistry. Therefore, we sampled
25 303 semi-natural springs across Catalonia (NE Iberian Peninsula) and analysed
26 the concentrations of 20 different ions and elements, and determined the impact of
27 SSA (using distance to the coast as a proxy) as well as climate, lithology and
28 human disturbances. We found that distance to the coast had a clear effect on the
29 water chemical composition of springs, while accounting for potentially confounding
30 factors such as anthropogenic water pollution (nitrate, NO_3^-), differences in
31 lithology and annual rainfall. Our results showed that springs located closer to the
32 coast had higher Cl^- , SO_4^{2-} , Na^+ , Mg^{2+} , K^+ and Ca^{2+} concentrations than those of
33 springs located further away. Precipitation was generally negatively correlated with
34 the concentration of almost all elements analysed. The concentration of NO_3^-
35 increased with distance to the coast, concurrently with farming activities, located
36 mainly inland in the study area. These results demonstrate that SSA has an
37 important effect on the groundwater of coastal zones, up to a distance of around 70
38 km from the coastline. This analysis reveals the main natural and human
39 processes that influence spring water chemistry in this Mediterranean region,
40 information that could be helpful in similar regions for ecological studies, water
41 quality policies, and for the improvement of predictions in the current context of
42 global change.

43 **1. Introduction**

44 Sea spray aerosol (SSA) is the collection of particles directly produced by wind
45 driven processes that leads to the ejection into the atmosphere of bursting bubbles
46 at the air-sea interface (Gorham, 1957; Quinn et al., 2015). SSA is one of the
47 largest pools of global atmospheric aerosols (Grythe et al., 2014; Quinn et al.,
48 2015) and the process of sea spray formation is favoured by wind speed that
49 exponentially increases the number and weight of salt particles in the atmosphere
50 (Woodcock, 1953). These particles can range in size from 0.02 to 60 μm , and
51 smaller particles can remain in suspension in the air for days at around 1000 and
52 2000 meters above the sea level (de Leeuw et al., 2011; Gong et al., 1997; Junge
53 and Gustafson, 1957). This process allows a potential translocation of SSA far
54 away from its original source. The majority of larger ($>1 \mu\text{m}$) particles are formed of
55 sea salt, meaning NaCl (and the ions Na^+ and Cl^-) and other alkali metals and
56 alkaline earth metals (e.g. K^+ , Mg^{2+} and Ca^{2+}) (Bertram et al., 2018; Cochran et al.,
57 2017). Fine particles ($<0.3 \mu\text{m}$) comprise around 90% of the particles (but around
58 5% of their total mass), and contain a higher proportion of organic species (e.g.
59 lipids and alkanes) (Bertram et al., 2018; Cochran et al., 2017).

60 These aerosols stay mainly in liquid form in the atmosphere and contribute to the
61 scattering of salts into inland waters, accounting for as much as 10% of the salts in
62 some regions (Starinsky et al., 1983) and having an important role for the
63 atmospheric cycles of scarce elements (Gong et al., 1997). The removal of sea
64 spray from the atmosphere occurs by three main processes: fallout by gravity,
65 retention by obstacles such as vegetation, and rain washout (Junge and

66 Gustafson, 1957). Additionally, rainfall also washes down salts retained by
67 vegetation, potentially increasing salt concentrations in lakes, rivers and
68 groundwater (Eriksson, 1955; McDowell et al., 1990).

69 The influence of sea salt deposition on coastal areas because of SSA has been
70 long studied from different disciplines. Several studies have pointed out that
71 coastal regions are subjected to higher rates of sea salt deposition, specifically of
72 Cl⁻, Na⁺, Mg²⁺ and K⁺ (Granatt, 1972; Hedin et al., 1994; McDowell et al., 1990; Vet
73 et al., 2014) especially when winds blow from the sea side (Dimitriou et al., 2017;
74 Izquierdo et al., 2014, 2013). Eventually, chronic deposition of sea salt can change
75 soil mineral composition (Dahms, 1993; Hedin et al., 1994; Kennedy et al., 1998;
76 Whipkey et al., 2000) and potentially affect soil weathering, something that could
77 affect the composition of groundwater (Silva et al., 2017; Starinsky et al., 1983),
78 lakes and rivers (Sullivan et al., 1988). Hence, SSA can potentially differentiate
79 water chemical composition of coastal regions from inland regions, which may
80 have large-scale impacts on ecosystem structure and function (Bes et al., 2018;
81 Fernández-Martínez et al., 2017, 2014) as well as water quality for human supply.
82 Although there are several studies that report an effect of SSA on the composition
83 of groundwater (Silva et al., 2017; Starinsky et al., 1983), lakes and rivers
84 (Eriksson, 1955; Sullivan et al., 1988), little attention has been devoted to its
85 influence on spring water chemistry, either influenced by deep groundwater or soil
86 and surface processes. For instance, Na⁺ and K⁺ deposition could force the
87 release of other cations captured in the cation exchange complex of the soil
88 (mostly occupied by Na⁺, K⁺, Mg²⁺, Ca²⁺, and H⁺) in a process called sodization

89 (Shainberg and Letey, 1984), potentially causing Ca^{2+} and Mg^{2+} enrichment of
90 groundwater. Additionally, human activities could mask the effect of SSA on
91 groundwater, for example, by increasing nitrate and levels of other ions because of
92 fertilization and other agricultural activities.

93 In this study, we analysed the concentration of a range of ions and elements (Na^+ ,
94 K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , Al, As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Hg, Ni
95 and Zn) in the water of 303 semi-natural springs distributed across the NE Iberian
96 Peninsula, (**Figure 1, Figure S1**) a region that is representative of the
97 Mediterranean basin. This allowed us to study the effect of SSA on groundwater
98 composition while taking into account the effects of other environmental factors
99 such as climate, lithology and human disturbances. Our main aim was to quantify
100 the net effect of SSA on water composition of springs, using the distance to the
101 coast as the proxy indicator of sea influence. We hypothesised that sea spray
102 could lead to substantial enrichment of water with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and
103 SO_4^{2-} in coastal springs compared to those located further inland, as well as
104 enrichment resulting from cation release from the cation exchange sites as a result
105 of Na^+ or K^+ intake to soils.

106

107 **2. Material and methods**

108 *2.1 Area of study*

109 We surveyed 303 water springs along a south-to-north and east-to-west gradient
110 across the north-eastern Iberian Peninsula from the Mediterranean sea to the Pre-

111 Pyrenees (**Figure 1**), with distance to the sea coast from 5 to 140 km. The
112 surveyed area comprised a wide geographical area and a variety of anthropogenic
113 and biophysical conditions. Climate differed considerably amongst sites, mostly
114 associated with altitude, with mean annual precipitation ranging from around 550 to
115 1200 mm, comprising maritime, continental, humid and sub-humid and Pyreneal
116 Mediterranean climate according to Martín-Vide (1992).

117 The surveyed springs were located over different types of lithology. The coastal
118 territory surveyed mostly consisted of granodiorites and other types of granitoids,
119 except for some regions dominated by shales and phyllites and other metamorphic
120 rocks (Fernández-Martínez et al., 2016; Sabater et al., 2015). Inland, we found
121 very rich lithology, with some of the springs located over granite, granodiorites,
122 shales, phyllites, silicic sandstones and micritic limestones, while some others
123 were located over sand and siltstones and marls, predominantly of calcareous
124 lithology. Further inland, and approaching the Pyrenees, the surveyed area
125 consisted of Quaternary volcanic field (basalts) developed over paleogene
126 conglomerate, sandstones, mudstones and marls. The Pyrenees area surveyed
127 was geologically complex, but most of the sampled springs were located over
128 limestones, shales or calcareous clastic rocks.

129 *2.2 Field sampling and analyses*

130 The springs surveyed were human-made constructions to force the water to flow
131 through a spout (**Figure S1**), which is a traditional practice of the area intended to
132 provide drinking water for humans and cattle. Some of the springs were built in

133 naturally occurring springs while others drained water mines (collecting water from
134 aquifers). None of the surveyed springs received any kind of sanitization. Surveys
135 of the springs were carried out during spring and autumn of the years 2013, 2015,
136 2016 and 2017. Only open flow springs were sampled, i.e. those not controlled by
137 a tap, although in some springs drought can interrupt water flow in dry periods.
138 Water pH and conductivity were analysed in the field with a pHmeter and
139 conductivity meter. Alkalinity was also measured *in situ* for a subset of 61 springs
140 using a strong acid (sulphuric acid, 0.02 mol L⁻¹), a fixed volume of water sample
141 (25 mL) and methyl blue as the indicator (changing colour at pH = 4.5). Main ions
142 were analysed in the laboratory following previously described protocols (Àvila,
143 1996; Àvila and Rodà, 2002). A sample of the flowing water was filtered through a
144 glass fibre filter disk of 0.7 µm and stored in the laboratory at -20 °C until the
145 moment of the analyses. Ion chromatography was used to determine the
146 concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻. Concentrations of
147 NH₄⁺ were undetectable in all springs (<0.1 µeq L⁻¹). Phosphate (PO₄³⁻)
148 concentration was analysed by colorimetry following the method developed by
149 Murphy and Riley (1962). We acidified the water samples with HNO₃⁻ (0.1 mL of
150 HNO₃⁻ for 10 mL of sample) to analyse elemental composition of Al, As, Cd, Co,
151 Cr, Cu, Fe, Mn, Pb, Hg, Ni, Zn by ICP-MS (Inductively Coupled Plasma - Mass
152 Spectrometry). Quality control included the repeated inclusion of blanks and
153 certified samples.

154 The geographical coordinates of the springs were obtained in the field with a global
155 positioning system (GPS). The coordinates were used to calculate the minimum

156 distance to the coast for each spring, and also to gather additional information
157 about climate and lithology from available digital maps. The mean annual
158 precipitation (MAP) was taken from the Digital Climatic Atlas of Catalonia (Pons,
159 1996; Ninyerola et al., 2000; available at
160 <http://www.opengis.uab.cat/acdc/index.htm>) with a resolution of 180 m, and the
161 lithology was obtained for each spring from the 1:50000 Geological map of
162 Catalonia (ICGC, 2016; available online at <http://www.icgc.cat/>). Eight categories of
163 lithology were defined based on the information provided by the map, being: 1)
164 carbonate-clastic (30 springs), 2) mixed clastic (31), 3) siliciclastic (7), 4)
165 granodiorite and other intrusive rocks (100), 5) marls and sandstones (44),
166 calcareous (7), 7) slates and phyllites (49) and 8) other or unknown bedrock (35).

167 *2.3 Statistical analyses*

168 A piper diagram (Piper, 1944) was constructed to represent the chemistry of the
169 water samples collected. These diagrams are commonly used to visualize the
170 relative abundance of common ions in multiple water samples on one plot. They
171 comprise three components: two ternary diagrams representing cations
172 (magnesium, calcium, and sodium plus potassium) and anions (chloride, sulfate,
173 and carbonate plus bicarbonate), plus a diamond plot that is a projection of the two
174 ternary diagrams. The diamond plot can be used to classify the type of water that
175 has been sampled. Samples in the top quadrant are calcium sulphate waters,
176 samples in the right quadrant are sodium chloride waters, samples in the left
177 quadrant are calcium bicarbonate waters, and samples in the bottom quadrant are
178 sodium bicarbonate waters.

179 Carbonate alkalinity ($CA = 2[CO_3^{2-}] + [HCO_3^-]$, hereafter alkalinity) was estimated
180 using a regression model between alkalinity and conductivity with a subset of 61
181 springs. Our model (described later in this section) showed that conductivity
182 explained 90% of the variance in alkalinity. We, therefore, estimated alkalinity as:
183 $Alkalinity = e^{-6.47 + 1.21 \times \ln(conductivity)}$, where alkalinity is measured in meq L⁻¹ and
184 conductivity in $\mu\text{S cm}^{-1}$. Next, we performed a principal component analysis (PCA)
185 to explore the relationship among the concentration of the different elements, using
186 the *pca* function of the R package *mixOmics* (Le Cao et al., 2017).

187 To explore the influence of SSA on the water chemistry composition of our springs,
188 we fitted linear models where the response variables were either the log-
189 transformed concentration of the different elements, the Na:Cl ratio or the scores of
190 the PCA, and the explanatory variables were the distance to the coast, NO_3^-
191 concentration and MAP, all log-transformed. Lithology was also included as a
192 categorical explanatory variable to control for endogenous variation of water
193 chemistry because of differences in lithology. The Na:Cl ratio has been suggested
194 as being a good indicator of SSA influence on water composition because the
195 predominant source of Cl⁻ in coastal areas is SSA and, therefore, Na:Cl ratio
196 approximates to that of seawater (0.86) in sources close to the coast (Sullivan et
197 al., 1988). Na:Cl then increases its value and its variability further inland. NO_3^- was
198 included in the models to account for chemistry composition disturbances due to
199 human activities such as farming or leaking of sewage (Sabater et al., 2015). The
200 existence of high values of NO_3^- indicates water pollution that is often accompanied
201 by other anthropogenic ions (e.g., Cl⁻) (Sabater et al., 2015). For the model in

202 which the response variable was NO_3^- , we used PO_4^{3-} to control for water pollution,
203 but NO_3^- was not included as a predictor in the models with the PCA scores.

204 To visualise the relationship between the response variables and the predictors we
205 used partial residuals plots, and the R package *visreg* (Breheny and Burchett,
206 2015). Partial residual plots show the relationship between the response and one
207 predictor at a time while keeping constant the other predictors included in the
208 model. We assessed the variance explained by each of the predictors using the
209 averaged over orderings method (Grömping, 2007), and the *lmg* metric in R
210 package *relaimpo* (Grömping, 2006). We also calculated the average percentage
211 of enrichment of those elements that showed a statistically significant effect of the
212 distance to the coast on their concentrations. To do so, we used our models to
213 predict the average concentration at 5 and 75 km from the coast and calculated the
214 percentage increase. All the statistical analyses were performed using R statistical
215 software (R Core Team, 2016).

216

217 **3. Results**

218 *3.1 Concentration of main ions of the springs*

219 We found a great diversity in the chemical composition of our springs, for both
220 cations and anions however, overall, the piper diagram showed that the majority of
221 the springs contained water that was classified as calcium bicarbonate or calcium
222 sulphate waters (**Figure 2**). The cation composition of most spring waters was

223 clearly dominated by Ca^{2+} and Mg^{2+} , while Na^+ + K^+ were dominant in very few
224 springs showing a tendency to being those closer to the coast (**Figure 2**). HCO_3^-
225 and, to a lesser extent SO_4^{2-} , dominated the anion composition in most of the
226 springs. Nonetheless, Cl^- had an important contribution in many springs, especially
227 those located closer to the sea line.

228 The first component of the PCA (PC1), explaining 30.1% of the variance in our
229 dataset, was primarily positively related to Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and NO_3^-
230 and Hg, and to a lesser extent to Cu, Ni and Co (**Figure 3**). Instead, PO_4^{3-} and Pb
231 were negatively related to PC1. The second component (PC2) was mainly
232 negatively related to Fe, Mn, Al, Cr, Pb, Co and Cd, and explained 14.4% of the
233 variance in the dataset. The third component (PC3), explaining 11.9% of the
234 variance of the dataset, was negatively related to Ni, Cu, Zn, As, Co and positively
235 related to Fe. Despite the scattering, colouring the site scores according to their
236 distance to the coast shows that positive values of PC1 and PC2 and negative
237 values of PC3 clearly comprise most of the springs located further inland (**Figure**
238 **3**). This observation was further supported when fitting linear relationships
239 controlling for lithology and annual precipitation. PC1 and PC3 were negatively
240 related to the distance to the coast ($P = 0.002$ and $P < 0.001$ respectively) while
241 PC2 was positively related to it ($P < 0.001$). Lithology was a significant predictor of
242 PC1 and PC3 but annual precipitation was only negatively related to PC1 (results
243 not shown).

244 *3.2 Controls of the concentration of main ions*

245 Our statistical models indicated that springs located closer to the sea line had
246 higher Cl⁻, SO₄²⁻, Na⁺, Mg²⁺, K⁺ and Ca²⁺ concentrations than those springs located
247 further away (**Figure 4 and Figure 5, Table 1**). Distance to the coast explained,
248 22% of the variance in water concentration of K⁺, 9% of both Cl⁻ and Na⁺ and 3% of
249 the rest of ions. This influence, though, practically disappeared at around 70 km
250 inland (**Figure 4 and Figure 5**). Based on our models, we estimate that the
251 concentration of Cl⁻, SO₄²⁻, Na⁺, Mg²⁺, K⁺ and Ca²⁺ in our springs located at 5 km
252 from the coast increases, respectively, by 487, 126, 161, 174, 124 and 114%
253 (**Table 2**) with respect to those located at 75 km inland. Instead, NO₃⁻
254 concentration increased with distance to the coast (**Table 1, Figure 4**),
255 concurrently with agricultural activities, which in this area are located mainly far
256 from the coast in the inland plains and highlands.

257 NO₃⁻ concentration was positively related to concentrations of Cl⁻, SO₄²⁻, Na⁺, and
258 K⁺, being an especially important predictor for Cl⁻ and SO₄²⁻ (explaining 14% of
259 their variance, **Table 1**). Annual precipitation decreased all ion concentrations
260 except PO₄³⁻, explaining from 11 (K⁺) to 29% (Cl⁻) of their variance. Instead, PO₄³⁻
261 presented a positive relationship with precipitation. Lithology also played an
262 important role determining ion concentration, being a significant predictor of the
263 concentration of all main ions except for PO₄³⁻. Lithology was the main predictor of
264 ion concentration of SO₄²⁻, K⁺, and Ca²⁺ (**Table 1**).

265 On the other hand, the ratio Na:Cl was significantly and positively influenced by the
266 distance to the coast, explaining 7% of its variance. Many springs located closer to
267 the sea line presented a Na:Cl ratio very close to that of the sea water (0.86,

268 **Figure 6**). Instead, further inland, springs presented higher ratios of Na:Cl. The
269 lithology explained 20% of the variance in Na:Cl ratio while NO_3^- was negatively
270 related to Na:Cl, explaining 11% of its variance.

271

272

273 *3.3 Controls of the concentration of minor elements*

274 Several elements (Al, Co, Cr, Fe, Mn, Hg) presented a negative relationship
275 between their water concentrations and the distance to the coast (**Table 3**). The
276 estimated enrichment factors related with distance to the coast for the
277 abovementioned elements are shown in **Table 2**. Among trace elements, Mn was
278 the element with the highest enrichment (439%), followed by Fe (211%) and Co
279 (167%).

280 Concentrations of Al, Fe and Mn were negatively related with NO_3^- concentration
281 while Cr and Hg presented a positive relationship with NO_3^- concentration (**Table**
282 **3**). Concentrations of Al, Cu, Hg and Ni were lower in springs with high annual
283 precipitation while Cr presented the opposite behaviour. Differences in lithology
284 between springs significantly explained differences in all trace elements, except for
285 Fe and Cr, explaining up to 37% of their variance (for As).

286

287 **4. Discussion**

288 We found that the distance to the coast had a clear effect on the water chemical
289 composition of coastal springs, while controlling for potentially confounding factors
290 such as anthropogenic water pollution (nitrate), differences in lithology, and annual
291 rainfall. Based on our results and previous literature, SSA is the most likely
292 mechanism that can explain this phenomenon. Additionally, the robustness of our
293 results makes them potentially up-scalable to any coastal region in the planet. Our
294 results agree with previous literature showing that sea aerosols are responsible for
295 the deposition of sea salt into coastal zones, affecting chemical composition of
296 precipitation (Granatt, 1972; Hedin et al., 1994; Izquierdo et al., 2014; McDowell et
297 al., 1990; Vet et al., 2014), lakes (Sullivan et al., 1988), soils (Dahms, 1993; Hedin
298 et al., 1994; Kennedy et al., 1998; Whipkey et al., 2000) and groundwater
299 (Starinsky et al., 1983). Moreover, in our study area, previous studies have already
300 pointed out that wet deposition of sea salt is commonly occurring, especially during
301 events of eastern winds and sometimes associated with intense rainfall events
302 (Izquierdo et al., 2014, 2013). Nonetheless, our study presents the first empirical
303 evidence of the sea spray effect on groundwater using a large geographical region
304 and a much larger dataset (303 different springs) than previous studies (Silva et
305 al., 2017; Starinsky et al., 1983).

306 *4.1 Mechanisms driving the effect of sea spray on groundwater composition*

307 Groundwater enrichment of main ions present in sea water, such as Cl^- , SO_4^{2-} ,
308 Na^+ , Mg^{2+} , K^+ and Ca^{2+} , occurs because of a higher atmospheric deposition of
309 those ions close to the sea coast compared to regions further inland (Vet et al.,
310 2014). However, different properties of ions can contribute to the differences of the

enrichments. Firstly, Cl^- is the most abundant ion in sea water, it does not get retained in soils and its presence in the lithology is usually very scarce. It is, therefore, logical that Cl^- is the ion that presents the highest enrichment in coastal areas (**Table 2**). Na^+ is the second most concentrated ion in sea water. However, it can be retained in the cation exchange complex of soil (clays and humus) while exchange with other cations, something that may contribute to reduce Na^+ enrichment in groundwater of coastal areas compared to Cl^- and other abundant ions in sea water. This was particularly evident when analysing the relationship between the Na:Cl ratio and the distance to the coast (**Figure 6**). SO_4^{2-} , Mg^{2+} , K^+ and Ca^{2+} are all similarly abundant in sea water, they are abundant in the lithology and K^+ and Ca^{2+} may also be potentially retained in the soil. This may explain why, despite the fact that they are also enriched in coastal areas, their enrichment factors are considerably lower than that for Cl^- .

Additionally, soil intake of Na^+ associated with SSA could change soil water and groundwater chemistry of other elements by i) promoting the release of cations (mostly H^+ , Ca^{2+} , Mg^{2+} , and K^+ , but also Mn^{2+} , Co^{2+} , or $\text{Fe}^{2/3+}$) from the soil exchange complex (clays and humic substances) by their substitution with Na^+ ; and alternatively ii) in acid soils, through the solubilisation of ions by dissolution of relatively insoluble mineral compounds (i.e. Fe, Al and Mn oxides and hydroxides, that can be released released as $\text{Fe}^{2/3+}$, Al^{3+} , and Mn^{2+}), because of the acidification caused by Na^+ through the so-called “neutral salt effect” (Sullivan *et al.*, 1988). The dissolution of those oxides and hydroxides is negligible at pH of 5 but increases under more acidic conditions (van Breemen *et al.*, 1983). The neutral

334 salt effect corresponds to the acidification caused by the release of H⁺ from the
335 exchange complex by substitution with Na⁺, in an effect that would only be possible
336 in acid soils, without acidity neutralization. It would not be possible in basic or
337 alkaline soils where the H⁺ concentration in exchange sites is low and where
338 carbonates might buffer any acidity release (van Breemen et al., 1983). This is a
339 plausible mechanism in the study area, as we measured springs in areas of acid
340 soils, either due to having non-carbonated lithology or decarbonation from high
341 rainfall.

342 Nonetheless, it is also possible that we are detecting a spurious correlation
343 between the distance to the coast and some trace elements, which could be
344 explained by a lithology or anthropogenic gradient. For example, Mn was found to
345 have the second highest enrichment factor, despite not being one of the main
346 elements present in sea water. In that case, it is well known that some parts of this
347 region have granitoids that are sometimes enriched with trace elements such as
348 Mn (Enrique, 2014, 1990). Our lithology variable did not account for such
349 particularities and it is possible that a spurious relationship between Mn
350 concentration and the distance to the coast could appear as a result. As an
351 example, the coastal enrichments in Cr and Hg may be more related to the
352 proximity of factories to the coast than to a natural SSA effect on the mobilisation
353 of these two trace elements (Kotaś and Stasicka, 2000; Losi et al., 1994; Navarro
354 et al., 1993; Xu et al., 2014; Zhang and Wong, 2007).

355 *4.2 Effect of precipitation, lithology and anthropogenic impacts on water chemistry*

356 The dilution effect of precipitation was evident in our study. We found a general
357 trend showing that precipitation decreased the concentration of almost all ions and
358 most of the elements analysed (**Table 1**, **Table 3**, **Figure 4** and **Figure 5**), in
359 agreement with previous studies (McDowell et al., 1990). Only PO_4^{3-} and Cr
360 presented positive significant relationships with annual precipitation. Additionally,
361 precipitation changed the proportion of elements as shown by its negative
362 significant relationship with the scores of PC1. Also, higher precipitation rates may
363 reduce groundwater residence time, allowing less salts to be dissolved into water
364 (Kapfer et al., 2012). In addition to the dilution effect, it is also plausible that the
365 higher precipitation has increased past nutrient leaching in soils, reducing the
366 current concentration of ions and trace elements in springs.

367 Parental material (rock substrate) is thought to be the main source of elements to
368 soils (Schlesinger, 1977) and water. However, the effect of lithology may have not
369 be fully captured in our analyses, which could imply that lithological differences
370 aligned with the distance to the coast or precipitation patterns could have been
371 confounded in our analyses (as discussed above regarding Mn). Nonetheless,
372 lithological differences explained a large proportion of the variance in ion and trace
373 elements concentrations (see **Table 1** and **Table 3**). Additionally, it was also a
374 significant factor explaining variance of PC1 and PC3. Therefore, lithology, despite
375 being a “coarse” variable already reflected important differences in water
376 composition.

377 Finally, our results showed that high concentrations of NO_3^- are related to higher
378 concentration of Cl^- , SO_4^{2-} , Na^+ , K^+ , Cr and Hg (**Table 1** and **Table 2**). High NO_3^-

379 concentration in groundwater is a good indicator of water pollution and
380 anthropogenic impacts on groundwater through agricultural activities and leaking of
381 sewage. It is therefore not surprising that in our study the same sites are also
382 exposed to other types of contamination, such as heavy metals from industry.
383 Governments, water supply companies, landowners and other stakeholders should
384 be aware of the risks of such activities to public health, as they have a clear impact
385 on spring water quality, which in turn is an indicator of the health of the whole
386 ecosystem.

387

388

389 **5. Conclusions**

390 Our results clearly demonstrated that SSA has an important impact on
391 groundwater of coastal zones, up to a distance of around 70 km from the coastline.
392 The most important effect of SSA on groundwater is the enrichment in Cl^- , SO_4^{2-} ,
393 Na^+ , Mg^{2+} , K^+ , and Ca^{2+} , although other elements such as Mn, Fe, Co, Al, Cr and
394 Hg may also increase close to the coastline either because of their release in soils
395 with high inputs of Na^+ deposition, pollution due to the proximity anthropogenic
396 activities, or particular lithologies that were not well captured in our models.
397 Additionally, we found that precipitation has a general effect of reducing the
398 concentration of almost all elements analysed. Thus, we reveal the main processes
399 (natural and anthropogenic) that affect the water chemistry of springs in this
400 Mediterranean region, which provides important information for studies in similar

401 regions that are related to terrestrial and aquatic ecology, water quality policy, and
402 predicting ecosystem changes.

403

404

405 **Acknowledgements**

406 M.F-M is a postdoctoral fellow of the Research Foundation – Flanders (FWO). We
407 acknowledge the Institució Catalana d'Història Natural (ICHN) and the Secció de
408 Ciències Biològiques de the Institut d'Estudis Catalans (IEC) for funding the
409 project. Also, to all the volunteers and “Teaming” supporters of the Delegation of
410 the Serralada Litoral Central, Grup de Naturalistes d'Osona (GNO-ICHN) and
411 Lluçanès Viu for helping with the survey of the springs. We also thank all those
412 people who helped us to find the springs.

413

414 **References:**

- 415 Àvila, A., 1996. Time trends in the precipitation chemistry at a mountain site in
416 northeastern Spain for the period 1983-1994. *Atmos. Environ.* 30, 1363–1373.
417 doi:10.1016/1352-2310(95)00472-6
- 418 Àvila, A., Rodà, F., 2002. Assessing decadal changes in rainwater alkalinity at a
419 rural Mediterranean site in the Montseny Mountains (NE Spain). *Atmos.*
420 *Environ.* 36, 2881–2890.
- 421 Bertram, T.H., Cochran, R.E., Grassian, V.H., Stone, E.A., 2018. Sea spray
422 aerosol chemical composition: Elemental and molecular mimics for laboratory
423 studies of heterogeneous and multiphase reactions. *Chem. Soc. Rev.* 47,
424 2374–2400. doi:10.1039/c7cs00008a
- 425 Bes, M., Corbera, J., Sayol, F., Bagaria, G., Jover, M., Preece, C., Viza, A.,
426 Sabater, F., Fernández-Martínez, M., 2018. On the influence of water
427 conductivity, pH and semi-natural springs On the influence of water
428 conductivity , pH and climate on bryophyte assemblages in Catalan semi-
429 natural springs. *J. Bryol.* 40, 1–10. doi:10.1080/03736687.2018.1446484
- 430 Breheny, P., Burchett, W., 2015. Visualization of Regression Models Using visreg,
431 R package version 2.2-0.
- 432 Cochran, R.E., Ryder, O.S., Grassian, V.H., Prather, K.A., 2017. Sea spray
433 aerosol: The chemical link between the oceans, atmosphere, and climate. *Acc.*
434 *Chem. Res.* 50, 599–604. doi:10.1021/acs.accounts.6b00603

- 435 Dahms, D.E., 1993. Mineralogical evidence for eolian contribution to soils of late
436 quaternary moraines, Wind River Mountains, Wyoming, USA. Geoderma 59,
437 175–196. doi:10.1016/0016-7061(93)90068-V
- 438 de Leeuw, G., Andreas, E., Anguelova, M., Fairall, C.W., Ernie, R., O'Dowd, C.,
439 Schulz, M., Schwartz, S.E., 2011. Production Flux of Sea-Spray Aerosol. Rev.
440 Geophys. 49, 1–39. doi:10.1029/2010RG000349.1
- 441 Dimitriou, K., Paschalidou, A.K., Kassomenos, P.A., 2017. Distinct synoptic
442 patterns and air masses responsible for long-range desert dust transport and
443 sea spray in Palermo, Italy. Theor. Appl. Climatol. 130, 1123–1132.
444 doi:10.1007/s00704-016-1957-9
- 445 Enrique, P., 1990. The Hercynian intrusive rocks of the Catalonian Coastal Ranges
446 (NE Spain). Acta Geol. Hisp. 25, 39–64.
- 447 Enrique, P., 2014. El paisatge geològic: origen i evolució de les roques i les
448 muntanyes del Maresme. L'Atzavara 23, 5–13.
- 449 Eriksson, E., 1955. Air borne salts and the chemical composition of river waters.
450 Tellus 7, 243–250. doi:10.3402/tellusa.v7i2.8782
- 451 Fernández-Martínez, M., Bagaria, G., Raya, I., Preece, C., Margalef, O., Domene,
452 X., 2016. Terra Negra: un sòl sobre pissarres al Montnegre. L'Atzavara 26,
453 67–72.
- 454 Fernández-Martínez, M., Vicca, S., Janssens, I.A., Ciais, P., Obersteiner, M.,
455 Bartrons, M., Sardans, J., Verger, A., Canadell, J.G., Chevallier, F., Wang, X.,

- 456 Bernhofer, C., Curtis, P.S., Gianelle, D., 2017. Atmospheric deposition, CO₂,
457 and change in the land carbon sink. *Sci. Rep.* 7:9632, 1–13.
458 doi:10.1007/s13398-014-0173-7.2
- 459 Fernández-Martínez, M., Vicca, S., Janssens, I.A., Sardans, J., Luyssaert, S.,
460 Campioli, M., Chapin III, F.S., Ciais, P., Malhi, Y., Obersteiner, M., Papale, D.,
461 Piao, S.L., Reichstein, M., Rodà, F., Peñuelas, J., 2014. Nutrient availability as
462 the key regulator of global forest carbon balance. *Nat. Clim. Chang.* 4, 471–
463 476. doi:doi:10.1038/nclimate2177
- 464 Gong, S.L., Barrie, L.A., Blanchet, J.-P., 1997. Modeling sea-salt aerosols in the
465 atmosphere: 1. Model development. *J. Geophys. Res. Atmos.* 102, 3805–
466 3818. doi:10.1029/96JD02953
- 467 Gorham, E., 1957. The influence and importance of daily weather conditions in the
468 supply of chloride, sulphate and other ions to fresh waters from atmospheric
469 precipitation. *Freshw. Biol. Assoc.* 244, 147–178. doi:10.1098/rstb.1958.0001
- 470 Granatt, L., 1972. On the relation between pH and the chemical composition in
471 atmospheric precipitation. *Tellus* 24, 550–560. doi:10.1111/j.2153-
472 3490.1972.tb01581.x
- 473 Grömping, U., 2006. Relative importance for linear regression in R: the package
474 relaimpo. *J. Stat. Softw.* 17, 1–27.
- 475 Grömping, U., 2007. Estimators of Relative Importance in Linear Regression
476 Based on Variance Decomposition. *Am. Stat.* 61, 139–147.

- 477 doi:10.1198/000313007X188252
- 478 Grythe, H., Ström, J., Krejci, R., Quinn, P., Stohl, A., 2014. A review of sea-spray
479 aerosol source functions using a large global set of sea salt aerosol
480 concentration measurements. *Atmos. Chem. Phys.* 14, 1277–1297.
481 doi:10.5194/acp-14-1277-2014
- 482 Hedin, L. o., Granatt, L., Likens, Gene E., Buishandll, T.A., Galloway, James N.
483 Butler, T.J., Rodhe, H., 1994. Steep declines in atmospheric base cations in
484 regions of Europe and North America. *Nature* 367, 351–354.
- 485 Izquierdo, R., Alarcón, M., Aguillaume, L., Ávila, A., 2014. Effects of teleconnection
486 patterns on the atmospheric routes, precipitation and deposition amounts in
487 the north-eastern Iberian Peninsula. *Atmos. Environ.* 89, 482–490.
488 doi:10.1016/j.atmosenv.2014.02.057
- 489 Izquierdo, R., Alarcón, M., Ávila, A., 2013. WeMO effects on the amount and the
490 chemistry of winter precipitation in the north-eastern Iberian Peninsula. *Tethys*
491 10, 45–51. doi:10.3369/tethys.2013.10.05
- 492 Junge, C.E., Gustafson, P.E., 1957. On the Distribution of Sea Salt over the United
493 States and its Removal by Precipitation. *Tellus* 9, 164–173.
494 doi:10.3402/tellusa.v9i2.9092
- 495 Kapfer, J., Audorff, V., Beierkuhnlein, C., Hertel, E., 2012. Do bryophytes show a
496 stronger response than vascular plants to interannual changes in spring water
497 quality? *Freshw. Sci.* 31, 625–635. doi:10.1899/11-037.1

- 498 Kennedy, M.J., Chadwick, O.A., Vitousek, P.M., Derry, L.A., Hendricks, D.M.,
499 1998. Changing sources of base cations during ecosystem development,
500 Hawaiian Islands. *Geology* 26, 1015–1018. doi:10.1130/0091-
501 7613(1998)026<1015:CSOBCD>2.3.CO
- 502 Kotaś, J., Stasicka, Z., 2000. Chromium occurrence in the environment and
503 methods of its speciation. *Environ. Pollut.* 107, 263–283. doi:10.1016/S0269-
504 7491(99)00168-2
- 505 Le Cao, K.-A., Rohart, F., Gonzalez, I., Dejean, S., Gautier, B., Bartolo, F., Monget,
506 P., Coquery, J., Yao, F., Liquet, B., Monget, Jeff Coquery, F.Y. and B.L., 2017.
507 mixOmics: Omics Data Integration Project.
- 508 Losi, M.E.E., Amrhein, C., Frankenberger, J.W., Frankenberger, W.T., 1994.
509 Environmental biochemistry of chromium. *Rev. Environ. Contam. Toxicol.* 136,
510 91–121. doi:10.1007/978-1-4612-2656-7_3
- 511 Martín-Vide, J., 1992. El clima, in: Carreras, C. (Ed.), *Geografia General Dels*
512 *Països Catalans*. Enciclopèdia Catalana. Barcelona, pp. 1–110.
- 513 McDowell, W.H., Sánchez, C.G., Asbury, C.E., Ramos Pérez, C.R., 1990.
514 Influence of sea salt aerosols and long range transport on precipitation
515 chemistry at El Verde, Puerto Rico. *Atmos. Environ. Part A, Gen. Top.* 24,
516 2813–2821. doi:10.1016/0960-1686(90)90168-M
- 517 Murphy, J., Riley, J.P., 1962. A modified single solution method for the
518 determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.

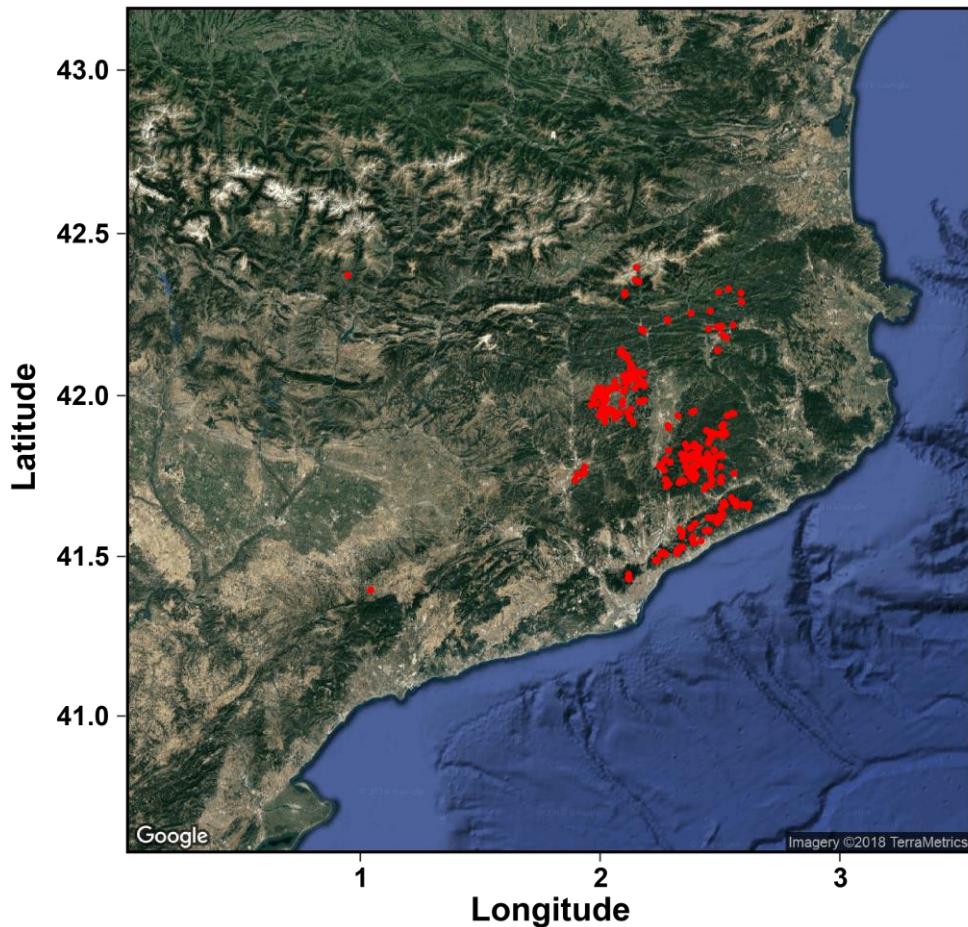
- 519 Navarro, M., López, H., Sánchez, M., López, M.C., 1993. The effect of industrial
520 pollution on mercury levels in water, soil, and sludge in the coastal area of
521 Motril, Southeast Spain, in: Archives of Environmental Contamination and
522 Toxicology. pp. 11–15. doi:10.1007/BF01061083
- 523 Ninyerola, M., Pons, X., Roure, J.M., Ninyerola, M., Pons, X., Roure, J.M., 2000. A
524 methodological approach of climatological modelling of air temperature and
525 precipitation through GIS techniques, A methodological approach of
526 climatological modelling of air temperature and precipitation through GIS
527 techniques. Int. J. Climatol. Int. J. Climatol. 20, 20, 1823, 1823–1841, 1841.
528 doi:10.1002/1097-0088
- 529 Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water
530 analyses. Eos, Trans. Am. Geophys. Union 25, 914–928.
531 doi:10.1029/TR025i006p00914
- 532 Pons, X., 1996. Estimación de la radiación solar a partir de modelos digitales de
533 elevaciones. Propuesta metodológica., in: Modelos y Sistemas de Información
534 Geográfica. pp. 87–97.
- 535 Quinn, P.K., Collins, D.B., Grassian, V.H., Prather, K.A., Bates, T.S., 2015.
536 Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol.
537 Chem. Rev. 115, 4383–4399. doi:10.1021/cr500713g
- 538 R Core Team, 2016. R: A Language and Environment for Stasitical Computing.
- 539 Sabater, F., Fernández-Martínez, M., Corbera, J., Calpe, M., Torner, G., Cano, O.,

- 540 Corbera, G., Ciurana, O., Parera, J.M., 2015. Caracterització hidrogeoquímica
541 de les fonts de la Serralada Litoral Central en relació a la litologia i als factors
542 ambientals. *L'Atzavara* 25, 93–104.
- 543 Schlesinger, W.H., 1977. Carbon Balance in Terrestrial Detritus. *Annu. Rev. Ecol.*
544 *Syst.* 8, 51–81. doi:10.1146/annurev.es.08.110177.000411
- 545 Shainberg, I., Letey, J., 1984. Response of soils to sodic and saline conditions.
546 *Hilgardia* 52, 1–57. doi:10.3733/hilg.v52n02p057
- 547 Silva, A.M., Campos, V.P., Domingues, R.S., Cruz, L.P.S., Santana, F.O., 2017.
548 Influence of the transport of sea spray on the salinization of the semiarid
549 region waters (Bahia, Brazil). *J. Braz. Chem. Soc.* 28, 2402–2411.
550 doi:10.21577/0103-5053.20170094
- 551 Starinsky, A., Bielski, M., Ecker, A., Steinitz, G., 1983. Tracing the origin of salts in
552 groundwater by Sr isotopic composition (the Crystalline Complex of the
553 southern Sinai, Egypt). *Chem. Geol.* 41, 257–267. doi:10.1016/S0009-
554 2541(83)80023-0
- 555 Sullivan, T.J., Ellers, J.M., Driscoll, C.T., Landers, D.H., 1988. Evaluation of the
556 role of sea salt inputs in the long-term acidification of coastal new england
557 lakes. *Environ. Sci. Technol.* 22, 185–190. doi:10.1021/es00167a009
- 558 van Breemen, N., Mulder, J., Driscoll, C.T., 1983. Acidification and alkalinization of
559 soils. *Plant Soil* 75, 283–308. doi:10.1007/BF02369968
- 560 Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.-U.U., Aas, W., Baker, A.,

- 561 Bowersox, V.C., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J.J., Gillett,
562 R., Forti, M.C., Gromov, S., Hara, H., Khodzher, T., Mahowald, N.M., Nickovic,
563 S., Rao, P.S.P.S.P., Reid, N.W., 2014. A global assessment of precipitation
564 chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic
565 acids, acidity and pH, and phosphorus. *Atmos. Environ.* 93, 3–100.
566 doi:10.1016/j.atmosenv.2013.10.060
- 567 Whipkey, C.E., Capo, R.C., Chadwick, O.A., Stewart, B.W., 2000. The importance
568 of sea spray to the cation budget of a coastal Hawaiian soil: A strontium
569 isotope approach. *Chem. Geol.* 168, 37–48. doi:10.1016/S0009-
570 2541(00)00187-X
- 571 Woodcock, A.H., 1953. Salt Nuclei in Marine Air As a Function of Altitude and Wind
572 Force. *J. Meteorol.* doi:10.1175/1520-
573 0469(1953)010<0366:SNIMAA>2.0.CO;2
- 574 Xu, J., Bravo, A.G., Lagerkvist, A., Bertilsson, S., Sjöblom, R., Kumpiene, J., 2014.
575 Sources and remediation techniques for mercury contaminated soil. *Environ.*
576 *Int.* 74, 42–53. doi:10.1016/j.envint.2014.09.007
- 577 Zhang, L., Wong, M.H., 2007. Environmental mercury contamination in China:
578 Sources and impacts. *Environ. Int.* 33, 108–121.
579 doi:10.1016/j.envint.2006.06.022
- 580

581 **Figure captions**

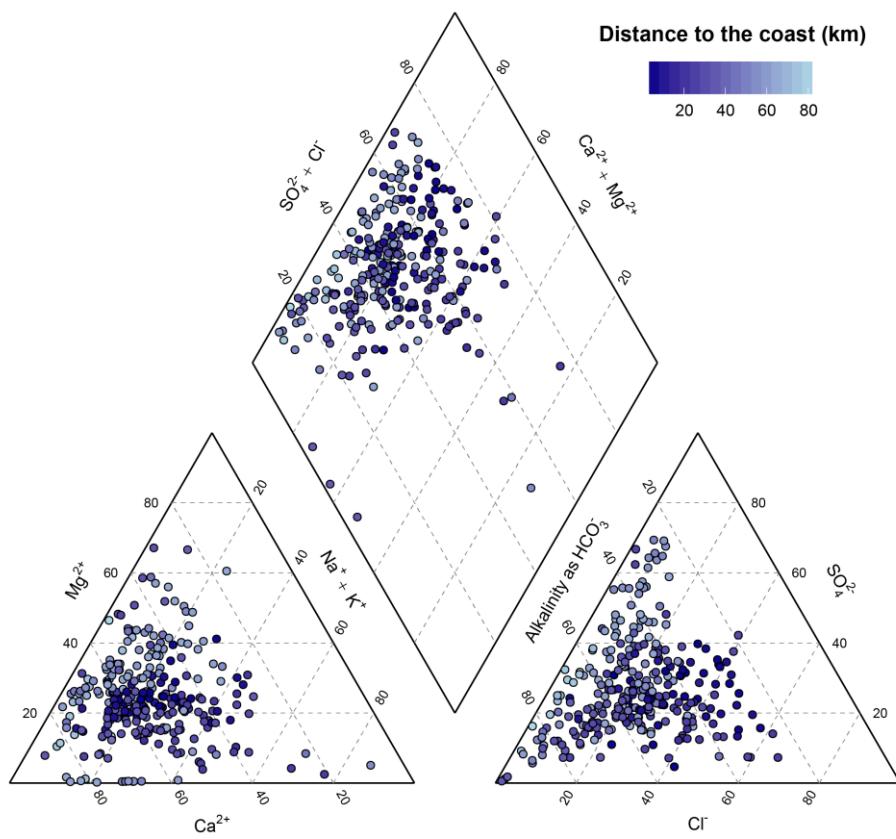
582 **Figure 1:** Map of studied region, showing the springs sampled (red dots).



583
584

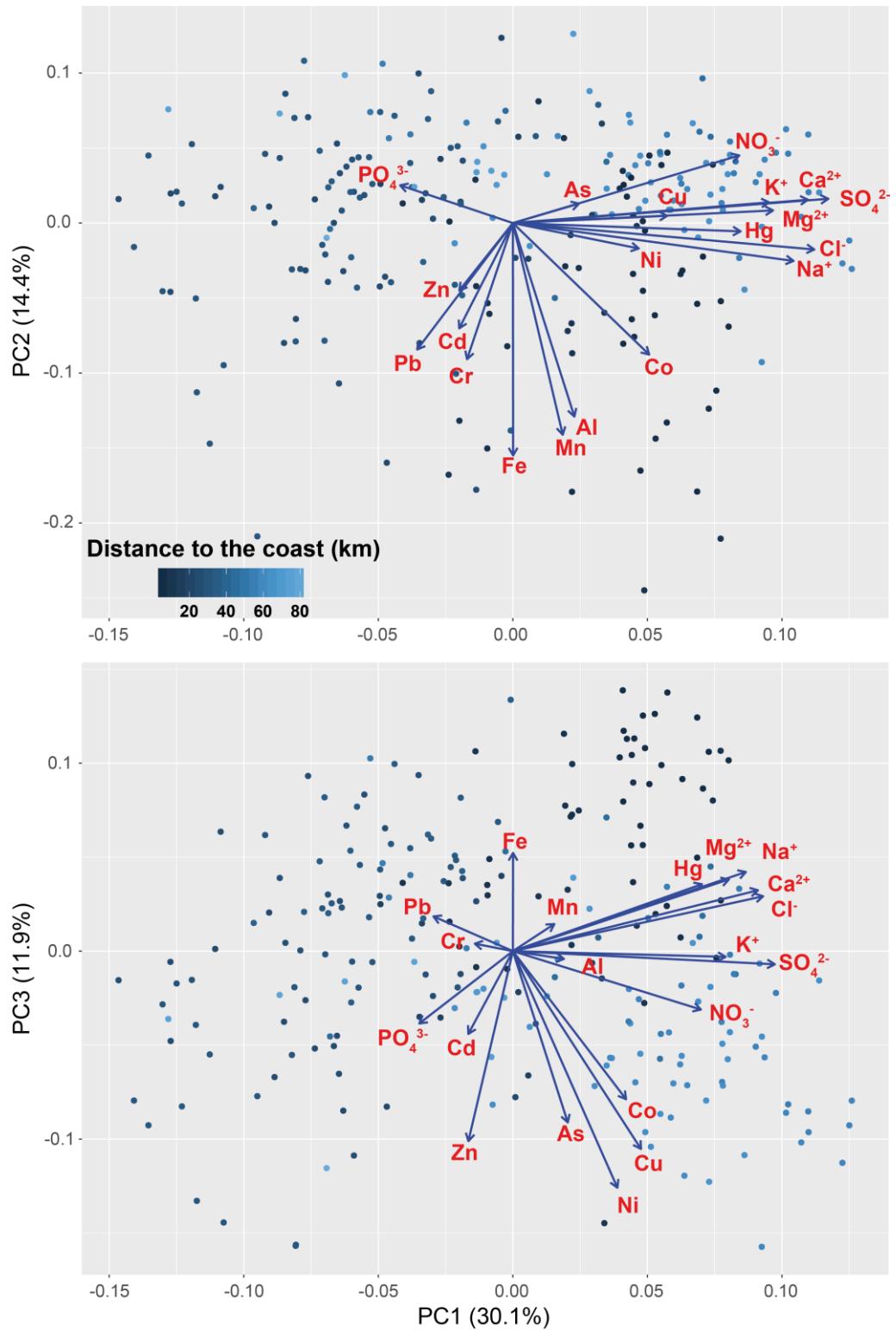
585 **Figure 2:** Piper diagram of the water samples collected. The colour of the points
586 shows the distance of each spring to the coastline in km. Samples in the top
587 quadrant of the diamond plot are CaSO_4 waters, samples in the right quadrant are
588 NaCl waters, samples in the left quadrant are CaHCO_3 waters, and samples in the
589 bottom quadrant are NaHCO_3 waters.

590

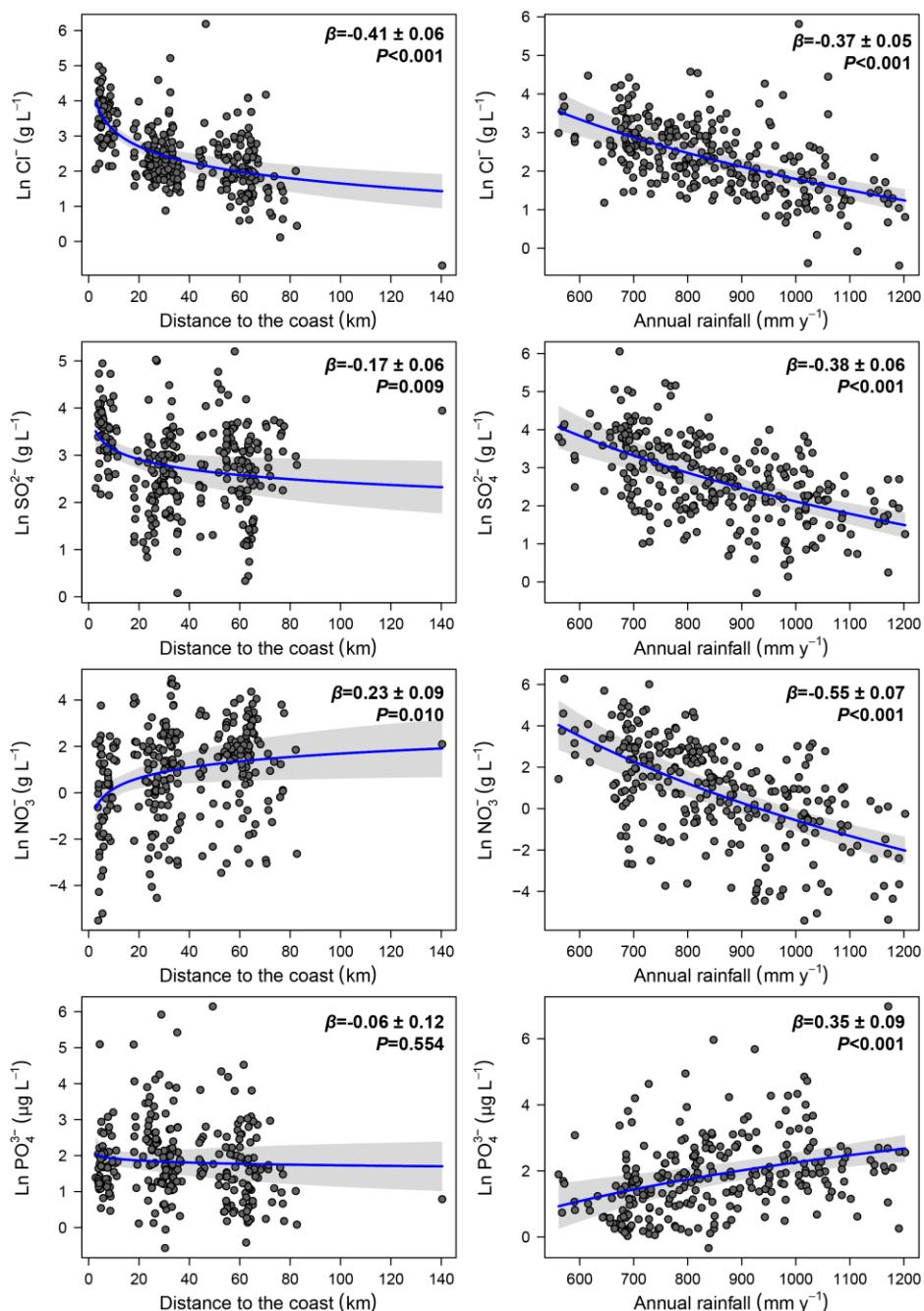


591
592

593 **Figure 3:** Biplots showing scores and loadings of the first three components
594 extracted by a principal component analysis performed with water chemical
595 composition. The colour of the points indicates the distance from the coast. Ions
596 and elements shown are: Na⁺ - sodium ion, K⁺- potassium ion, Mg²⁺ - magnesium
597 ion, Ca²⁺ - calcium ion, Cl⁻ - chloride ion, NO₃⁻ - nitrate ion, SO₄²⁻ - sulphate ion,
598 PO₄³⁻ - phosphate ion, Al - aluminium, As - arsenic, Cd - cadmium, Co - cobalt, Cr -
599 chromium, Cu - copper, Fe - iron, Mn - manganese, Pb - lead, Hg - mercury, Ni –
600 nickel, and Zn – zinc.

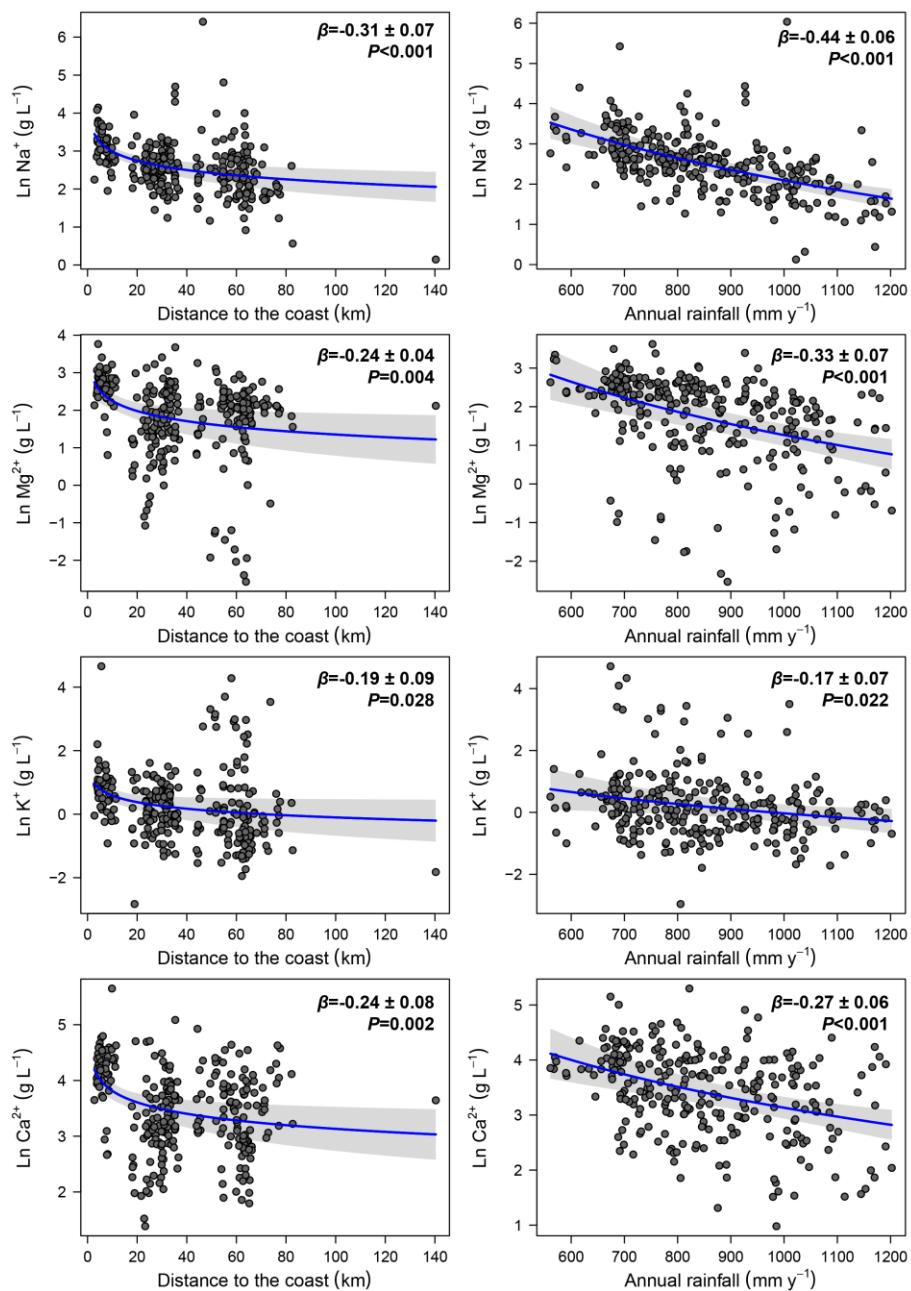


602 **Figure 4:** Partial residual plots showing the relationship of distance from the
 603 coastline and mean annual precipitation with main anions. Standardized (β)
 604 coefficients and P values and partial residuals were extracted from a model
 605 containing distance from the coast, chemistry of the lithology, nitrate and annual
 606 rainfall as predictors of anion concentration.



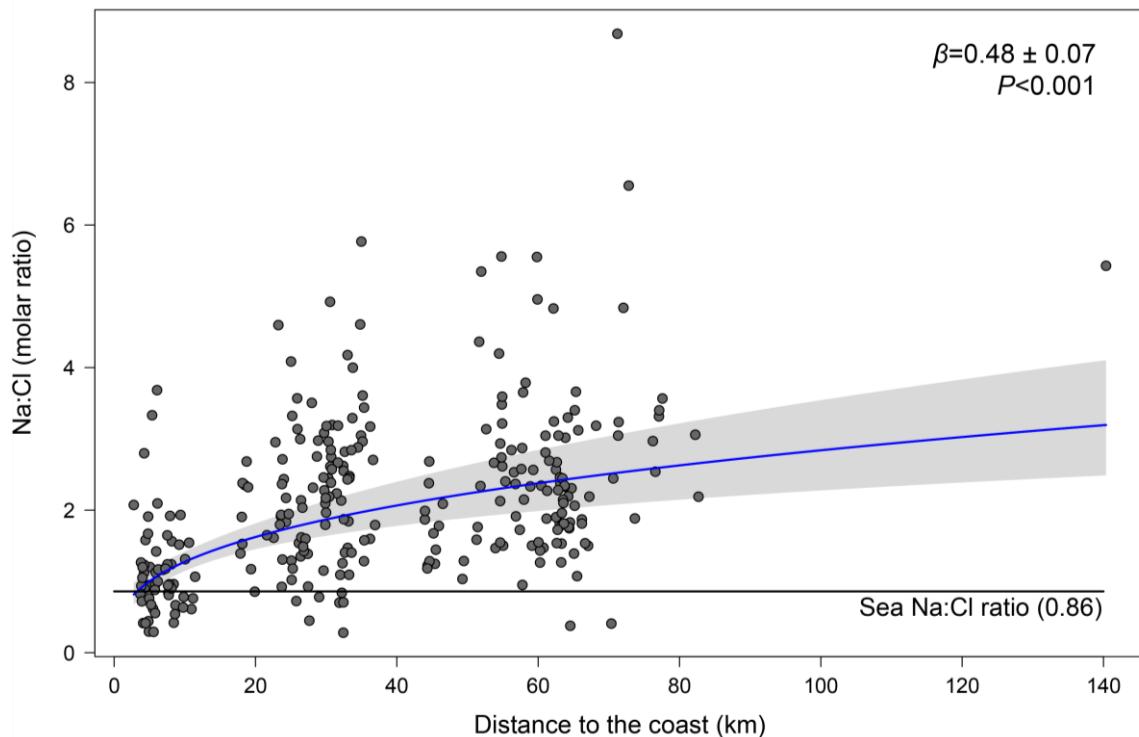
607

608 **Figure 5:** Partial residual plots showing the relationship of distance from the
 609 coastline and mean annual precipitation with main cations. Standardized (β)
 610 coefficients and P values and partial residuals were extracted from a model
 611 containing distance from the coast, chemistry of the lithology, nitrate and annual
 612 rainfall as predictors of cation concentration.



613

614 **Figure 6:** Partial residual plots showing the relationship between the distance from
615 the coastline and the Na:Cl ratio on a molar basis. β coefficients and P values and
616 partial residuals were extracted from a model containing distance from the coast,
617 lithology and nitrate concentration as predictors, explaining 39% of its variance.



618

619 **Table 1:** Standardized (β) coefficients and percentage of variance explained (R^2) of each of the statistically significant
 620 predictors explaining variability in water concentration of main anions and cations. For lithology, only R^2 is shown. See
 621 **Methods** for further information about the models. Significance levels: * $P<0.05$; ** $P<0.01$; *** $P<0.001$.

	Distance to coast	R^2	Nitrate	R^2	Precipitation	R^2	Lithology
Anions							
Cl ⁻	-0.41 ± 0.06 ***	0.09	0.23 ± 0.04 ***	0.14	-0.37 ± 0.05 ***	0.29	0.18 ***
SO ₄ ²⁻	-0.17 ± 0.06 **	0.03	0.16 ± 0.04 ***	0.14	-0.38 ± 0.06 ***	0.24	0.26 ***
NO ₃ ⁻	0.23 ± 0.09 **	0.03			-0.55 ± 0.07 ***	0.21	0.15 *
PO ₄ ³⁻					0.27 ± 0.06 ***	0.07	
Cations							
Na ⁺	-0.31 ± 0.07 ***	0.09	0.13 ± 0.05 **	0.09	-0.44 ± 0.06 ***	0.26	0.16 ***
Mg ²⁺	-0.23 ± 0.08 **	0.03			-0.36 ± 0.06 ***	0.22	0.21 ***
K ⁺	-0.19 ± 0.09 *	0.22	0.15 ± 0.06 *	0.08	-0.17 ± 0.07 *	0.11	0.22 ***
Ca ²⁺	-0.23 ± 0.07 **	0.03			-0.30 ± 0.06 ***	0.21	0.32 ***

622

623 **Table 2:** Average percentage enrichment between springs near the coast (5 km)
624 and springs far from the coast (75 km) for all the ions and elements studied. Ratios
625 were calculated by dividing the difference between modelled concentrations at 5
626 and 75 km from the coast and the modelled values at 75 km from the coast. Values
627 have been calculated based on models from **Tables 1** and **3** and maintaining other
628 significant factors constant.

	Enrichment	2.50%	97.50%
Cl ⁻	487.2%	470.0%	504.5%
Mn	439.1%	424.0%	454.3%
Fe	211.4%	209.1%	213.7%
Mg ²⁺	173.7%	163.1%	183.9%
Co	166.5%	161.8%	171.2%
Na ⁺	160.5%	154.2%	166.6%
SO ₄ ²⁻	126.4%	118.5%	133.7%
K ⁺	124.2%	115.0%	132.7%
Ca ²⁺	113.5%	107.6%	119.0%
Al	99.9%	94.5%	104.9%
Cr	82.9%	81.6%	84.2%
Hg	76.3%	72.8%	79.5%

629

630 **Table 3:** Standardized (β) coefficients and percentage of variance explained (R^2) of each of the statistically significant
 631 predictors explaining variability in water elemental concentration of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Hg, Ni and Zn. For
 632 lithology only R^2 is shown. See **Methods** for further information about the models. Significant levels: * $P<0.05$; ** $P<0.01$;
 633 *** $P<0.001$.

634 **Supplementary material**

635 **Figure S1:** Example of one of the semi-natural springs surveyed.



636