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

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Abstract

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

1. Introduction

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

These aerosols stay mainly in liquid form in the atmosphere and contribute to the scattering of salts into inland waters, accounting for as much as 10% of the salts in some regions (Starinsky et al., 1983) and having an important role for the atmospheric cycles of scarce elements (Gong et al., 1997). The removal of sea spray from the atmosphere occurs by three main processes: fallout by gravity, retention by obstacles such as vegetation, and rain washout (Junge and Gustafson, 1957). Additionally, rainfall also washes down salts retained by vegetation, potentially increasing salt concentrations in lakes, rivers and groundwater (Eriksson, 1955; McDowell et al., 1990).

The influence of sea salt deposition on coastal areas because of SSA has been long studied from different disciplines. Several studies have pointed out that coastal regions are subjected to higher rates of sea salt deposition, specifically of Cl^-, Na^+, Mg^{2+} and K^+ (Granatt, 1972; Hedin et al., 1994; McDowell et al., 1990; Vet et al., 2014) especially when winds blow from the sea side (Dimitriou et al., 2017; Izquierdo et al., 2014, 2013). Eventually, chronic deposition of sea salt can change soil mineral composition (Dahms, 1993; Hedin et al., 1994; Kennedy et al., 1998; Whipkey et al., 2000) and potentially affect soil weathering, something that could affect the composition of groundwater (Silva et al., 2017; Starinsky et al., 1983), lakes and rivers (Sullivan et al., 1988). Hence, SSA can potentially differentiate water chemical composition of coastal regions from inland regions, which may have large-scale impacts on ecosystem structure and function (Bes et al., 2018; Fernández-Martínez et al., 2017, 2014) as well as water quality for human supply. Although there are several studies that report an effect of SSA on the composition of groundwater (Silva et al., 2017; Starinsky et al., 1983), lakes and rivers (Eriksson, 1955; Sullivan et al., 1988), little attention has been devoted to its influence on spring water chemistry, either influenced by deep groundwater or soil and surface processes. For instance, Na^+ and K^+ deposition could force the release of other cations captured in the cation exchange complex of the soil (mostly occupied by Na^+, K^+, Mg^{2+}, Ca^{2+}, and H^+) in a process called sodization (Shainberg and Letey, 1984), potentially causing Ca^{2+} and Mg^{2+} enrichment of groundwater. Additionally, human activities could mask the effect of SSA on groundwater, for example, by increasing nitrate and levels of other ions because of fertilization and other agricultural activities.

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

2. Material and methods

2.1 Area of study

We surveyed 303 water springs along a south-to-north and east-to-west gradient across the north-eastern Iberian Peninsula from the Mediterranean sea to the Pre-Pyrenees (**Figure 1**), with distance to the sea coast from 5 to 140 km. The surveyed area comprised a wide geographical area and a variety of anthropogenic and biophysical conditions. Climate differed considerably amongst sites, mostly associated with altitude, with mean annual precipitation ranging from around 550 to 1200 mm, comprising maritime, continental, humid and sub-humid and Pyreneeal Mediterranean climate according to Martín-Vide (1992).

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

2.2 Field sampling and analyses

The springs surveyed were human-made constructions to force the water to flow through a spout (**Figure S1**), which is a traditional practice of the area intended to provide drinking water for humans and cattle. Some of the springs were built in naturally occurring springs while others drained water mines (collecting water from aquifers). None of the surveyed springs received any kind of sanitization. Surveys of the springs were carried out during spring and autumn of the years 2013, 2015, 2016 and 2017. Only open flow springs were sampled, i.e. those not controlled by a tap, although in some springs drought can interrupt water flow in dry periods. Water pH and conductivity were analysed in the field with a pHmeter and conductivity meter. Alkalinity was also measured *in situ* for a subset of 61 springs using a strong acid (sulphuric acid, 0.02 mol L^{-1}), a fixed volume of water sample (25 mL) and methyl blue as the indicator (changing colour at pH = 4.5). Main ions were analysed in the laboratory following previously described protocols (Àvila, 1996; Àvila and Rodà, 2002). A sample of the flowing water was filtered through a glass fibre filter disk of 0.7 μm and stored in the laboratory at -20 ºC until the moment of the analyses. Ion chromatography was used to determine the concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}. Concentrations of NH_4^+ were undetectable in all springs (<0.1 μeq L^{-1}). Phosphate (PO_4^{3-}) concentration was analysed by colorimetry following the method developed by Murphy and Riley (1962). We acidified the water samples with HNO_3^- (0.1 mL of HNO_3^- for 10 mL of sample) to analyse elemental composition of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Hg, Ni, Zn by ICP-MS (Inductively Coupled Plasma - Mass Spectrometry). Quality control included the repeated inclusion of blanks and certified samples.

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

2.3 Statistical analyses

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

Carbonate alkalinity (CA = $2[CO_3^{2-}] + [HCO_3^-]$, hereafter alkalinity) was estimated using a regression model between alkalinity and conductivity with a subset of 61 springs. Our model (described later in this section) showed that conductivity explained 90% of the variance in alkalinity. We, therefore, estimated alkalinity as:

$Alkalinity = e^{-6.47 + 1.21 \times \ln(conductivity)}$, where alkalinity is measured in meq L^{-1} and conductivity in µS cm^{-1}. Next, we performed a principal component analysis (PCA) to explore the relationship among the concentration of the different elements, using the *pca* function of the R package *mixOmics* (Le Cao et al., 2017).

To explore the influence of SSA on the water chemistry composition of our springs, we fitted linear models where the response variables were either the log-transformed concentration of the different elements, the Na:Cl ratio or the scores of the PCA, and the explanatory variables were the distance to the coast, NO_3^- concentration and MAP, all log-transformed. Lithology was also included as a categorical explanatory variable to control for endogenous variation of water chemistry because of differences in lithology. The Na:Cl ratio has been suggested as being a good indicator of SSA influence on water composition because the predominant source of Cl^- in coastal areas is SSA and, therefore, Na:Cl ratio approximates to that of seawater (0.86) in sources close to the coast (Sullivan et al., 1988). Na:Cl then increases its value and its variability further inland. NO_3^- was included in the models to account for chemistry composition disturbances due to human activities such as farming or leaking of sewage (Sabater et al., 2015). The existence of high values of NO_3^- indicates water pollution that is often accompanied by other anthropogenic ions (e.g., Cl^-) (Sabater et al., 2015). For the model in which the response variable was NO_3^-, we used PO_4^{3-} to control for water pollution, but NO_3^- was not included as a predictor in the models with the PCA scores.

To visualise the relationship between the response variables and the predictors we used partial residuals plots, and the R package *visreg* (Breheny and Burchett, 2015).

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

3. Results

3.1 Concentration of main ions of the springs

We found a great diversity in the chemical composition of our springs, for both cations and anions however, overall, the piper diagram showed that the majority of the springs contained water that was classified as calcium bicarbonate or calcium sulphate waters (**Figure 2**). The cation composition of most spring waters was clearly dominated by Ca^{2+} and Mg^{2+}, while Na^{+} + K^{+} were dominant in very few springs showing a tendency to being those closer to the coast (**Figure 2**). HCO_3^- and, to a lesser extent SO_4^{2-}, dominated the anion composition in most of the springs. Nonetheless, Cl^- had an important contribution in many springs, especially those located closer to the sea line.

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

3.2 Controls of the concentration of main ions

Our statistical models indicated that springs located closer to the sea line had higher Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, K^+ and Ca^{2+} concentrations than those springs located further away (**Figure 4 and Figure 5, Table 1**). Distance to the coast explained, 22% of the variance in water concentration of K^+, 9% of both Cl^- and Na^+ and 3% of the rest of ions. This influence, though, practically disappeared at around 70 km inland (**Figure 4 and Figure 5)**. Based on our models, we estimate that the concentration of Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, K^+ and Ca^{2+} in our springs located at 5 km from the coast increases, respectively, by 487, 126, 161, 174, 124 and 114% (**Table 2**) with respect to those located at 75 km inland. Instead, NO_3^- concentration increased with distance to the coast (**Table 1, Figure 4**), concurrently with agricultural activities, which in this area are located mainly far from the coast in the inland plains and highlands.

NO_3^- concentration was positively related to concentrations of Cl^-, SO_4^{2-}, Na^+, and K^+, being an especially important predictor for Cl^- and SO_4^{2-} (explaining 14% of their variance, **Table 1**). Annual precipitation decreased all ion concentrations except PO_4^{3-}, explaining from 11 (K^+) to 29% (Cl^-) of their variance. Instead, PO_4^{3-} presented a positive relationship with precipitation. Lithology also played an important role determining ion concentration, being a significant predictor of the concentration of all main ions except for PO_4^{3-}. Lithology was the main predictor of ion concentration of SO_4^{2-}, K^+, and Ca^{2+} (**Table 1**).

On the other hand, the ratio Na:Cl was significantly and positively influenced by the distance to the coast, explaining 7% of its variance. Many springs located closer to the sea line presented a Na:Cl ratio very close to that of the sea water (0.86, **Figure 6**). Instead, further inland, springs presented higher ratios of Na:Cl. The lithology explained 20% of the variance in Na:Cl ratio while NO_3^- was negatively related to Na:Cl, explaining 11% of its variance.

3.3 Controls of the concentration of minor elements

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

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

4. Discussion

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

4.1 Mechanisms driving the effect of sea spray on groundwater composition

Groundwater enrichment of main ions present in sea water, such as Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, K^+ and Ca^{2+}, occurs because of a higher atmospheric deposition of those ions close to the sea coast compared to regions further inland (Vet et al., 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 $Fe^{2/3+}$) 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 $Fe^{2/3+}$, 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 salt effect corresponds to the acidification caused by the release of H^+ from the exchange complex by substitution with Na^+, in an effect that would only be possible in acid soils, without acidity neutralization. It would not be possible in basic or alkaline soils where the H^+ concentration in exchange sites is low and where carbonates might buffer any acidity release (van Breemen et al., 1983). This is a plausible mechanism in the study area, as we measured springs in areas of acid soils, either due to having non-carbonated lithology or decarbonation from high rainfall.

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

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

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

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

Finally, our results showed that high concentrations of NO_3^- are related to higher concentration of Cl^-, SO_4^{2-}, Na^+, K^+, Cr and Hg (**Table 1** and **Table 2**). High NO_3^- concentration in groundwater is a good indicator of water pollution and anthropogenic impacts on groundwater through agricultural activities and leaking of sewage. It is therefore not surprising that in our study the same sites are also exposed to other types of contamination, such as heavy metals from industry. Governments, water supply companies, landowners and other stakeholders should be aware of the risks of such activities to public health, as they have a clear impact on spring water quality, which in turn is an indicator of the health of the whole ecosystem.

5. Conclusions

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

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Figure captions

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

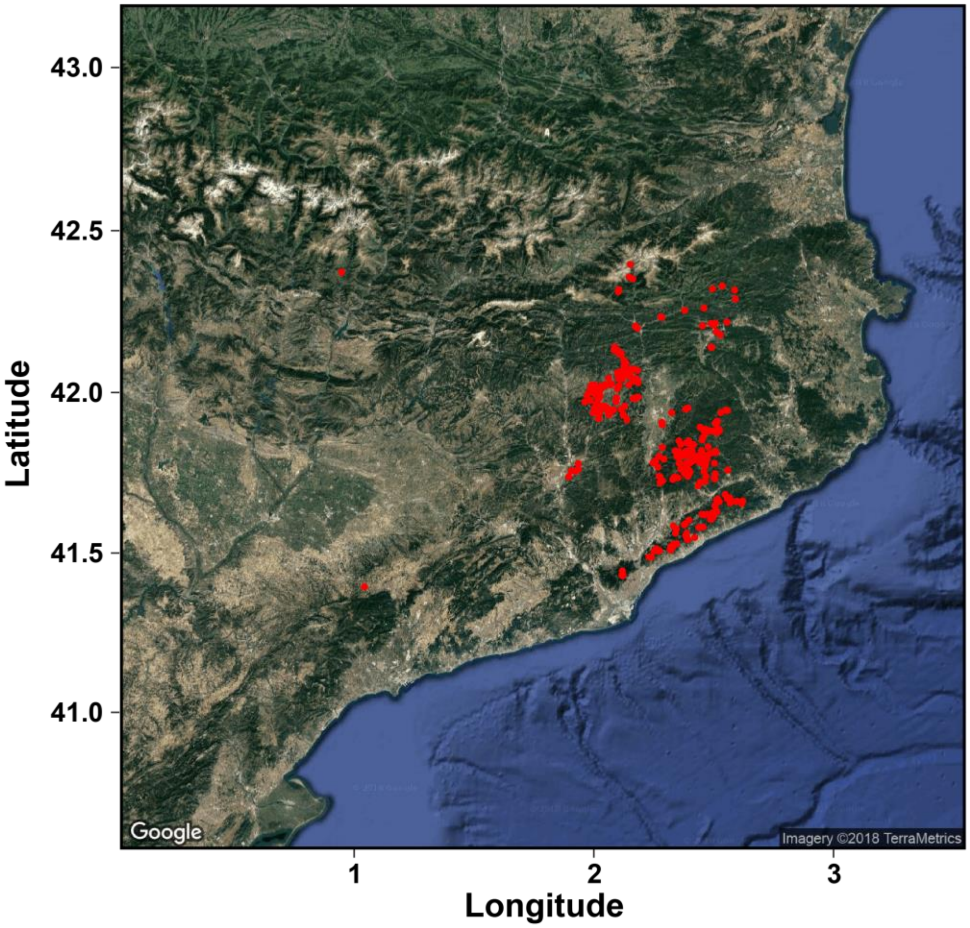

Figure 2: Piper diagram of the water samples collected. The colour of the points shows the distance of each spring to the coastline in km. Samples in the top quadrant of the diamond plot are $CaSO_4$ waters, samples in the right quadrant are NaCl waters, samples in the left quadrant are $CaHCO_3$ waters,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

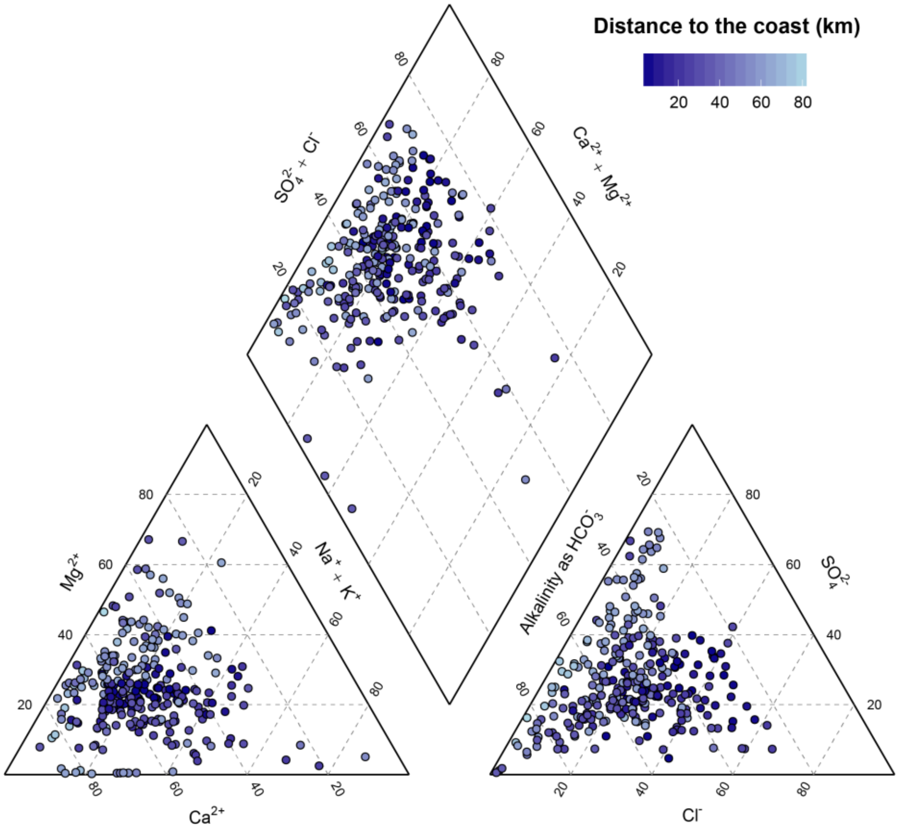

Figure 3: Biplots showing scores and loadings of the first three components extracted by a principal component analysis performed with water chemical composition. The colour of the points indicates the distance from the coast. Ions and elements shown are: Na^+ - sodium ion, K^+- potassium ion, Mg^{2+} - magnesium ion, Ca^{2+} - calcium ion, Cl^- - chloride ion, NO_3^- - nitrate ion, SO_4^{2-} - sulphate ion, PO_4^{3-} - phosphate ion, Al - aluminium, As - arsenic, Cd - cadmium, Co - cobalt, Cr - chromium, Cu - copper, Fe - iron, Mn - manganese, Pb - lead, Hg - mercury, Ni – nickel, and Zn – zinc.

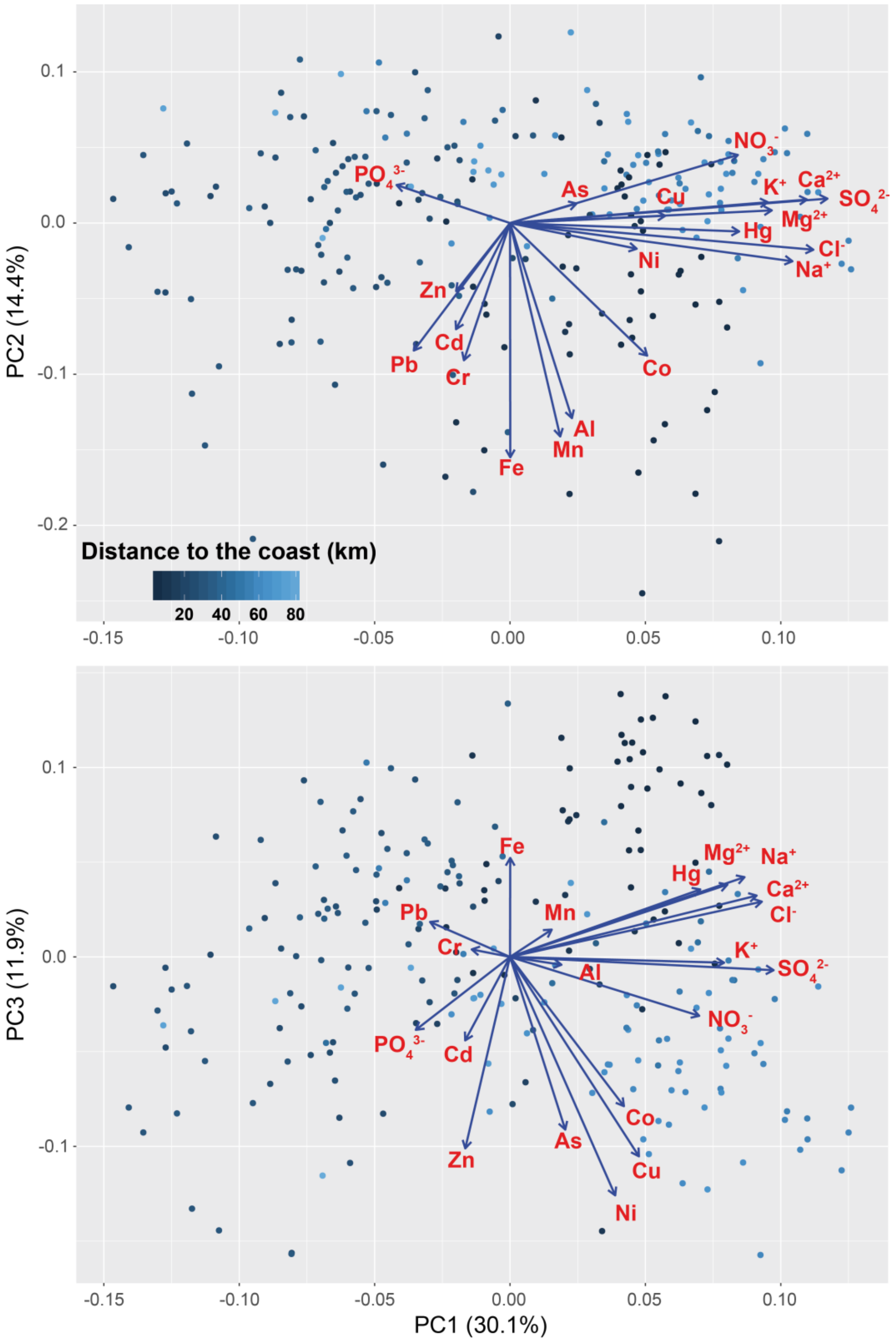
PC2 (14.4%)
0.1
0.0
-0.1
-0.2
NO$_3^-$
As
Cu
K$^+$
Ca^{2+}
SO$_4^{2-}$
Mg^{2+}
Hg
Cl$^-$
Na$^+$
Ni
PO$_4^{3-}$
Zn
Cd
Pb
Cr
Co
Al
Mn
Fe
Distance to the coast (km)
20
40
60
80
-0.15
-0.10
-0.05
0.00
0.05
0.10
PC3 (11.9%)
0.1
0.0
-0.1
Fe
Mg^{2+}
Na$^+$
Hg
Ca^{2+}
Cl$^-$
Mn
Pb
K$^+$
Cr
SO$_4^{2-}$
Al
NO$_3^-$
PO$_4^{3-}$
Cd
Co
As
Cu
Zn
Ni
-0.15
-0.10
-0.05
0.00
0.05
0.10
PC1 (30.1%)

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

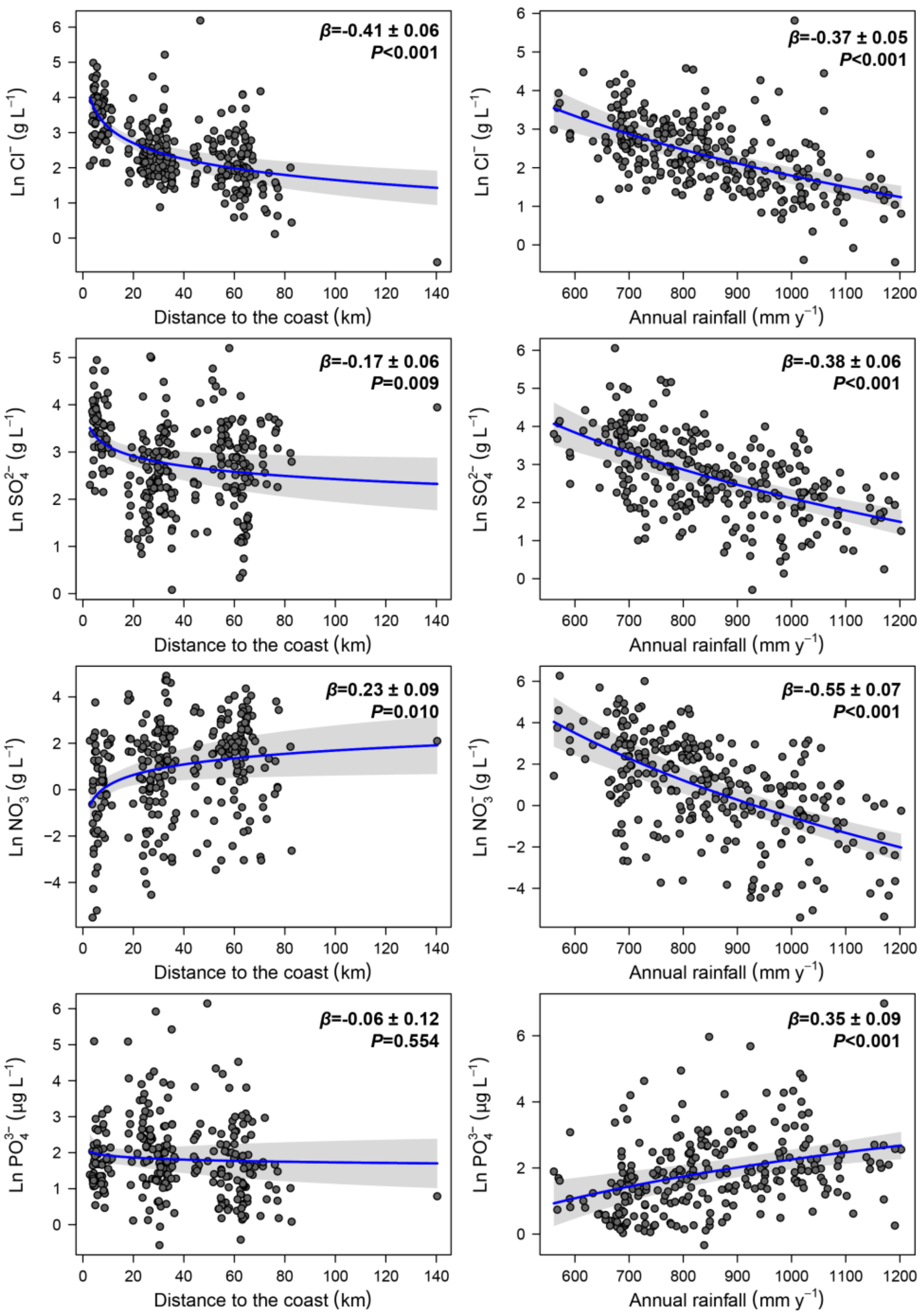

Figure 5: Partial residual plots showing the relationship of distance from the coastline and mean annual precipitation with main cations. Standardized (*β*) coefficients and *P* values and partial residuals were extracted from a model containing distance from the coast, chemistry of the lithology, nitrate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

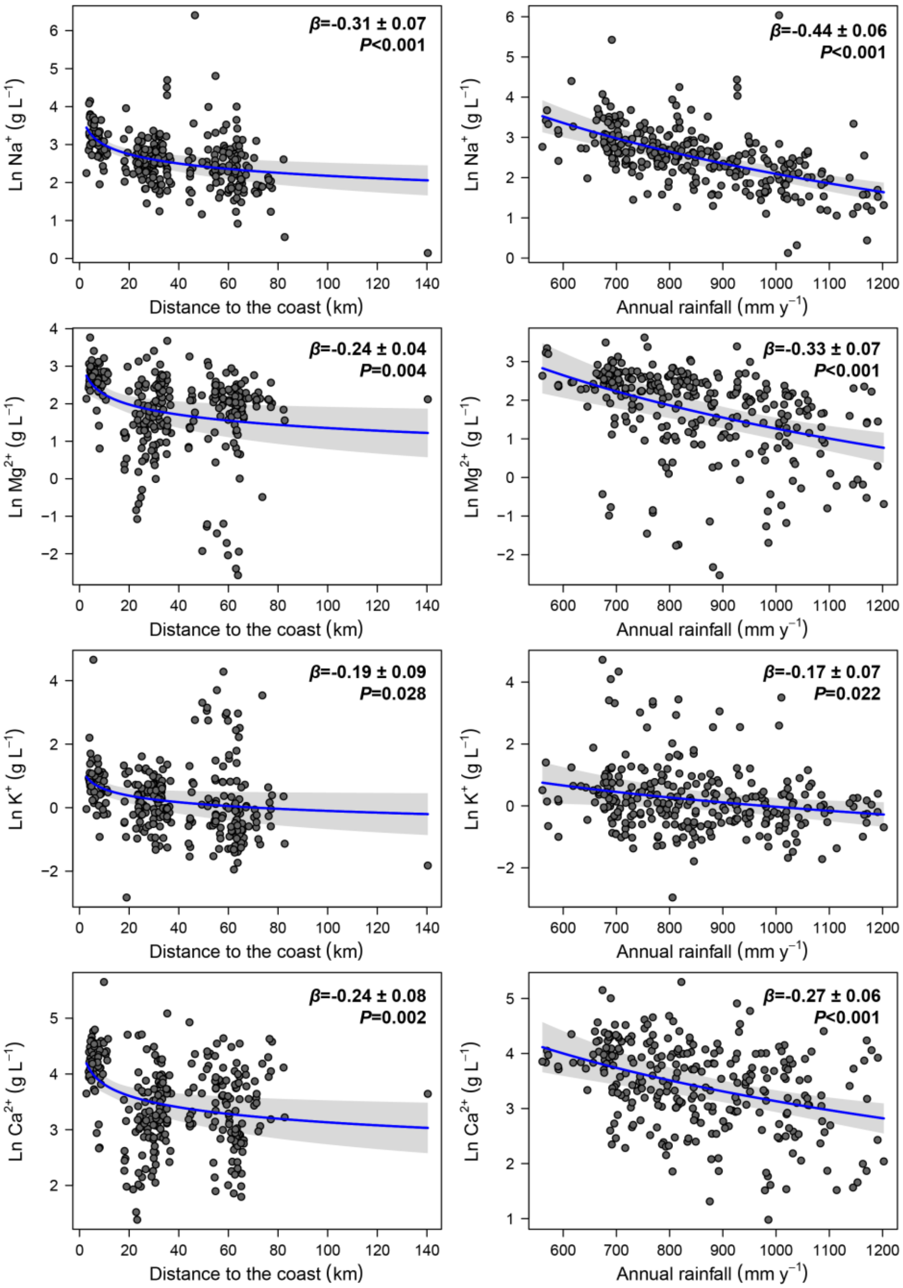

Figure 6: Partial residual plots showing the relationship between the distance from the coastline and the Na:Cl ratio on a molar basis. *β* coefficients and *P* values and partial residuals were extracted from a model containing distance from the coast, lithology and nitrate concentration as predictors,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

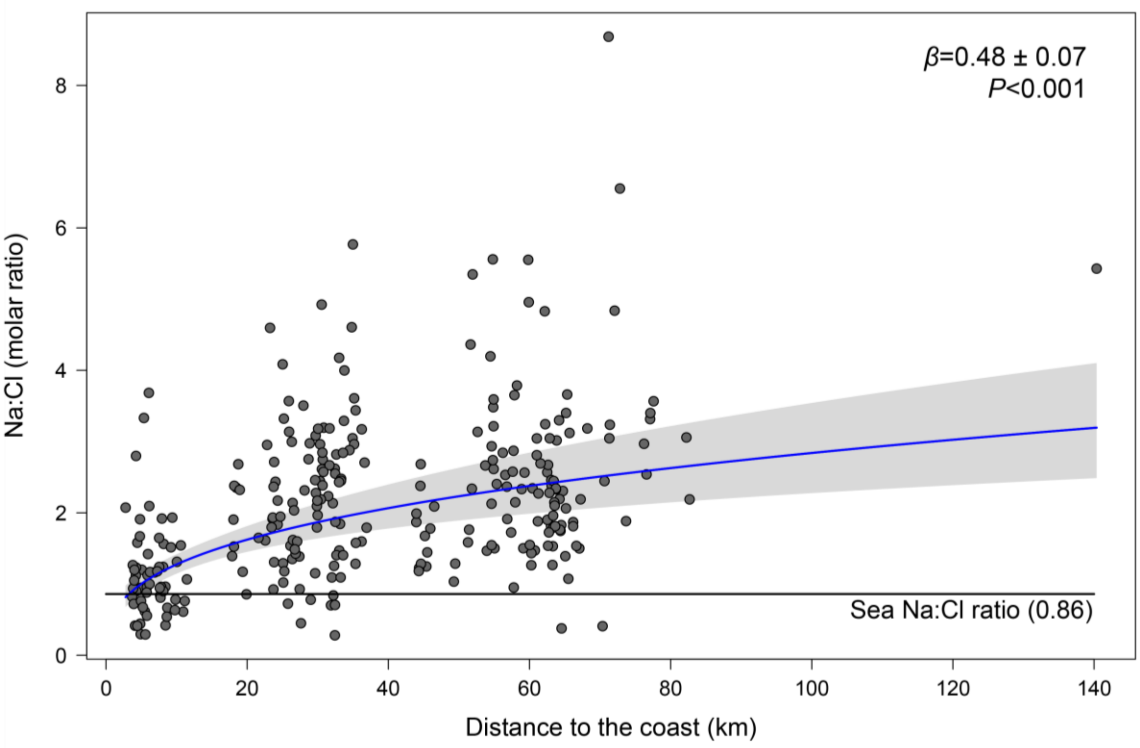

Table 1: Standardized (β) coefficients and percentage of variance explained (R^2) of each of the statistically significant predictors explaining variability in water concentration of main anions and cations. For lithology, only R^2 is shown. See **Methods** for further information about the models. Significance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

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

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

	Distance to coast	***R^2***	**Nitrate**	***R^2***	**Precipitation**	***R^2***	**Lithology**
Al	-0.32 ± 0.11 **	5	-0.18 ± 0.07 *	1	-0.20 ± 0.09 *	5	7 ***
As							37 ***
Cd							11 ***
Co	-0.30 ± 0.08 ***	2					10 ***
Cr	-0.39 ± 0.07 ***	8	0.20 ± 0.07 **	1	0.30 ± 0.08 ***	2	
Cu					-0.13 ± 0.05 *	4	34 **
Fe	-0.46 ± 0.08 ***	22	-0.18 ± 0.06 **	4			
Mn	-0.37 ± 0.07 ***	10	-0.17 ± 0.07 **	2			10 ***
Pb							15 ***
Hg	-0.31 ± 0.10 **	7	0.14 ± 0.06 *	7	-0.39 ± 0.08 ***	20	6 *
Ni					-0.11 ± 0.05 *	2	28 ***
Zn							12 ***

Supplementary material

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