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Trace elements in the water column of high-altitude Pyrenean lakes: Impact of local weathering and long-range atmospheric input

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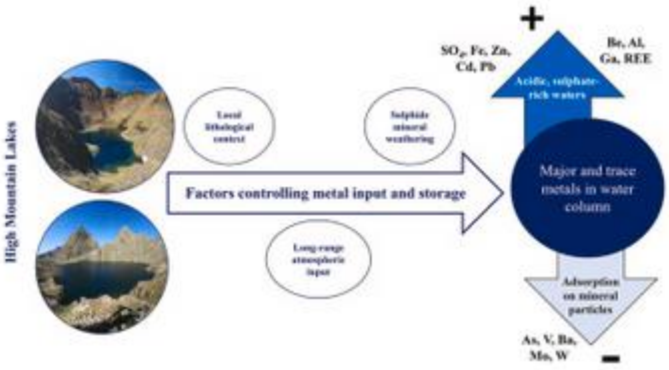
Abstract :

High altitude (alpine) lakes are efficient sentinels of environmental processes, including local pollution and long-range atmospheric transfer, because these lakes are highly vulnerable to ongoing climate changes and increasing anthropogenic pressure. Towards improving the knowledge of trace element geochemistry in the water column of alpine lakes, we assessed 64 physico-chemical parameters, including macro- and micronutrients, major and trace element concentrations in the water column of 18 lakes in the Pyrenees, located along the border between France and Spain.

Lake depth, morphology, retention time and watershed rock lithology did not exhibit sizable impact on major and trace element concentrations in the water column. However, acidic (pH = 4.7 ± 0.2) lakes were distinctly different from circumneutral lakes (pH = 6.8 ± 0.5) as they exhibited >10 times higher concentrations of SO42− and trace metals (Fe, Mn, Zn, Cd, Pb, Co, Ni, Be, Al, Ga and REEs). While some of these elements clearly mark the presence of sulphide-rich minerals within the watershed (Fe, Zn, Cd and Pb), the increased mobility of lithogenic elements (Be, Al, Ga and REEs) in acidic lakes may reflect the leaching of these elements from silicate dust derived from atmospheric deposits or surrounding granites. At the same time, compared to circumneutral lakes, acidic lake water displayed lower concentrations of dissolved oxyanions (As, Mo, V, B and W) and elevated SO42− concentrations. The latter could lead to efficient Ba removal from the water column. The exploitation of metal ores within the watershed of three lakes clearly impacted high Zn and Cd concentrations observed in their water column, despite two of these lakes not being acidic. We conclude that local impacts have a greater effect on the water column than long-range atmospheric inputs and that dissolved trace element concentration measurements can be used for revealing sulphide-rich minerals or acid mine drainage within the lakes' watershed.

Graphical abstract



Highlights

► Dissolved major and trace elements in water column of 18 alpine lakes. ► Solute sensitivity to local lithological context and long-range atmospheric input. ► Sulphide mineral weathering controls trace metals in the water column. ► Acidic, sulphate-rich waters are rich in trace metals and trivalent lithogenic elements. ► Oxyanions are depleted in acidic lakes due to adsorption on mineral particles.

Keywords : Alpine lakes, Pyrenees, Trace metals, Sulfide, Pollution, Atmospheric dust

1. INTRODUCTION

Alpine lakes, typically located above 2000 m altitudes and subject to seasonal freezing, are considered sentinels of environmental processes including local pollution (Shen et al., 2022) and long-range atmospheric transfer (Catalan et al., 2013). These lakes are typically seasonally stratified, are low-humic and low-mineralized, due to the dominance of rain and snow feeding their water balance. Because the watershed of alpine lakes exhibits relatively low vegetation biomass, compared to typical lakes of the plains, such lakes can be helpful in tracing direct impact of rock lithology on the hydrochemistry of surface waters. Furthermore, lakes at high altitudes are particularly sensitive to climate change and modification in their carbon biogeochemistry (Adrian et al., 2009; Mladenov et al., 2011); these lakes are highly vulnerable to any type of external impact.

In order to assess the level of local and global pollution impact on alpine lakes, spatially resolved measurements for both major and trace components are necessary. Compared to lake sediments, which were used for a long time as reliable environmental archives of past and contemporary pollution (i.e., Bacardit and Camarero, 2010a; Camarero et al., 1998; Camarero, 2003; Ruiz-Fernández et al., 2003; Williamson et al., 2009), the water column of lakes can be considered more sensitive and as a fast reacting medium with respect to environmental input of various contaminants (Moser et al., 2019).

Over the past decades, sizable research efforts were devoted to biogeochemical cycling of trace elements in the water column in seasonally stratified lakes of the temperate zone (Achterberg et al., 1997; Hamilton-Taylor et al., 1996, 2005), boreal regions including Scandinavian (Kortelainen et al., 2006; Tranvik et al., 2009), Canadian (Alfaro-De la Torre et al., 2000; Gibson et al. 2002; Johannesson and Lyons, 1995; Johannesson and Zhou, 1999; Laurion et al., 2010), European (Moiseenko and Gashkina, 2007; Pokrovsky et al., 2012; Shirokova et al., 2013a, 2020) and Siberian subarctic lakes (Manasypov et al., 2015, 2020, 2023; Pokrovsky et al., 2013, 2016; Shirokova et al., 2013b). Although these seasonally stratified high-latitude lakes can be used as analogues for alpine lakes, mainly in terms of their temperature regime (seasonal stratification, a period of approximately one half year ice coverage), most of them are highly humic (i.e., rich in dissolved organic matter (DOM) which is derived from surrounding bogs, tundra and forest litter). As a result, the concentrations and speciation of most trace elements suitable for determination of environmental properties in these lakes are drastically different from those of alpine lake with low dissolved organic carbon (DOC).

Up to present time, few studies on trace element geochemistry in typical alpine lakes are available. These include glacial lakes of the Himalayas (Khan et al., 2022) and alpine lakes in New Zealand (Reid et al., 1999; Sander et al., 2007; Zhu et al., 2020). European high latitude lakes were only occasionally studied from the view point of water column chemistry (Bacardit and Camarero 2010b; Zaharescu et al., 2009), notably for trace metal concentrations, with most information on lake sediments versus solutes (i.e., Camarero et al., 2009; Koining et al., 2003; Lavilla et al., 2006; Thevenon et al., 2011; Yang et al., 2002). In this study, we selected alpine lakes located along the French – Spanish border in the Pyrenees Mountains. The interest in this region is two-fold. First, these lakes can serve as efficient sentinels of long-range atmospheric pollution, given that the Pyrenees lie on the boundary of the Atlantic and Mediterranean air mass transition zone. It is known that long-range transport of trace metal pollutants through the atmosphere (Bacardit, 2011; Bacardit and Camarero, 2009; Camarero, 2017) is followed by their delivery to lake watersheds in the form of both wet and dry deposition (Camarero et al., 2017; Gioda et al., 2011; Groeneveld et al., 1993; Marques et al., 2004). Therefore, long-range atmospheric transfer (Camarero et al., 2009) impacts all alpine lakes globally (Catalan et al., 2013). Perhaps the most spectacular examples are Saharan dust outbreaks, which distribute significant amounts of trace metals and metalloids—in the form of solid aerosol materials—worldwide (Escudero et al., 2005). Local range atmospheric pollution can be also pronounced, given the presence of large cities (Bilbao, Bordeaux, Zaragoza, Toulouse and Barcelona) surrounding the Pyrenees. Second, the water column of lakes can allow tracing of local mining activities or specific heavy-metal bearing ores within their watershed. In this regard, the pH of lake water is known to be the best sentinel for tracing acidic and metal sources (i.e., Gammons et al., 2005). Extreme examples of lake contamination derived from mining activity include acid mine drainage (AMD) impacted pits in metal ore provinces (Bozau et al., 2004; Gammons et al., 2003; Viers et al., 2023). Similarly high acidity and dissolved metal concentrations are observed in lakes located in the vicinity of active volcanoes (Gammons et al., 2005; Pedrozo et al., 2001, 2002; Takano et al., 2004).

Only a few studies exist that examine and address trace metal patterns in Pyrenean lakes. Lake Marboré (Central Pyrenees) exhibited elevated concentrations of Fe, Zn and sulphate which indicated localized sulphide oxidation processes (Sanchez-Espana et al., 2018), despite its circumneutral pH (7.0 to 7.8). Bueno et al. (2022) reported major ions and selenium (Se) concentrations in 20 neutral (pH = 6.0-7.5) central-western Pyrenean lakes and demonstrated that the dissolved Se originates from S-enriched bedrock and long-range atmospheric deposition. Zaharescu et al. (2009) studied a dammed lake in the central Pyrenees and revealed the source for numerous trace elements (As, Cd, Co, Cu, Mn, Ni, Pb and Zn) in the water column and lake catchment to be linked to local geology. Finally, Duval et al. (2023) addressed the behavior of Hg in 19 high-altitude pristine lakes from the western and central Pyrenees. Outside these studies, information regarding trace element concentrations of Pyrenean lakes remains extremely limited.

To fill this knowledge gap, the present study focuses on the assessment of major and 40 trace element concentrations in the water columns of 18 representative and contrasting high altitude lakes throughout the Pyrenees. This work reports results of extensive sampling campaign conducted in summer 2013 which included thorough study of lake sediments for chemical composition (Rodriguez-Iruretagoiena et al., 2023) and microbiological assessment of the water column and sediments (Compte-Port et al., 2018). Here, through encompassing both deep and shallow lakes and sampling surface and bottom horizons, we aim to characterize the role of local metal sources, which is present in several pre-identified lakes, versus global atmospheric transfer, which is pronounced for all selected lakes. For this, we tested the role of lake morphology, retention time and other hydrological parameters and watershed lithology on the dissolved element concentration. We hypothesize that the acidity of the lake water is the main factor controlling trace element patterns in the water column and that, together with dissolved sulphate, it can be evidence of the dissolution of sulphide minerals on the lake watershed, be it natural or anthropogenic (acid mine drainage).

2. MATERIAL AND METHODS

2.1. Study site and sampling

From August through September of 2013, we sampled 18 high-altitude (> 2000 m) Pyrenean lakes (**Fig. 1**; **Table 1** as adapted from Del Castillo, 2004). These lakes are located in France [Anglas (AN), Aubé (AU), Bersau (BE), Compte (CO), Estelat (ES) and Siscar (SI)] and Spain [Airoto (AIr), Aixeus (AIx), Baiau (BA), Eriste (ER), Gran del Pessó (GR), Llosás (LL), Mariola (MA), Monges (MO), Montoliu (MT), Plan (PL), Pica Palomèra (PP) and Romedo de Dalt (RO)]. Most lakes are located in pristine regions, without known agricultural and/or industrial activity on their catchments. The exceptions are sites exploiting metal (Pb, Zn) ores since ancient times within the catchments of lakes Montoliu, Pica Palomèra and Anglas (Birch et al., 1996; Subias et al., 1999). Lakes Aixeus and Baiau Superior also have some mines in the lower part of their valleys. These are old iron mines that were exploited in an artisanal fashion from the 2nd century BC until the 19th century. The lithology of Aixeus and Baiau Superior lakes catchment is represented by Cambro-Ordovician schists that are pyrite enriched.

Given that the lakes are free of ice from June through October, August is the optimal time for sampling of a seasonally stratified water column, in order to avoid the period of spring and autumn overturn. Sampling was performed in the deepest (usually central) part of the lakes reached via inflatable boat. The surface (0.5 m) and bottom (approx. 0.5 m above the sediment-water interface) horizons were sampled using Aquatic Research® horizontal water sampler.

The water temperature, O_2 level and specific conductivity were measured on-site. Water temperature was measured using a PT100 thermistor (Digiterm) while conductivity was measured in the laboratory with a WTW 3110 meter. The pH was measured using CRISON 5221 electrode, suitable for low ionic strength solutions and an Orion 720 m pH-meter. Dissolved oxygen was measured using the Winkler method.

The water was filtered on-site through a 0.22 µm membrane filter, previously acid cleaned, for analyses of major and trace elements and the filtrate was acidified with bi-distilled HNO_3. Another filtration was performed through a GFF pyrolyzed filter for DOC analyses.

2.2. Water sample analyses

Major anions and nutrients (PO_4^{3-}, Cl^-, SO_4^{2-}, NH_4^+ and NO_3^-) were measured in non-acidified samples. Soluble Reactive Phosphorous (SRP) was determined by colorimetry using a segmented flow autoanalyzer (AA3HR, Seal/Bran + Luebbe) with an automated method based on Murphy and Riley's (1962) method (Bran + Luebbe method G-175-96). NH_4^+ was determined by an automated version of the blue indophenol (Berthelot reaction) method (B + L G-171-96) using a segmented flow autoanalyzer. The concentrations of Cl^-, SO_4^{2-} and NO_3^- were measured by capillary electrophoresis according to Method 6500 of the US Environmental Protection Agency (2007). DOC was measured using a Shimadzu TOC 5000 with an uncertainty of 5%. To characterize the phytoplankton parameters, we measured IFEO which is the index of phaeopigments and ICARO which is the index of carotenoids. These indices were measured as absorbance ratios in the visual range (Abs_{433}/Abs_{413} and Abs_{472}/Abs_{664} respectively), after extraction by 90 % acetone from phytoplankton collected on filters.

Filtered solutions for cations and trace element analyses were acidified (pH = 2) with ultrapure double-distilled HNO_3 and stored in HDPE bottles previously washed with 1 M HCl (Merck) and rinsed with Milli-Q deionized water. The bottle preparation for sampling was performed in a class A-10,000 clean room under a class A-100 laminar hood. Filtered water samples for anions were not acidified and stored in HDPE bottles previously washed according to the above-described procedure for cations.

Milli-Q blanks were routinely processed in parallel to lake water to account for possible contamination during sampling, transport, storage, handling and analyses.

Trace elements (TE) were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500) with indium and rhenium as internal standards and a precision better than ±5%. Detection limits of TE were set as 3× the blank signal. The uncertainty for elemental concentration measurements ranged from 5 to 10 % at 1–1000 µg L^{-1} to 10–20 % at 0.001–0.1 µg L^{-1}. The international geostandard SLRS-5 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. Good agreement was obtained between our replicated measurements of SLRS-5 and the certified values (relative difference $\leq$ 10%). In addition to SLRS-5, we analysed in-house water standard which was obtained by ten-fold dilution of SLRS-5. This allowed testing the limits of quantification for elements present in trace amounts of the lake water. Note that although the 10× diluted SLRS-5 sample is not certified, it could be used as a surrogate for assessing elementary concentrations in low-mineralized lakes of circum-neutral pH samples. We accepted 20% agreement as satisfactory between the calculated concentrations of this diluted standard and the actual measured concentrations for all elements.

2.3. Data treatment

The Shapiro-Wilk test demonstrated that the data on solute concentrations in the water column were abnormally distributed, and thus non-parametric statistics were used. The Kruskal-Wallis test was used to check for possible existence of significant differences between major and trace element concentrations in different lakes as well as between surface and bottom horizons of lakes. The level of significance was fixed at

0.05 (95% confidence level) to consider a result as statistically significant. Pairwise (Pearson) correlations were used to assess the relationship between lake water pH and concentration of other solutes.

More thorough statistical analyses were applied to get a distinctive view as to the influence of landscape parameters of the watershed, lake morphology, lake depth and lithology on major and trace element variations among lakes, separating for surface and bottom horizons. In order to eliminate redundancy of variables, Principal Component Analysis (PCA) was used as it supplies scores for observations (samples in each location and each horizon) and loadings for variables (elemental concentrations) which could be interpreted together (Holmes, 2006; Viers et al., 2023). An Eigenvalue graph (not shown here) suggested 2 to 4 dimensional scores. The appropriate number of principal components (PCs) used in the multivariate analysis was determined by a scree plot. Scores for observations (lakes and their watershed parameters) and loadings for variables (biplots of element concentrations) were interpreted together (De la Cruz and Holmes, 2011). Furthermore, inertia ellipses regrouping samples by site, by lithological context or by lake water type (acidic, neutral) were used to visualize data structures (Chessel et al., 2004). For this, we used the ADE4 package developed with The Comprehensive R Archive Network® for statistical computing and graphics (Thioulouse et al., 1997).

In some cases, the number of physico-chemical variables (nutrients, major and trace elements) was superior to the number of individuals (lakes). For this, instead of classic PCA, we used a Sparce PCA (SPCA) to select the sub-group of coordinates with maximal sample variability, and then we ran the PCA on the sub-group (e.g., Johnstone and Lu, 2009). In order to obtain the highest stability of results, variables were selected by 10 sub-group and decomposed on subsets of 5 pairs. The mean and standard deviation of each run was recorded. The calculation was performed using a library of mixOmics (Lê Cao et al., 2009). Further, to relate the physical, lithological and physico-chemical parameters of lakes, we used a M-fold cross-validation procedure. For this, we subdivided the data into 10 groups with arbitrary distribution of lakes. After that, one criterion was calculated for each group and this operation was repeated 5 times. We used a Q2 total criterion to evaluate the prediction performance of the model following:

$$Q2 = 1 - SS_E/SS_O$$

where SS_O is the sum of squares of deviations from the mean of observations:

$$\sum(y_i - \bar{y})^2$$

and SS_E is the sum of squares of deviations from the mean of predictions:

$$\sum(y_i - \hat{y})^2$$

3. RESULTS AND DISCUSSION

3.1. Multiparametric treatment of physico-chemical variables (solutes of the water column)

The full data set of physico-chemical parameters for the lakes, concentrations of nutrients, major and trace elements is provided in the Mendeley data portal (Pokrovsky and Gonzalez, 2023). The SPCA analysis restricted the data set to three dimensions. The correlation between the factors demonstrated that the dataset can be expressed by seven variables for axis 1 and one variable for axes 2 and 3 (**Fig. S1** of the Supplement). Dominant factor 1 therefore separated lakes Aixeus and Baiau Superior from other lakes. These two acidic lakes are enriched in sulphate, Al, Co, Ni, Ga and REEs (**Fig. 2 A, B**).

Factor 2 separated the lakes into two groups. Group 1 included Airoto, Siscar, Compte and Estelat and was different from group 2 which comprised all other lakes (**Fig. 3 A,**

B). Lakes of the first group were rich in dissolved phosphorus and poor in trace metals (Cu, Fe, Cs, Pb, Zn and Cd). Factor 3 differentiated the surface and bottom horizons of all lakes. The bottom waters were rich in all forms of dissolved nitrogen whereas the warmer surface waters were enriched in O_2. The IFFO value, which is an indication of the proportion of phaeopigments as result of chlorophyll degradation, was higher in warmer surface waters compared to bottom waters.

The SPCA and M-fold cross-validation procedure was also used to investigate the relationships between physical parameters of lakes, lithology of their watersheds and major and trace solute concentrations in both surface and bottom waters. The factorial structure was rather weak and no significant controlling factor in addition to those identified among solutes could be revealed. The Q2 criterion was negative (**Fig. S2**), hence demonstrating weak relationships between the two groups of variables. A simultaneous representation of the two groups of variables (environmental and physico-chemical) demonstrated a sizable length of arrows (**Fig. S3**) thereby suggesting that the physical and lithological parameters of the lakes are weakly linked to their physico-chemical variables. Similarly, the correlation circle (**Fig. S4**) did not evidence any significant correlations between the two groups of variables. Summarizing the results of multi-parametrical statistics, the global lithology of the lake's watershed and physical parameters of the lake do not exert any sizable control over physico-chemical parameters (solutes) of the water column.

3.2. Mechanisms of element mobilization and enrichment in the water column

The relationships identified via the SPCA approach were further detailed by pairwise correlation analysis. The pH of the lake water was found to be the main factor controlling the concentration of other solutes. Thus, sulfate, divalent metals (Be, Mg, Cu, Co, Ni and Mn) and trivalent cations (Fe, Al, Ga and REEs) strongly—by a factor of 10 to 100—decreased their concentration in both surface and bottom water horizons of the lakes at pH > 5.5 (**Fig. 4**). A histogram illustrating the difference in solute concentrations between acidic (pH = 4.7±0.2, *n* = 3) and circumneutral (pH = 6.5±0.2, *n* = 15) lakes demonstrates a clear distinction between the two groups of lakes for various elements. In particular, some heavy metals – micronutrients and pollutants (Zn, Cd, Fe, Mn, Pb, Cu, Co, Ni), divalent alkaline-earth metals (Be, Mg), trivalent hydrolysates – geochemical tracers (Al, Ga, REEs), Cs and sulfate were significantly ($p < 0.05$) enriched in acidic lakes relatively to other lakes (**Fig. 5**). Rare earth elements exhibited the strongest contrast (up to 3 orders of magnitude) between acidic and neutral lakes, as illustrated by REE patterns normalized to average world river values (from Gaillardet et al., 2004) for Baiau Superior, Aixeus and the mean of all circumneutral rivers (**Fig. 6**). The patterns were generally flat with slight enrichment in light REE (LREE) in acidic lakes. In circumneutral lakes, there was a weak (factor of 3) positive Eu anomaly and a slight enrichment in heavy REE (HREE) relative to LREE. Among possible causes of such patterns could be *i*) preferential desorption of LREE from sediment particles and suspended solids in the acidic environment, given the higher affinity of LREE to mineral surfaces as compared to HREE (Bau, 1999) and *ii*) preferential retention of HREE in solution in circumneutral waters, where these elements are more strongly complexed with carbonate ions and organic ligands, compared to LREE. The weak Eu anomaly in circumneutral lakes may stem from granitic (plagioclase-rich) host rocks.

Note that although Zn, Cd and Pb also followed the trend where concentration decrease with increasing pH, two circumneutral lakes (Anglas and Montoliu) exhibited 1 to 2 orders of magnitude higher concentrations of these metals compared to other circumneutral lakes (**Fig. 7**). We believe that the anomalously high concentrations of heavy metals (especially Zn and Pb) in the water column of these lakes reflect past ore mining activities within the lake watersheds, as evidenced by sedimentary records (see section 3.3 below).

Another exception for the metal concentration – pH trend is Ba, which exhibited about 10 times lower concentrations in acidic sulphate-rich lakes compared to circumneutral lakes (**Fig. 5**). A likely mechanism for such a peculiar Ba behavior is its precipitation in the form of barite ($BaSO_4$) given that the acidic lakes exhibited > 10 times higher sulphate concentrations compared to circumneutral lakes.

In contrast to metal cations, oxyanions demonstrated an increase in concentration between acidic and circumneutral lakes in both surface and bottom water horizons (**Fig. 8**). This difference, up to a factor of 10, was statistically significant for As, Mo, V, B, W and phosphate (**Fig. 5**). The restricted mobility of anionic forms of trace metals in acidic ($pH < 5$) relative to circumneutral solutions is a very well-known phenomenon in natural waters (Stumm and Morgan, 1995) and can be explained by retention of oxyanions in the form of adsorbed complexes onto positively charged mineral particles such as Fe or Mn hydroxides and clays. A likely scavenging mechanism would therefore include adsorption of anions onto the mineral surfaces of atmospheric dust particles, inflowing riverine particulate suspended material (PSM) or lake sediments.

In accordance with Factor 3 of SPCA, only a few solutes demonstrated distinctly different concentrations between surface and bottom water horizons, as the chemical stratification in studied lakes was generally low. When averaged among all 18 sampled lakes, surface waters were only weakly enriched, by a factor of 1.5 to 2, in DOC, Al and Cu relative to deep waters. The reasons for the elevated DOC concentration in surface waters include but are not limited to 1) exometabolites of phytoplankton, given that primary productivity was the highest in summer especially in warmer surface horizons of the photic layer; 2) spreading of allochthonous DOM from inlet rivers over the lake surface, and 3) DOM consumption by microbial respiration in the bottom horizons. Dissolved Al and Cu followed an increase in DOC because these elements form quite strong complexes with autochthonous organic ligands (Aiken et al., 2011; Karlsson et al., 2006). Thus, elevated DOM in the surface layers of Pyrenean lakes could promote the leaching of Al and Cu from incoming atmospheric dust or riverine particulate suspended matter that is being spread over the surface layers of the lakes. Excluding shallow lakes (< 5 m depth), the bottom waters of deep lakes were enriched in total and particulate phosphorus (x 2-3), ammonia (x 4), Fe (x 3), Mn (x 10) and Co (x 15) relative to their surface horizons. The other solutes did not exhibit any sizable (> x 1.5) enrichment.

Vertical stratification of nutrients (N and P), which are depleted in the surface layers due to active uptake by phytoplankton and enriched in the bottom horizons due to diffusion from sediments, represents a typical feature of seasonally stratified lakes (Goldman et al., 1996; Pokrovsky et al., 2012). Similarly, Fe and Mn enrichment in the bottom horizon may stem from (partially) anoxic pore waters that provide elevated concentrations of these elements into the bottom water, after the bacteria-driven reduction of Fe and Mn hydroxides, as is known for seasonally stratified lakes (e.g., Pokrovsky et al., 2012; Taillefert et al., 2002). Among all micronutrients, Co exhibited the strongest stratification during summer stagnation, which likely stems from its scavenging with Mn oxy(hydr)oxides via oxidation of Mn(III)- or Mn(IV)-oxide particles (Murray, 1975) of biological origin (Lienemann et al., 1997) within the water column followed by its release (upward diffusion) during bacterial dissolution of Mn oxy(hydr)oxides at the sediment-water interface or in the upper horizons of lake sediments (Taillefert et al., 2002). Similar coupled stratification of redox-sensitive Fe, Mn, Co and ammonia is observed in deep seasonally stratified lakes of the boreal zone (e.g., Pokrovsky et al., 2012).

3.3. Comparison between sediments and water column

A recent study of trace metal in the upper (0-1.5 cm) layer of sediments of Pyrenean lakes demonstrated extreme concentrations of Cd, Mo, Pb, Sb and Zn in Montoliu and Pica Palomera, whereas the sediments of Anglas were enriched in Cd, Cr, Hg, Sr and Zn (Rodriguez-Iruretagoiena et al., 2023). The exploitation of Pb and Zn rich ores has been carried out since ancient times within the catchments of these lakes (Birch et al., 1996; Subias et al., 1999). Thus, the extreme values found for those metals in surface sediments are probably related to mining activity within the lake catchments. This is further corroborated by analysis of the water column in this study; despite their circumneutral waters (pH = 7.2-7.4), Montoliu and Anglas lakes exhibited the highest Zn and Cd concentrations.

The dominant role of pH in metal leaching from sediments is illustrated via comparison of metal concentration in the sediments (Rodriguez-Iruretagoiena et al., 2023) and in the water column (this study). Sediments of the acidic lakes Baias Superior and Aixeus (pH = 4.8) presented significantly higher concentrations of Al, Co, Cu, Fe and Ni in comparison to the rest of the lakes (Rodriguez-Iruretagoiena et al., 2023). Additionally, the bottom layer of the water column in these two lakes was also strongly enriched in Al, Mn, Co, Cu and Ni. In contrast, despite the circumneutral pH (7.1), Lake Bersau exhibited higher concentrations of these metals in the upper sediments yet the water column of this lake was not particularly enriched in trace metals. We therefore suggest both desorption of trace metal cations from lake sediment particles and dissolution of alumosilicates minerals, strongly favoured at $pH < 5$ compared to $pH > 6.5$ (i.e., Schott et al., 2009; Stumm and Morgan, 1995), as the two main mechanisms responsible for elevated concentrations of trace metal cations in the water column of acidic lakes.

3.4. Global significance of trace element geochemistry in Pyrenean lake water and research perspectives

Similar to Pyrenean lake sediments (Rodriguez-Iruretagoiena et al., 2023), the water column of these lakes is also enriched in trace elements reflecting *i*) the lithogenic background (Al, Ga and REEs) of the lake watershed mother rocks, *ii*) atmospheric dust deposits (divalent heavy metals, Sb) and *iii*) the presence of sulphide ore minerals within the watershed (Zn, Pb and Cd). A combination of lake water acidity (originated from chemical weathering of sulphide-rich ores) and the specific granitic environment of the watershed produces strong enrichment in lithogenic, usually immobile elements such as trivalent hydrolysates, Be and Cs. Added to this is relative proximity of the Pyrenees to Sahara dust province, given that the reactivity of such dust deposits is strongly pH-dependent (i.e., Desboeufs et al., 1999). Thus, Camarero et al. (2009) highlighted that, due to a sizable atmospheric input, concentrations of metals and metalloids usually found in high-altitude Pyrenean lakes are higher than those that could be expected for remote pristine areas. In this regard, the alpine lakes of southern Europe clearly present an example of a pristine local environment affected by both local (terrestrial) sources of high-metal sulphide minerals and long-range atmospheric input. However, within relatively small distances between trace metal-rich acidic and trace metal-poor circumneutral lakes, the atmospheric input should not be drastically different among neighboring lakes. Therefore, we argue for the overwhelming control of local lithology and ore mining activity rather than long-range atmospheric pollution, as the primary external factor that controls the chemistry of the lake water column. We suggest that, in order to constrain the dual impact of local and global sources of pollution in other alpine lakes of the world, combined studies of water column, sediments and parameters of lake watersheds across a large number of lakes should be envisaged.

For further interpretation of biogeochemical reactions controlling trace metal cycling in the water column and at the sediment – water interface (e.g., Lopes et al., 2010; Moreira et al., 2010), one has to distinguish between two main controlling processes: (1) mobilization during leaching from settling mineral and organic particles of either external (atmospheric dust, riverine PSM) or autochthonous (biological) origin or (2) diffusion of trace elements from the sediments into the overlying water layer. For this, porewater solutes (e.g., Audry et al., 2011; Tessier et al., 1989) and sediment trap materials (e.g., Sigg, 1985; Sigg et al., 1995; Viollier et al., 1997) should be analysed in order to constrain elemental mass balance within the lake body. Furthermore, measurements of dissolved and particulate concentrations of TE in incoming springs and atmospheric depositions (e.g., Hamilton-Taylor and Willis, 1990) should allow for the elemental mass balance assessment at the scale of the lake watershed.

4. CONCLUSIONS

Towards better understanding the environmental factors controlling major and trace solutes, notably trace metals in alpine lakes, we measured ~45 dissolved (< 0.22 µm) major and trace elements in the water column of 18 high-altitude (> 2000 m) lakes of the Pyrenees along the border of Spain and France. Sulphate-rich, acidic (pH = 4.7±0.2) lakes were strongly enriched, relative to circumneutral lakes, in heavy metals (Zn, Cd, Pb, Cu, Co and Ni) that probably originated from the sulphide minerals within the lake watershed and in lithogenic elements (Al, Ga and REEs) that were likely to be leached by acidic waters from surrounding granites or silicate dust from far-range atmospheric transfer. There was a clear impact of metal-enriched lake sediments on the dissolved metal concentrations found in the water column, and this impact was detected even in circumneutral lakes. This suggests that the water column can inherit the long-term enrichment of the lake with respect to trace metals. The influence of metal input from the watershed remains visible over a long period of time, after neutralisation of the acidic impact from sulphide minerals weathering or acid mine drainage.

The results also demonstrate that the input of trace metals to the lake via long-range atmospheric deposits is sub-ordinary relative to local lithological aspects, notably the presence of highly reactive sulphide minerals. The latter largely control the input of acidic waters from the lake watershed, which *i*) is accompanied by delivery of sulphide-associated heavy metals (Zn, Cd, Pb and Cu) and *ii*) promotes metal desorption and leaching from silicate particles, thereby enriching the fluid in low-mobility lithogenic elements.

We further argue that complex studies of lakes' water columns, sediments and their pore waters, together with incoming rivers and their particulate suspended material as well as both solid and liquid atmospheric deposition are necessary to constrain the elemental balance of pristine alpine lakes. Due to the high sensitivity of the water column to external acidic water inputs, the knowledge of sulphide ore location (or acid mine drainage) within the lake watershed is of primary importance for assessing the degree of lake vulnerability to anthropogenic impact.

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Table 1. List of sampled lakes, their location, maximal depth and physical parameters. WRT is water residence time.

Lake	**sampling date**	**Latitude**	**Longitude**	**Depth (m)**	**Size (ha)**	**Altitude (m)**	**Catchment area (ha)**	**WRT (months)**
Anglas	25/09/2013	43.783	-0.8333	35.0	12.3	2077	61	31.4
Bersau	26/09/2013	42.8387	-0.4945	9.0	3.0	2068	125	1.3
Eriste	04/09/2013	42.6445	0.4681	21.0	3.8	2411	540	0.6
Llosás	03/09/2013	42.6157	0.6548	32.0	4.2	2480	334	1.8
Pica Palòmera	07/09/2013	42.7918	0.8688	10.0	4.9	2308	69	3.2
Monges	06/09/2013	42.6211	0.877	51.0	14.7	2418	110	30.1
Gran del Pessó	26/08/2013	42.5107	0.9156	38.0	9.2	2493	115	13.4
Montoliu	27/08/2013	42.7827	0.9261	16.5	11.2	2375	123	6.6
Plan	28/08/2013	42.6205	0.9307	11.0	5.0	2188	23	11.1
Airoto	29/08/2013	42.7009	1.0392	42.0	18.9	2210	175	21.0
Mariola	21/09/2013	42.7154	1.2243	46.0	17.8	2276	122	30.8
Romedo de Dalt	20/09/2013	42.7041	1.3247	40.0	11.9	2110	260	8.8
Aubé	11/09/2013	42.746	1.338	48.0	8.2	2094	72	26.8
Aixeus	23/09/2013	42.609	1.3718	15.5	3.4	2370	82	2.9
Baiau Superior	22/09/2013	42.5943	1.4319	22.0	7.9	2480	112	6.8
Siscar	12/09/2013	42.5995	1.7472	3.9	4.2	2187	358	0.2
Compte	14/09/2013	42.6317	1.7931	4.6	3.4	1726	1047	0.1
Estelat	13/09/2013	42.6444	2.2135	3.8	4.6	2021	150	0.5

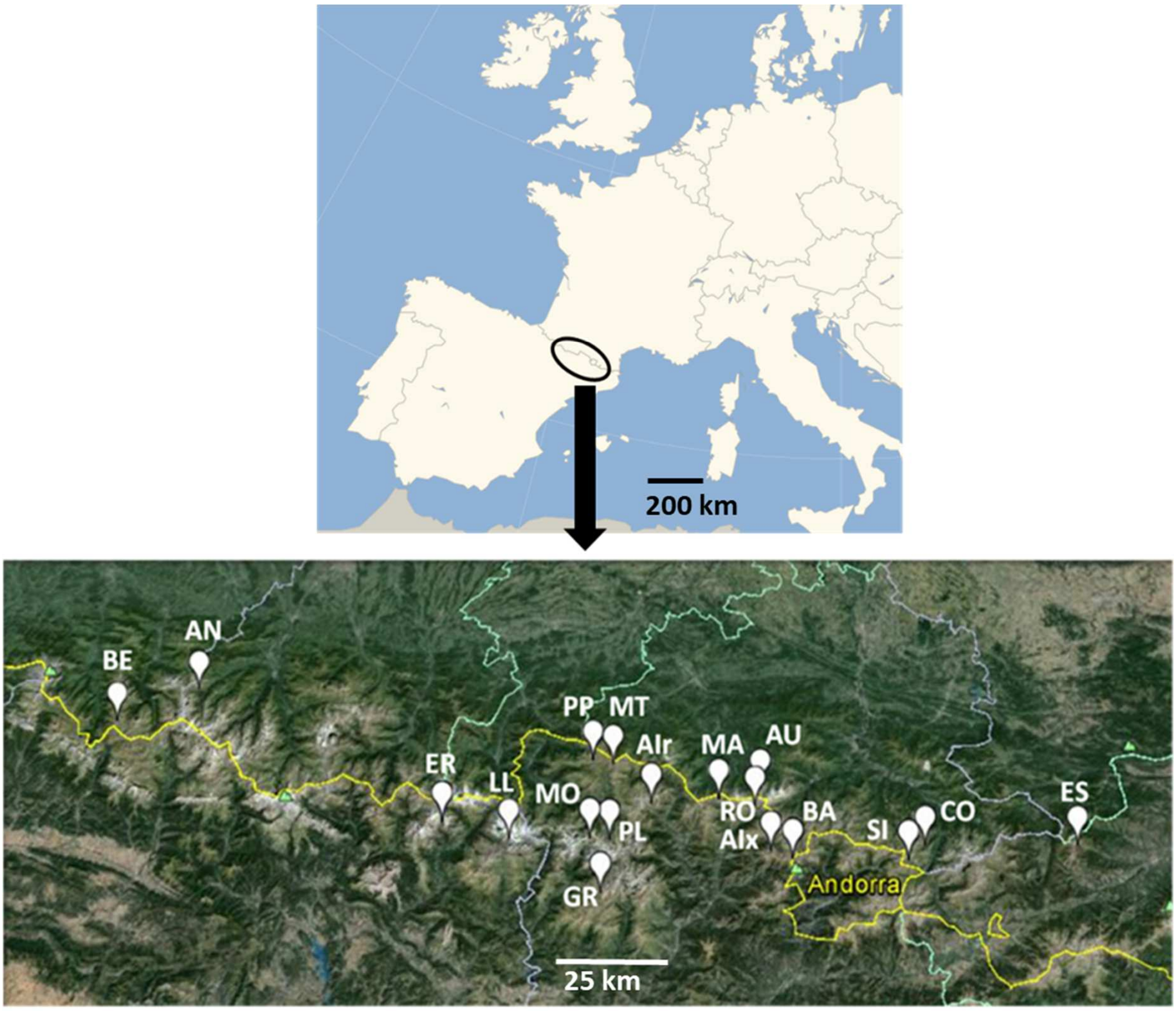


Fig. 1. General position of studied Pyrenean lakes in SW Europe and their locations at the border between Spain and France.

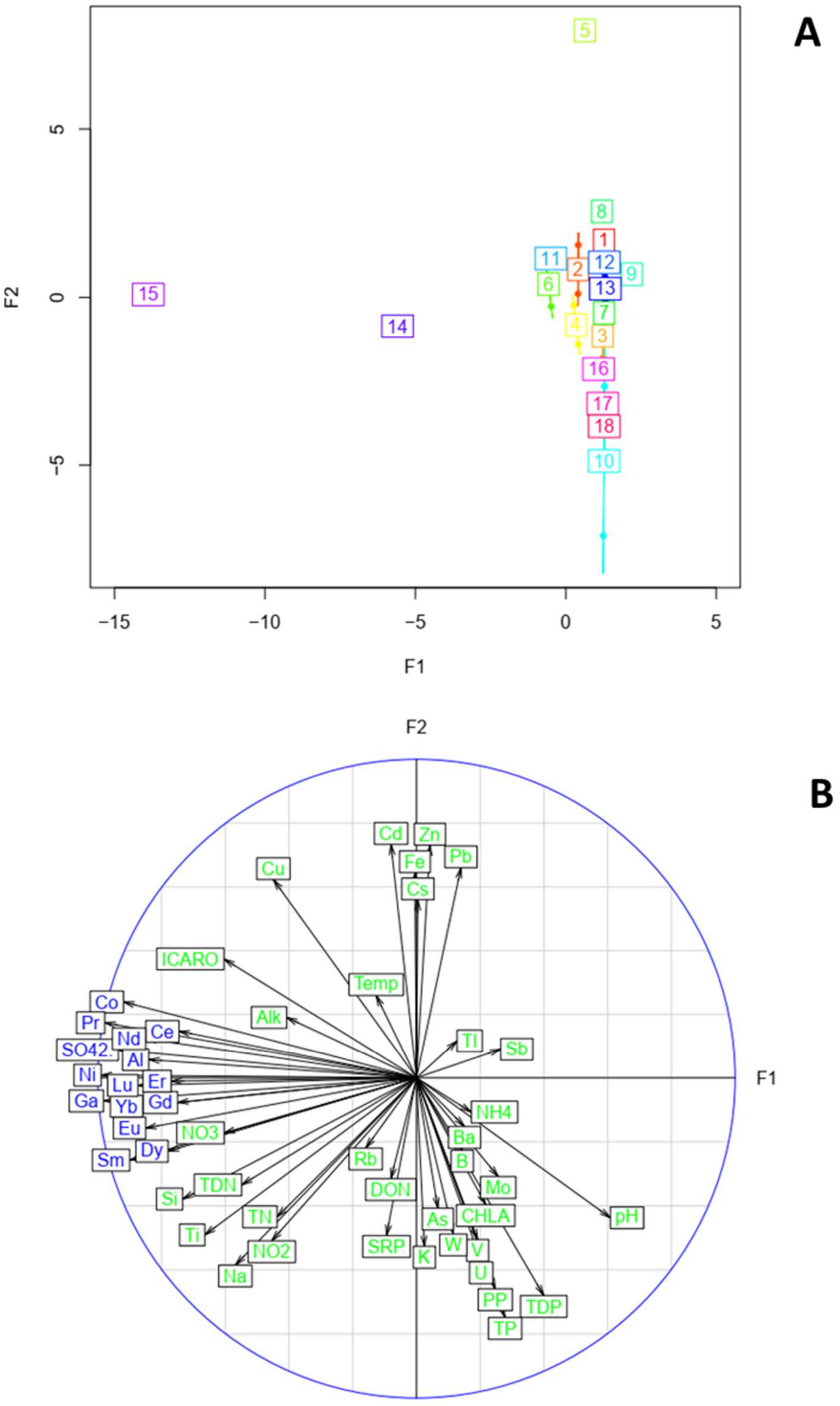


Fig 2. A: PCA plot of F1 X F2 for individual lakes. Three acidic lakes (No 15, 14, 5 corresponding to B. Superior, Aixeus and Pica Palomera, respectively) stay clearly apart of other lakes and are strongly enriched in SO_4, Al, Co, Ni, Ga and REE.

B: Circle of F1 X F2 correlations. The variables in blue and in green constitute Factor 1 and Factor 2, respectively.

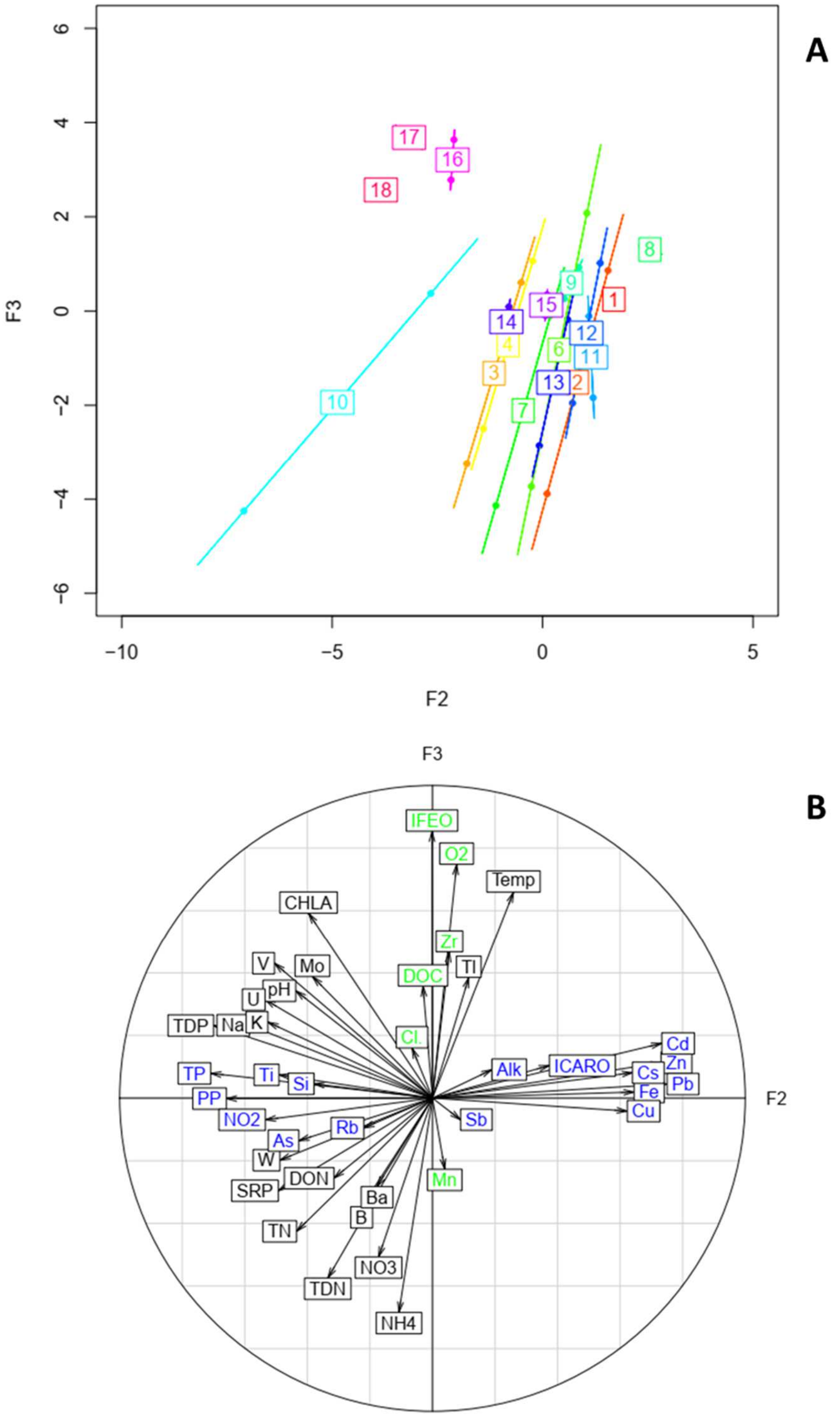


Fig. 3. A: PCA plot of F2 X F3 of individual lakes. These factors are of much lower importance compared to F1. Factor 2 separates the lakes into two groups. The first group comprises lakes No 10, 16, 17 and 18, which are enriched in PP, TP, TDP and depleted in Cu, Fe, Cs, Pb, Zn and Cd. Factor 3 differentiates the surface and bottom waters; the latter are rich in NH_4, TDN, TN and NO_3 (see text).

B: Circle of F2 X F3 correlations. The variable in blue and in green constitute Factor 2 and Factor 3, respectively. Variables in black participate in construction of both factors.

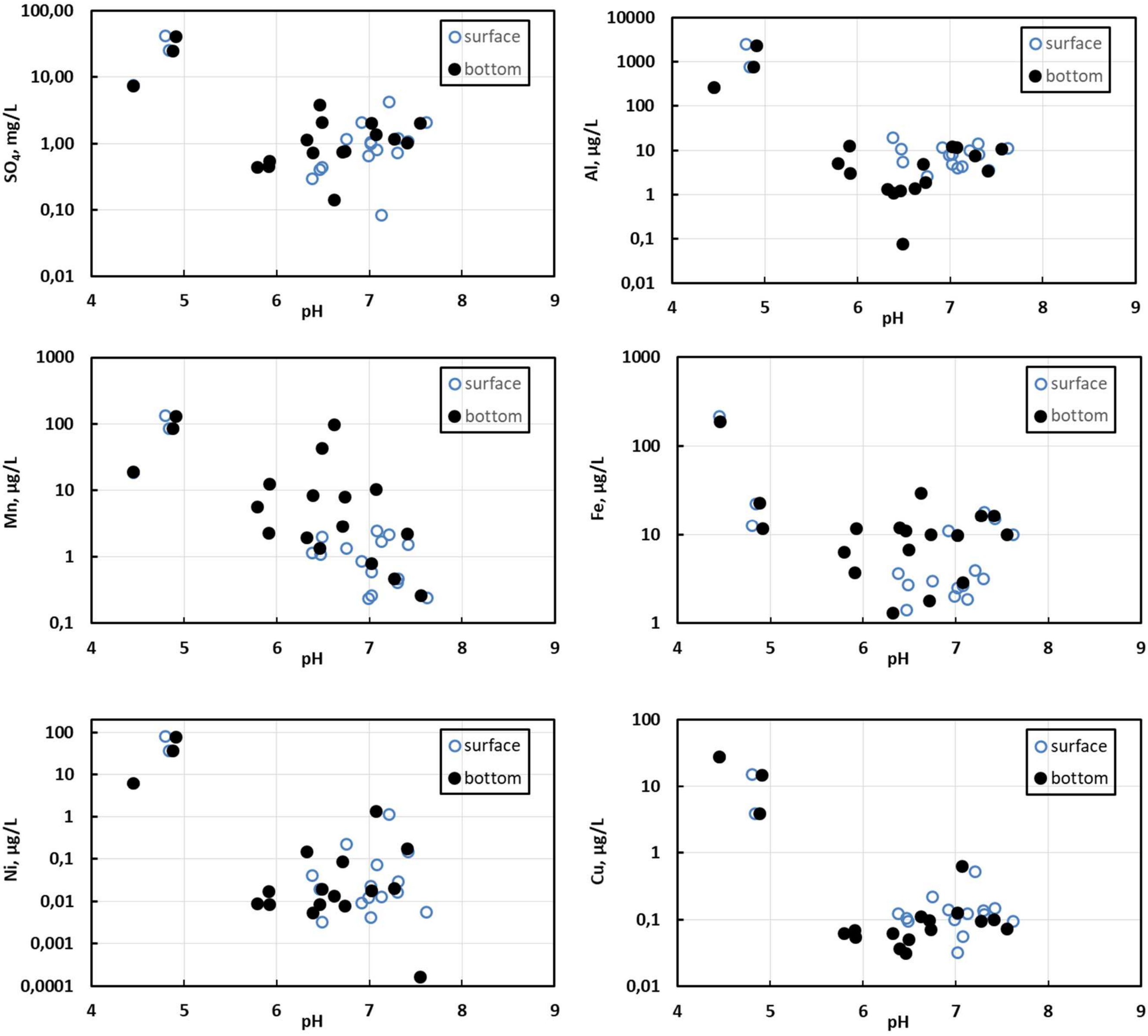


Fig. 4. Dissolved (< 0.22 µm) concentrations (log scale, Y axis) of SO_4, Al, Mn, Fe, Ni and Cu in the surface and bottom horizons of the water column (open and closed circles, respectively) as a function of lake water pH. Two clusters of lakes identified via SPCA treatment (see Fig. 2A) are clearly detected: 1) metal- and sulphate- rich acidic lakes No 15, 14 and 5 corresponding to B. Superior, Aixeus and Pica Palomera, respectively, and 2) all other, metal-poor circumneutral lakes.

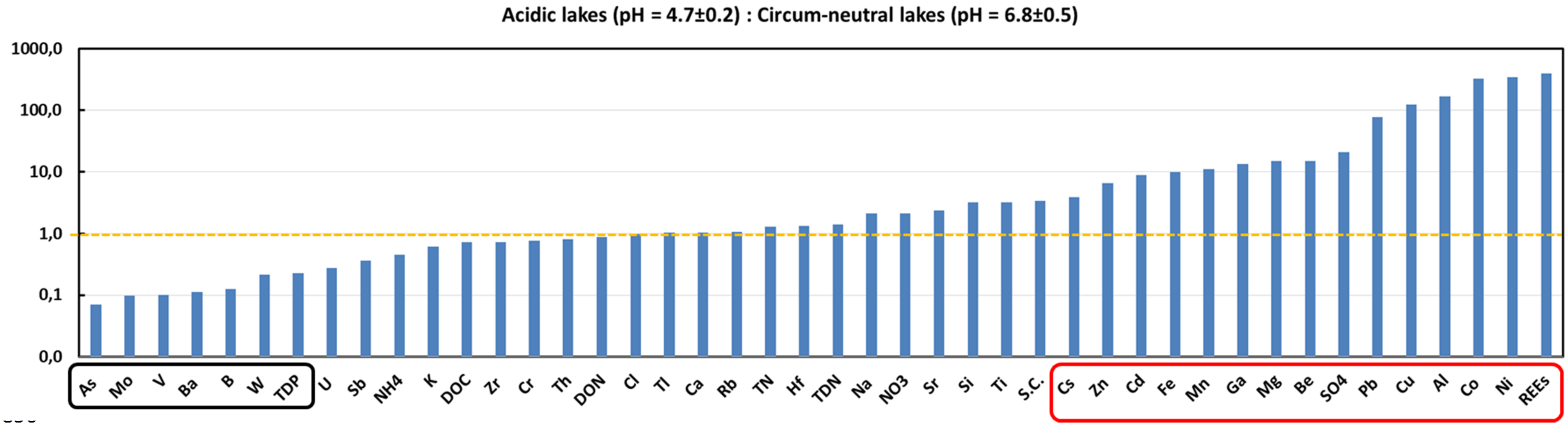


Fig. 5. A histogram of the mean ratio of solute concentration (averaged between surface and deep horizons) in three acidic lakes to that in 15 circumneutral lakes. Highlighted in black (left rectangle) and red (right rectangle) are solutes exhibiting significant ($p < 0.05$) deviations from 1, considering the variation of concentrations among lakes. Note that Ba is impoverished in acidic, high-sulphate lakes due to barite precipitation.

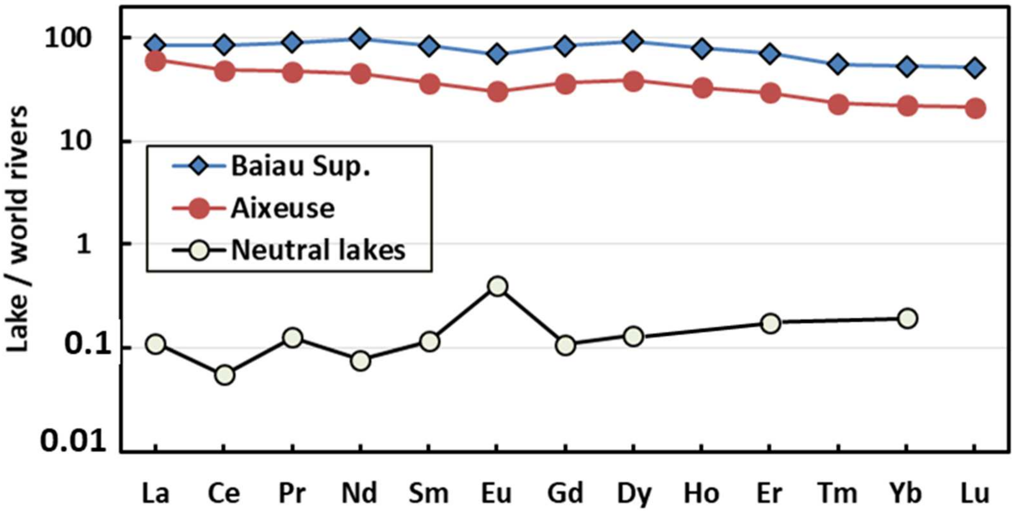


Fig. 6. REE pattern on two acidic lakes (Baiau Superior and Aixeus; blue and red symbols, respectively) and mean of 15 neutral lakes (open circles) normalized against mean world river compositions (Gaillardet et al., 2004).

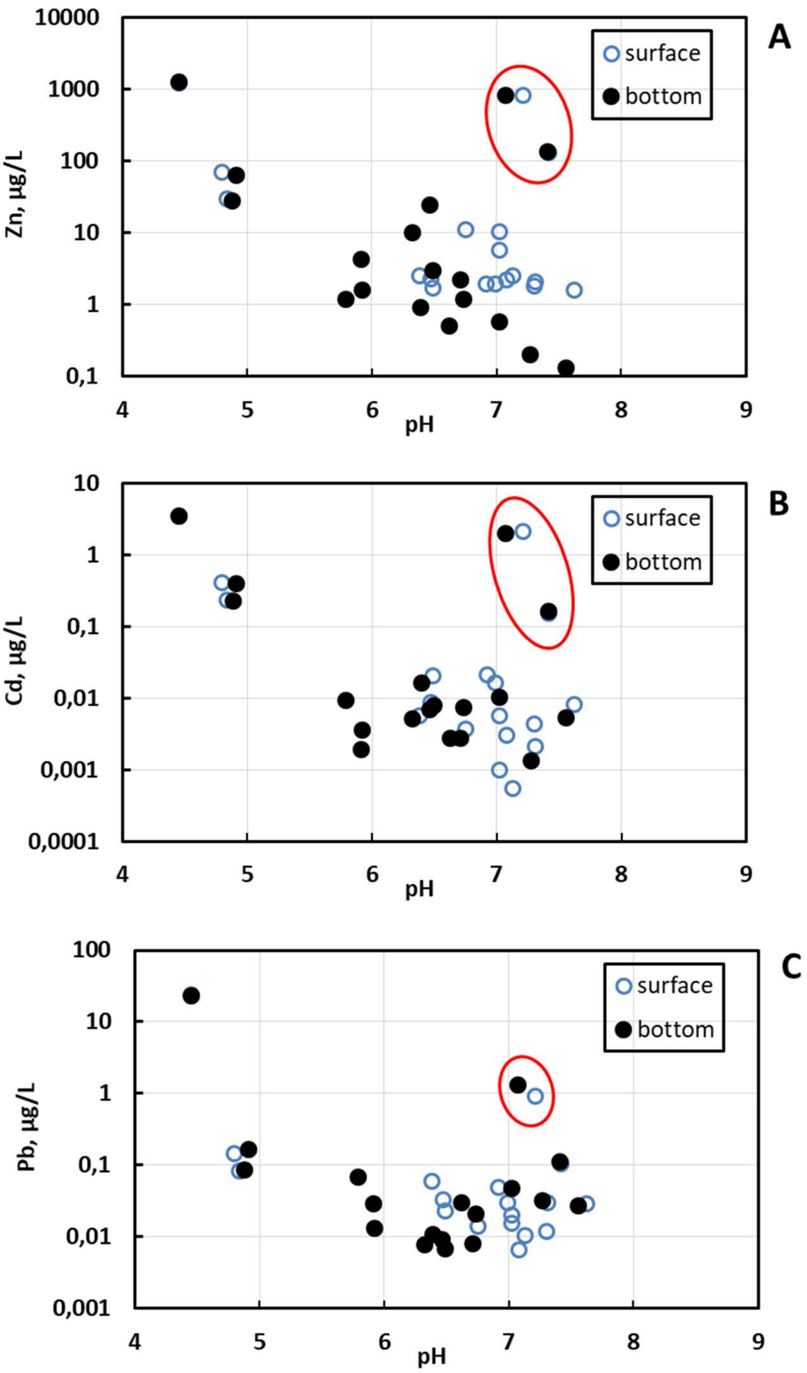


Fig. 7. Typical metal pollutants (Zn, Cd and Pb) decreasing their concentration (log scale, Y axis) with pH of the lake water. Two groups of lakes (acidic and circumneutral) exhibit distinctly different metal concentration, as consistent with SPCA treatment. In addition, we note high dissolved metal concentrations in two lakes of neutral pH (Anglas, Montoliu), with past mining activity within the watershed.

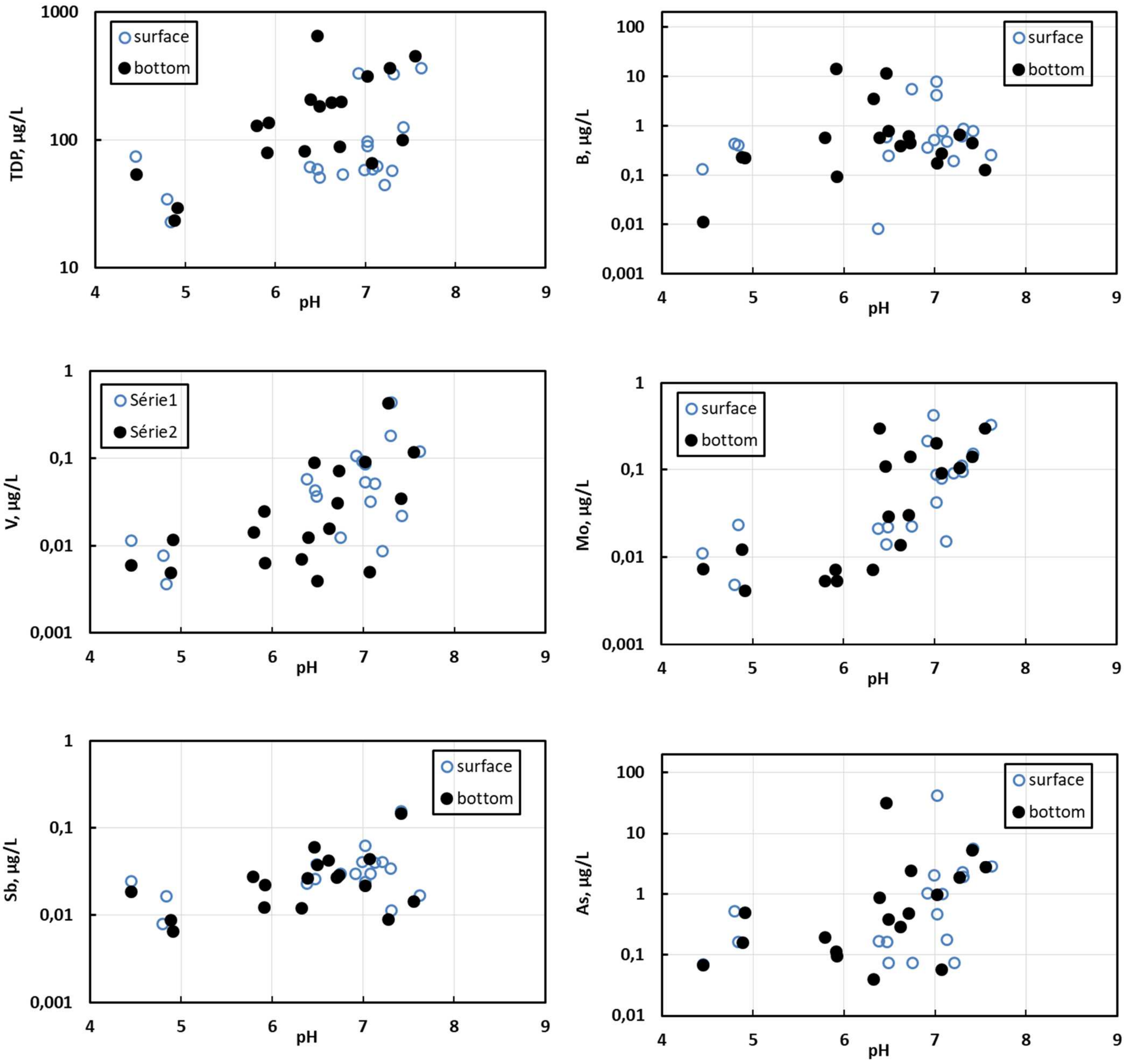
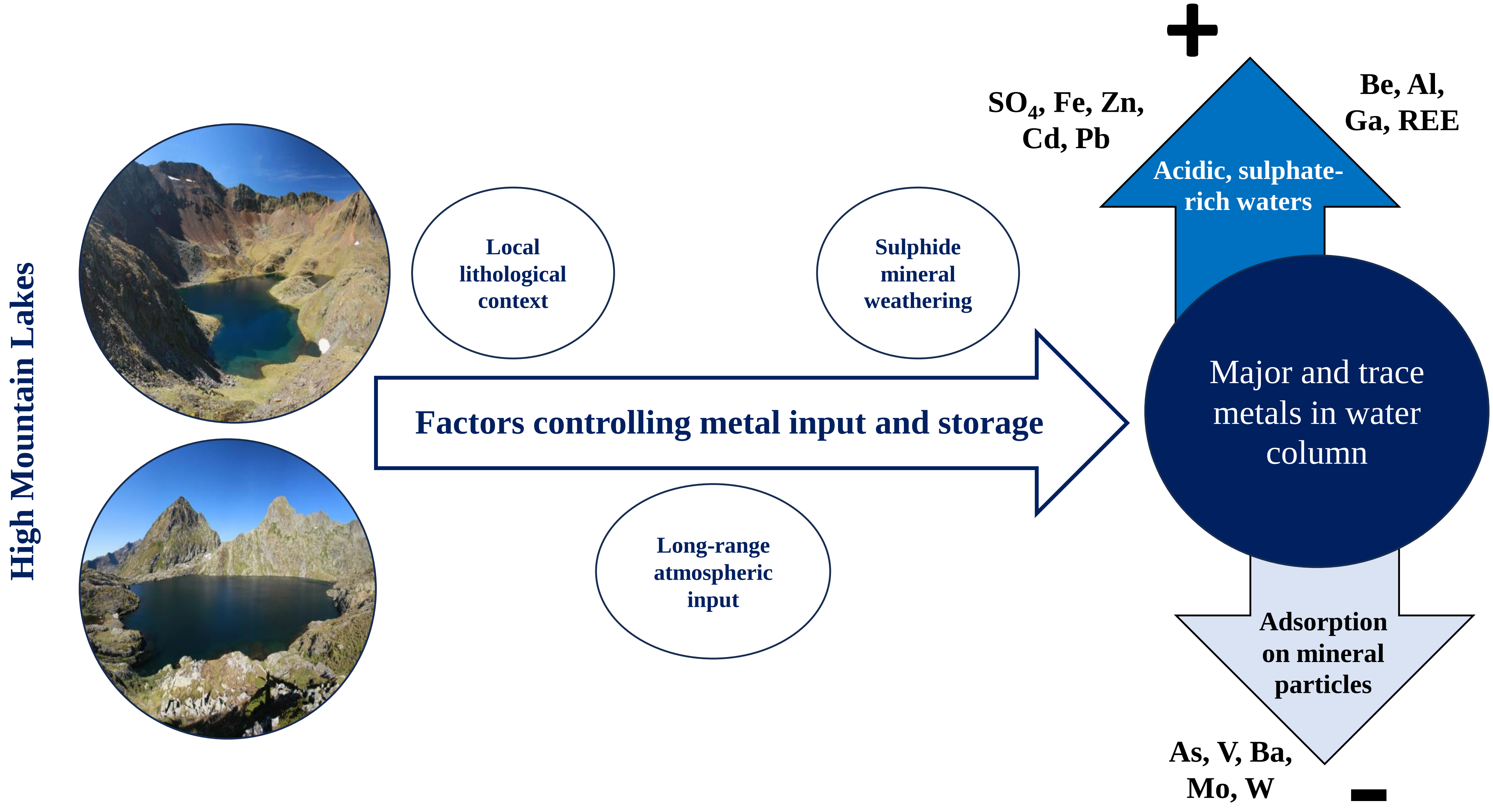


Fig. 8. Dissolved (< 0.22 µm) concentrations of phosphorus (TDP) and oxyanions (B, V, Mo, Sb and As) in the surface and bottom horizons of the water column (open and closed circles, respectively) increase with an increases in lake water pH.



High Mountain Lakes

Local lithological context

Sulphide mineral weathering

Long-range atmospheric input

Factors controlling metal input and storage

Major and trace metals in water column

+

Acidic, sulphate-rich waters

SO_4, Fe, Zn, Cd, Pb

Be, Al, Ga, REE

Adsorption on mineral particles

As, V, Ba, Mo, W

−