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Addressing Quality and Usability of Surface Water Bodies in Semi-Arid Regions with Mining Influences

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Abstract

Water resources management has considerable importance, specifically in the context of climate change. This subject has introduced new challenges in semi-arid regions with water quality problems, such as the Iberian Pyrite Belt, which is one of the largest metallogenetic provinces in the world and one of the driest regions in Europe. Positioned in the Mediterranean context, the region has a high density of polymetallic sulphide mines that promote the degradation of water systems. The present study aims to assess the water quality in the Pyrite Belt, considering a total of 34 surface water bodies, including constructed reservoirs, permanent and ephemeral streams, and mining facilities with accumulated water (e.g., pit lakes and mining dams). The water samples were analysed for physico-chemical properties, including field parameters (pH, electrical conductivity), alkalinity/acidity, hardness, anions, and potential toxic elements. The results were used for hydrochemical classifications and the assessment of suitability for public uses. Statistical methods, such as hierarchical cluster analysis and nearest centroid classifier, were used for grouping and evaluating the similarity between water bodies. Two groups were generated from the analysis: i) constructed lakes with alkaline and sodium signatures; and ii) waters suffering from the influence of mining wastes, e.g., showing high acidity, sulphate and metal contents. Therefore, the loss of water quality in the vicinity of mines reflects the impact of acid mine drainage. The methodological approach used may be applied to the integrated management of water resources in regions with mining influences and where it is necessary to combat drought and water scarcity scenarios.

Keywords Surface water · Reservoirs · Water quality · Mining contamination · Scarcity

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1 Introduction

Water quality is a key resource for human living, especially for drinking and irrigation purposes; thus, water is one of the most critical factors influencing human health (Zhang et al. 2012). Increasingly frequent and intense drought episodes, which are markers of anticipated climate change, lead to water scarcity in semi-arid regions (Tiri et al. 2014). This is the case in the Mediterranean region, where these scenarios of water shortages have made water quality a major concern.

Water quality is controlled by many natural and anthropogenic factors, as well as by the type of land use (Suthar et al. 2010), such as mining activity. In fact, one of the most serious problems of environmental contamination worldwide is the formation of acid mine drainage (AMD) in mining regions (Valente et al. 2015). The process occurs when sulphide minerals are exposed to weathering, which generates acidity, sulphates and elements of toxicological concern, such as metals (Gomes et al. 2016; Valente and Leal Gomes 2009). When these contaminated leachates reach river networks, the complete degradation of the aquatic ecosystems may occur. Additionally, if the impacted rivers drain into natural or artificial lakes, the precipitation of metals can occur due to the increase in water pH promoted by the mixture. Moreover, this process leads to the accumulation of toxic elements on the lake bottom, which can reduce the storage capacity and the general functioning of the water reservoirs (Santisteban et al. 2015; Grande et al. 2015).

Therefore, water quality management is an issue of concern, especially in mining regions with semi-arid climates. In such conditions, the construction of water reservoirs is one of the most common alternatives used to meet the increasing water demands required for agricultural expansion and growing populations (Santisteban et al. 2015). Nevertheless, in the context of scarcity, all water bodies deserve careful management because they may be used to satisfy permanent or temporary water shortages, namely, for irrigation purposes. In these scenarios, as stated by Geller et al. (2013), even pit lakes that are storage facilities of very acidic water could be important for nature and wildlife as well as for public uses. This is the case for the Iberian Pyrite Belt (IPB) in southwestern Europe, one of the most important metallogenic provinces in the world (Fig. 1). In this metallogenic province, which covers a large area of cross-border territory between Portugal and Spain, many abandoned mines prevail without corrective measures (Grande et al. 2013a; Rodrigues 2011); these mines generate AMD, and thus represent a potential focus related to water quality degradation.

Depending on the water uses, certain quality standards must be achieved in Portugal, e.g., in accordance with the implementation of the Water Framework Directive (WFD). Therefore, the concentration of toxic elements, such as metals and arsenic, cannot exceed legal limits, which could be a critical factor in the geological and mining backgrounds, such as in the IPB setting.

The general aims of the present study were to analyse the hydrochemical characteristics and evaluate the environmental quality of surface water in the IPB based on the legal standards for drinking and irrigation. Taking into account the mining heritage of the region, one of the specific objectives is related to the AMD process; specifically, the objective is to assess its potential impact on hydrochemistry and quality of surface waters in mining provinces. Hence, the current study covered a total of 34 surface water bodies, including: i) constructed reservoirs that configure artificial lakes with an area greater than 10 ha; ii) rivers and streams; and iii) mining facilities (e.g., pits lakes and mining dams).

Graphical methods, such as the trilinear Piper diagram (Freeze and Cherry 1979; Piper 1944) and the sodium adsorption ratio (SAR), enabled the interpretation of water chemistry and the
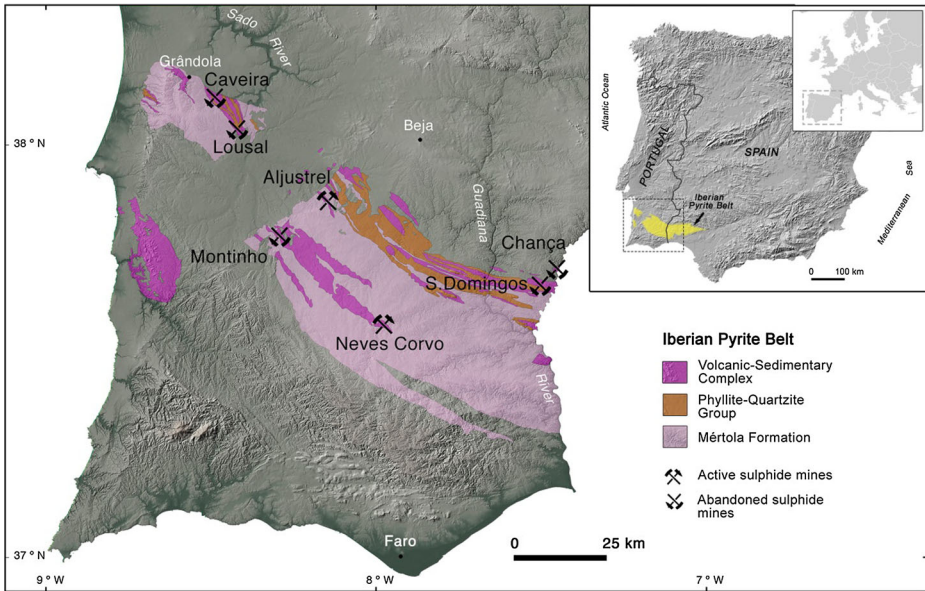
Fig. 1 Location of study area in southwestern Europe – Iberian Pyrite Belt. The geology and locations of mines are provided

assessment of water quality with respect to irrigation suitability, respectively. The application of statistical methods, such as hierarchical cluster analysis, revealed the similarity between water bodies, allowing their classification into different groups, which reflect the properties and quality of the water as well as the influence of contamination sources related to mining activity.

The obtained results can support water resources management decisions in the context of water scarcity by considering the information provided about the availability and quality of water in mining regions, thus meeting the United Nations Sustainability Development Goals (SDG-UN, Agenda, 2030).

2 Study Area

The study area is in the southwest region of the Iberian Peninsula, covering the entire sector of the Portuguese IPB. Thus, the region under study is part of a geological formation with a high density of polymetallic sulphide deposits, which extends from Seville (in Spain) to the coast of Portugal (Fig. 1). The IPB is subdivided into several tectonostratigraphic units (Leistel et al. 1994; Sáez et al. 1999), categorised from the oldest to the most recent: the Phyllite-Quartzite (PQ) group, which is composed of phyllites, siltstones, quartzites and quartzwackes; the volcano-sedimentary complex (VSC), which consists of a volcano-sedimentary sequence with volcanic felsic, intermediate and mafic rocks and sediments such as black shales, siliceous shales, jasper and chert; and the Flysch (Mértola Formation), which covers the VSC (Fernandes et al. 2008), that is widely scattered in the eastern part of the IPB and is composed of shale, greywacke and conglomerates (Fig. 1).

The presence of more than 90 polymetallic sulphide deposits associated with the VSC gives the Pyrite Belt a status of being a world-class metallogenic province (Barriga et al. 1997;

Leistel et al. 1994; Matos et al. 2008; Relvas et al. 2002). The massive sulphide bodies contain pyrite, sphalerite, galena and chalcopyrite and are associated with many minor phases (Sáez et al. 1999). The geological and mineralogical characteristics of the region reflect the existence of AMD-producing wastes that are dispersed by the numerous mining complexes and once discharged into the river network, and may affect the quality of the water bodies.

With typical characteristics of the Mediterranean semi-arid climate, precipitation occurs mostly in the autumn and winter months, producing drought situations in summer and part of spring, and this area is one of the driest regions in southwestern Europe (Silva et al. 2011). The annual precipitation is highly variable, with an oscillation of 330 to 1140 mm registered between 1981 and 2010. The average annual value is 595 mm, and severe droughts occur regularly. There were two severe droughts in 2003–2005 and 2011–2012 (Nunes et al. 2017). More recently, another severe drought episode occurred in 2017 (IPMA - Instituto Português do Mar e da Atmosfera 2018). In accordance with Nunes et al. (2017), current agricultural land use consists of a combination of pastures and cereals, which require large volumes of water.

There are several reservoirs in the IPB with considerable capacity to supply substantial irrigation areas, which are of great importance to the region (e.g., 20 of these artificial lakes have an area greater than 10 ha). The surface water bodies, including rivers and constructed reservoirs, have multiple uses, such as drinking, irrigation, fishing, recreational and industrial activities. The water bodies are spread along the basins of the Guadiana and Sado rivers (Fig. 2).
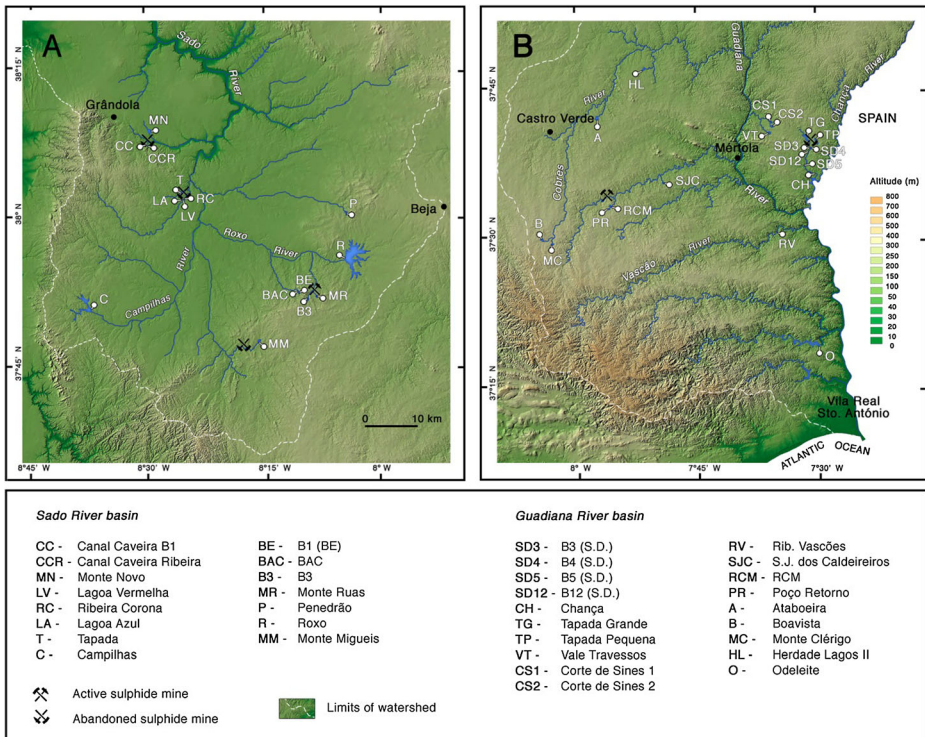

Fig. 2 Location of the sampling sites in the Sado and Guadiana river basins

3 Materials and Methods

3.1 Sampling and Analytical Methods

Sampling was performed in the dry season, specifically in July 2016. Thirty-four surface water samples were collected in different contexts, representing 20 reservoirs that were constructed for water supply, three river and stream waters and several mining facilities (e.g., pit lakes and mining dams). The locations of the sampling sites are shown in Fig. 2.

The samples were collected in 1-L pre-washed polyethylene bottles and were analysed immediately. The parameters of pH, electrical conductivity (EC), total dissolved solids (TDS), and water temperature (T) were measured in the field using a multiparameter portable meter (CRISON MM40+, Barcelona, Spain). Potential redox (Eh) was measured using a multiparameter portable meter (Thermo Scientific Orion, Massachusetts, EUA). The probes were calibrated according to standard methods and were kept submerged until the parameter reading was stable. Two 50-mL polyethylene bottles were used, and samples were filtered through 0.45-μm Millipore membrane filters to separate the suspended matter. One bottle was acidified with HNO_3 to pH~ 2 for cation determination. The other bottle was kept un-acidified for the analysis of anions. All bottles were kept in a portable refrigerator at a temperature below 4 °C.

In the laboratory, the major anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) were determined by ion chromatography with suppressed conductivity detection (761 Compact IC Metrohm, Herisan, Switzerland), and raw data were processed with Metrohm Metrodata 1.1 (Valente and Leal Gomes 2009). The IC method n°. S-03, which was developed by Metrohm for the determination of anions in water, was used for low-medium mineralized samples. Analytical conditions included the use of a 6.1006.100 Metrosep anion dual 2 column, with a flow of 0.8 mL/min and an injection volume of 20 μL. An internal calibration was performed in the range of 1–40 mg/L using multielement chromatography solutions (Fluka Analytical). During the analysis sequence, standard solutions of 1 mg/L and 10 mg/L (depending on the concentration range) were included periodically amongst the samples (i.e., every five samples). Between samples, ultrapure water (Milli-Q) was injected to clean the system. The detection limit was 0.03 mg/L for PO_4^{3-} and 0.01 mg/L for the other anions, and the measurement precision was within relative standard deviation (RSD) of 5% for all determinations.

The sulphate (SO_4^{2-}) of the water samples with high mineralization (EC > 1500 μS/cm) was determined by turbidimetry (Standard Methods 4500 E) using a turbidimeter (Eutech Instruments, TB 1000; Thermo Fisher Scientific, Massachusetts, EUA), which assured that the measurement precision was within 5% RSD. The total acidity and alkalinity were analysed within 24 h after sampling by volumetric determination (ASTM 1992).

The following trace elements were analysed by inductively coupled plasma optical emission spectrometry (Actlabs, Ontario, Canada): Co, Cr, Fe (total), Cu, Zn, Mn, Ca, Mg, Al, Ni, As, Na, and K (detection limit of 0.1 mg/L). Mo, Cd, and Pb were analysed by inductively coupled plasma-mass spectrometry (detection limit of 0.001 mg/L). The accuracy of the methods was verified using certified reference samples. The measurement precision was greater than 5% RSD. All reagents used were of analytical grade or of *Suprapur* quality (Merck, Darmstadt, Germany). The standard solutions were Merck AA Certificate; Milli-Q water was used in all experiments.

3.2 Statistical Analysis

Data resulting from analytical procedures were submitted to statistical treatment (SPSS Release 24.0 software), namely, to detect the grouping of samples by applying hierarchical

cluster analysis. The dendrogram was obtained using Ward's linkage method to calculate the mean of all the variables for each cluster (Ward 1963). Additionally, the Euclidean distance was the measure used between each variable and the mean of each cluster. This approach produced the most distinctive groups, where each member within the group was more similar to its fellow members than to any member outside the group (Shrestha and Kazama 2007).

The nearest centroid classifier distance (Christopher et al. 2009) was calculated between the centroid vector of each cluster and the characteristic vector of the two quality classes defined by the water quality framework (i.e., drinking and irrigation).

The cluster analysis was performed using the following variables: pH, EC, Eh, acidity, HCO_3^-, Cl^-, Na, SO_4^{2-}, Al, Ca, Fe (total), Cu, Zn, Mg, Mn, and As. The variables were normalized to more closely correspond to the distributed data. The normalization was defined by the calculation between the value used to normalize, the mean and the standard deviation.

3.3 Graphical Methods

The graphic treatment (i.e., the Piper and SAR diagrams) was conducted using the AquaChem software 5.1. For the water irrigation quality assessment, the SAR was calculated using the following equation (US Salinity Laboratory Staff 1954):

$$\text{Sodium absorption ratio } (SAR) = \frac{r\text{Na}^{2+}}{\sqrt{r(Ca^{2+} + Mg^{2+})/2}} \quad (1)$$

4 Results and Discussion

4.1 Hydrochemical Properties

The hydrochemical properties of the 34 surface water samples are shown in Table 1 using descriptive statistical parameters. The pH reveals large variability within the samples, with the minimum indicating an extremely acidic medium. In this region, acidic values (i.e., pH below 3.5) have been reported by several authors in the mining area surroundings as a result of AMD processes (e.g., Abreu et al. 2010; Ferreira da Silva et al. 2015; Gomes et al. 2016). In the present work, both streams that receive acid leachates and pit lakes are among the most acidic environments (e.g., the CCR sample, which receives leachates from a sulphide-rich mine, Fig. 2). The maximum pH (Table 1) is also related to mining activity. This value was collected from a mining dam with water that has been subjected to alkaline treatment (BAC sample, Fig. 2).

The highest anion concentration is displayed by SO_4^{2-}, followed by Cl^- and HCO_3^-. However, NO_3^- and PO_4^{3-} had minimum concentrations below the detection limit. As measured for pH and EC, the highest acidity and SO_4^{2-} were observed in mining contexts.

From the cationic pattern, it is possible to observe the dominance of Ca and Na, which were measurable in all samples. It should be noted that elements such as Fe (total), Mg, and Al had high concentrations in some samples. However, those elements, except for Mg, had low or even below-detection concentrations in other water samples. Therefore, samples show important variation, indicating there was abundant diversity related to different hydrochemical sources.

Table 1 Descriptive statistical summary of surface water hydrochemistry ($N = 34$)

Parameters	Min	Max	Mean	SD	Cv
pH	1.9	10.4	6.5	2.3	0.4
EC	202.0	28,600.0	2887.1	5189.5	1.8
TDS	2.1	6720.0	1244.5	1633.4	1.3
Eh (mv)	−3.0	555.0	188.3	165.5	0.9
T (°C)	13.0	32.5	27.7	4.1	0.1
HCO$_3$	0.0	2735.9	160.4	460.2	2.9
Acidity	0.0	28,437.5	1146.3	4871.3	4.2
Cl	17.8	644.1	162.9	154.0	0.9
NO$_3$	0.01	10.87	1.68	2.95	1.76
PO$_4$	0.03	0.66	0.06	0.13	2.17
SO$_4$	1.6	23,739.9	1577.4	4168.0	2.6
Al	0.1	687.0	46.1	131.1	2.8
As	0.1	37.9	1.2	6.5	5.2
Ca	5.7	968.5	149.1	257.5	1.7
Cu	0.1	44.1	3.2	9.1	2.8
Fe	0.1	8676.4	287.2	1484.6	5.2
K	1.3	96.7	11.8	22.6	1.9
Mg	2.4	995.1	90.4	183.4	2.0
Mn	0.1	184.9	12.5	33.8	2.7
Na	13.5	1153.9	125.5	205.7	1.6
Zn	0.1	298.9	18.0	53.9	3.0

All values are in mg/L except pH, EC (μS/cm), T (°C), and Eh (mV)

Min minimum, *Max* maximum, *SD* standard derivation, *Cv* coefficient of variation, *EC* Electrical conductivity, *TDS* Total dissolved solids

Figure 3 shows the hydrochemical facies of the sampled water bodies. The Piper diagram confirms the variability in water chemistry with respect to the presence of major ions. Most of the waters are mixed chloride and bicarbonate with a Na-Mg signature. However, there is a set of samples that are clearly of the sulphate type. Thus, most surface waters contain high amounts of HCO$_3^-$ and Cl$^-$, but there is also a trend of SO$_4^{2-}$-rich waters. Both anionic and cationic characteristics highlight the existence of different geochemical sources: one related to SO$_4^{2-}$-enriched waters, most likely indicating AMD influence, and the other related to more alkaline waters that are sodium in nature.

4.2 Water Quality Assessment

The present section provides information on the water quality of the various water bodies, which have distinctive physical and hydromorphological conditions, namely, lotic (ephemeral and permanent streams) and lentic (reservoirs, pit lake, and mining dams) systems.

There is some information about the large reservoirs in the south of Portugal (Silva et al. 2011). Additionally, the Spanish sector of the IPB is well documented, with the literature indicating high levels of contamination by AMD (Santisteban et al. 2015; Santisteban et al. 2016). However, for the most southwestern part of the IPB, there has been no overall assessment for the different types of surface water bodies (EU 2015).

The constructed reservoirs are the main source of water. However, in conditions of extreme shortages, large reservoirs can be depleted, and there are consequent restrictions on water use (Nunes et al. 2006). Therefore, other possible sources of surface water, such as the water accumulated in mining facilities, must be considered to increase the resource availability in the case of risky prolonged drought.
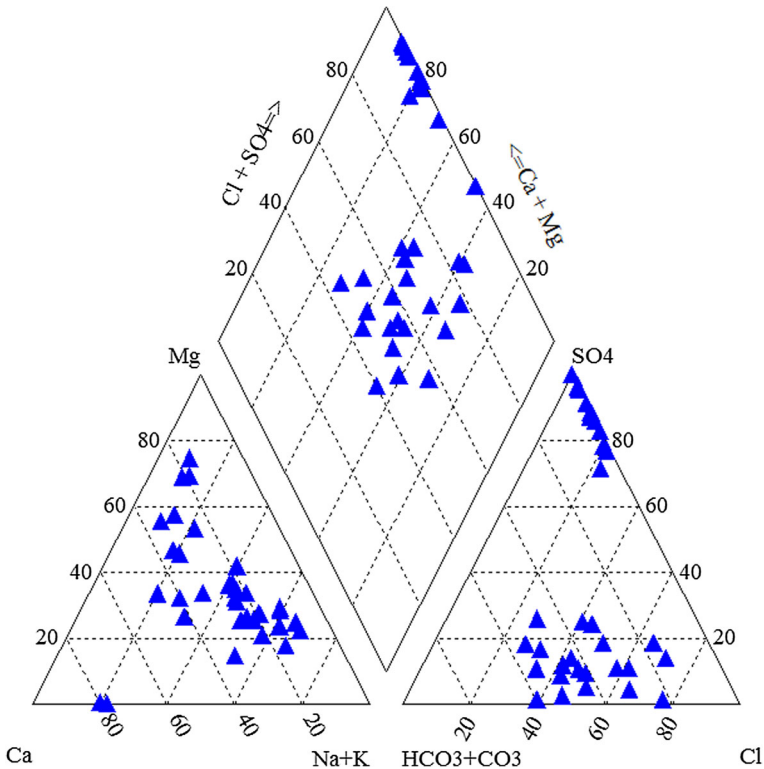
Fig. 3 Piper diagram for surface water samples

The suitability of water for irrigation and drinking was evaluated according to the European and national standards (Table 2). Regarding irrigation, all samples had Sn and NO_3^- values below the recommended maximum value (RMV). However, the maximum admissible value (MAV) of most elements was exceeded. Both pH and EC presented samples with values that were outside the permissible values for the two types of water uses.

Specifically, for drinking purposes, there were samples outside the guideline values for all the analysed elements. Chloride deserves special consideration because 91% of the samples were above the MAV. In fact, Cl^- and SO_4^{2-} were key indicators that had a high percentage of non-compliant samples. These two parameters indicate anthropogenic impacts, such as those related to mining. The formation of sulphate-rich waters through the complex chain of AMD reactions is a typical problem arising from the evolution of mining waste (Rimstidt and Vaughan 2003). It is important to note the existence of seven important polymetallic mines (Fig. 1). Here, AMD originates from waste dumps, old cementing basins and open pits, and is discharged into the watercourses, promoting river contamination (Valente et al. 2015).

4.2.1 Water Classification According to EC and SAR Values

By considering the non-compliance with legislation for many parameters regarding irrigation use (Table 2), the samples were classified according to the EC and SAR values. Figure 4 presents a classical tool that is used to assess the water quality for irrigation use (Wilcox 1955). Salinity and sodium risks are among the main factors affecting the suitability of water for irrigation (Mirabbasi

Table 2 Recommended Maximum Value (RMV) and Maximum Admissible Value (MAV) for irrigation and drinking waters, according to the European and National standards for water quality and percentage of samples in each range

Parameters	Irrigation water					Drinking water				
	RMV	MAV	<RMV	[RMV; MAV]	> MAV	RMV	MAV	<RMV	[RMV; MAV]	> MAV
Al	5	20	73%	9%	18%	0.05	0.2	53%	18%	29%
As	0.1	10	88%	9%	3%	0.05[a]	0.05	88%	–	12%
Be	0.5	1	79%	0%	21%	–	–	–	–	–
Cd	0.01	0.05	68%	0%	32%	0.005[a]	0.005	68%	–	32%
Pb	5	20	65%	9%	26%	0.05[a]	0.05	53%	–	47%
Cl	70	70[b]	39%	–	61%	25	25[b]	9%	–	91%
Co	0.05	10	68%	32%	0%	–	–	–	–	–
Cu	0.2	5	71%	18%	12%	3	3[b]	85%	–	15%
Cr	0.1	20	97%	3%	0%	n.a.	n.a.	n.a.	n.a.	n.a.
Sn	2	2[b]	100%	–	0%	n.a.	n.a.	n.a.	n.a.	n.a.
Fe	5	5[b]	79%	–	21%	0.05	0.2	47%	18%	35%
Li	2.5	5.8	53%	9%	38%	n.a.	n.a.	n.a.	n.a.	n.a.
Mn	0.2	10	62%	15%	24%	0.02	0.05	62%	0%	38%
Mo	0.005	0.05	91%	0%	9%	n.a.	n.a.	n.a.	n.a.	n.a.
Ni	0.5	2	94%	6%	0%	0.05[a]	0.05	82%	–	18%
Zn	2	10	71%	6%	24%	0.005	0.005[b]	62%	–	38%
NO$_3$	50	50[b]	100%	–	0%	25	50	82%	6%	12%
SO$_4$	575	575[b]	65%	–	35%	25	250	18%	0%	82%
NO$_2$	n.a.	n.a.	0%	0%	0%	0.1[a]	0.1	18%	–	82%
Hardness	n.a.	n.a.	0%	0%	0%	500[a]	500	82%	–	18%
EC	1000	1000[b]	53%	–	47%	400	400[b]	18%	–	82%
pH	6.5–8.4	4.5–9.0	26%	65%	9%	6.5–8.5	9.5	47%	47%	6%

All values are in mg/L except pH and EC (μS/cm)

n.a. not applicable

[a] the legislation does not provide RMV, so MAV was used

[b] the legislation does not provide MAV, so RMV was used

et al. 2008). As stated by Ayers and Westcot (1985), excessive sodium ions in water can replace calcium and magnesium, reduce permeability and cause soil degradation. Therefore, the combined effect of sodium risk and salinity risk is represented in the diagram by using EC to compute salinity risk and SAR to compute alkalinity risk, because SAR is related to the extent to which sodium is adsorbed by the soil. Samples can be classified as of low, medium, high, very high or exceptionally high salinity (x-axis) or sodium adsorption (y-axis) (Singh et al. 2005).

Most of the analysed samples fall into the group of medium to very high risk of salinization and low risk of sodium (Fig. 4). The majority of the reservoirs and one river water (RV - Rib. Vascões, Fig. 2) are included in the group (C2-S1), which corresponds to a medium risk of salinization. Following group C3-S1 were some reservoirs and two mining dams (BE and CC, Fig. 2). The most problematic waters are those with very high (C4-S1) or exceptionally high risks of salinization (C5), representing the influence of mining waste. Therefore, as expected, this last category included samples from a pit lake and mining dams, with the sample RCM (Fig. 2) positioned in the most extreme category (C5-S4). Furthermore, it should be noted that the sample CCR (i.e., the stream water in the vicinity of mining wastes, Fig. 2) was outside the limits of the diagram due to an extreme degree of contamination, with an EC value of 28,000 μS/cm. On the other hand, only two samples from constructed reservoirs presented a low risk
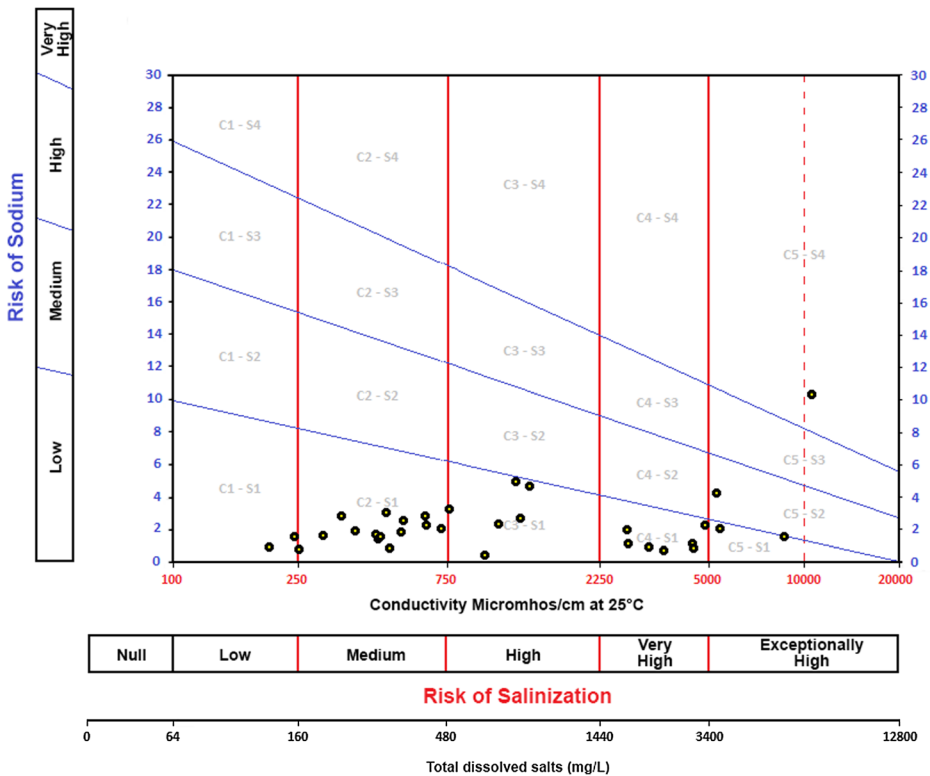
Fig. 4 Irrigation water classification diagram (after Richards 1954)

of salinization and sodium. Therefore, they can be directly used for irrigation, with no danger of the exchangeable development of sodium and salinity.

Globally, this classification indicates that the majority of surface waters present medium, high or very high risks of salinization, thus requiring treatment before use. Despite this result, most of the analysed reservoirs are extensively used for irrigation. This usage in cultivated land is of major concern in the Mediterranean region, where there is a considerable risk of soil salinization and land desertification (Zalidis et al. 2002; Verheye and de la Rosa 2005; AllEnvi 2016).

4.2.2 Cluster Analysis

Given the spatial distribution of the samples (Fig. 2) and their hydromorphological, physical, and hydrochemical variabilities, cluster analyses were performed to expose the existence of similarity between them. One of the most efficient grouping methods is hierarchical cluster analysis, which enables the ability to find proximity relationships between variables. This method has been extensively applied for classification purposes in different types of water environments (Shrestha and Kazama 2007; Kamble and Vijay 2011; Perrin et al. 2018). The efficiency of this cluster analysis has also been demonstrated when applied to extreme types of environments, such as AMD-affected systems (Grande et al. 2013b; Cerón et al. 2014; Valente et al. 2016).

From the output of the dendrogram (Fig. 5), two major classes are revealed to the level of clustering: Group 1 (G1), which is composed of samples from constructed reservoirs and rivers, and Group 2 (G2), which includes samples influenced by mining, namely dams, pit lakes, and ephemeral streams.

Most of the samples are classified as G1, including the constructed reservoirs, one river water (RV - Rib. Vascões) and a mining dam (B3). In turn, this major group comprised two subgroups (G1SG1 and G1SG2), which represent differences in terms of mineralization. In fact, G1SG2 includes reservoirs with higher EC and Cl⁻. The inclusion of the mining dam B3 in G1SG2 together with the constructed reservoirs used for irrigation and drinking is in accordance with the physico-chemical treatment that this water undergoes to reduce pollution; therefore, this treatment minimizes the environmental impact of the mining effluents generated in the Aljustrel mine.

Group G2 consisted of three major subgroups (G2SG1, G2SG2, and G2SG3) that included mining dams, pit lakes and stream waters. The G2SG1 subgroup, which was composed of only stream water from Canal Caveira Ribeira, emerged immediately due to its higher distance relative to the other leaves of the dendrogram. This independent classification reflects the strong AMD contamination of this sample because the stream receives the leachates from the waste dumps of a polymetallic sulphide mine (Canal Caveira, Figs. 1, and 2).

Subgroup G2SG3 is composed mainly of a set of samples from the same site, i.e., the São Domingos mine (B3 (S.D.); B4 (S.D.); B5 (S.D.); and B12 (S.D.)). This discrimination revealed similar hydrochemistry, highlighting the same paragenetic signature that was associated with the mining wastes accumulated in this mining complex.

Finally, subgroup G2SG2 included the remaining waters that experience mining influence. At a lower level (distance <5), it was possible to discriminate between two alkaline mining dams (BAC and B1 (BE)). Although these dams experience environmental control, the waters had high levels of sulphate that attested their mining signature. With less similarity, there is the leaf of Lagoa Vermelha, which corresponded to a pit lake with strongly acidic water.

Figure 6 shows the centroid vector of each subgroup identified by the hierarchical classifier. In accordance with the dendrogram, these vectors illustrate the distinction between the types of water samples, although the different parameters reveal different discriminating vocations. For example, group G2 shows the influence of mining contamination, including most acidic and sulphate-rich waters. Thus, SO_4^{2-}, EC, Fe (total) and acidity are the major distinguishing factors, with increasing concentrations along the subgroups.

Possible differences between lotic and lentic waters as well as general physical and hydromorphological features are not reflected in these cluster analyses. Thus, a permanent stream (Ribeira de Vascões), which represents the general features of the regional background, appears to be grouped with several constructed reservoirs. On the other hand, the ephemeral streams are mainly discriminated by the influence of mining. Therefore, the existence or not of mining contamination overlaps the physical and hydromorphological differences.

Considering these five clusters, an overall assessment of the water quality for the region is now proposed, attending to the legal framework for irrigation and drinking water (Table 2). Thus, the nearest centroid classifier was applied to the vector that represented each subgroup centroid and to the vector that represented the recommended maximum value (RMV) for irrigation and drinking water classes. Figure 7 shows the result of this classification algorithm. At this point, it is possible to observe the segregation of surface waters based on distinctive levels of contamination. The y-axis represents the distance from the subgroup centroid to the quality parameter that defined the irrigation and drinking classes. As the value on the y-axis increases, the distance to the class increases; this was associated with degraded water quality. Therefore, Fig. 7 shows that the level of contamination increases on the x-axis from G1SG1 to G2SG1. Additionally, the line corresponding to the irrigation class is below the line corresponding to the drinking class; thus, these waters have characteristics closer to irrigation usage.
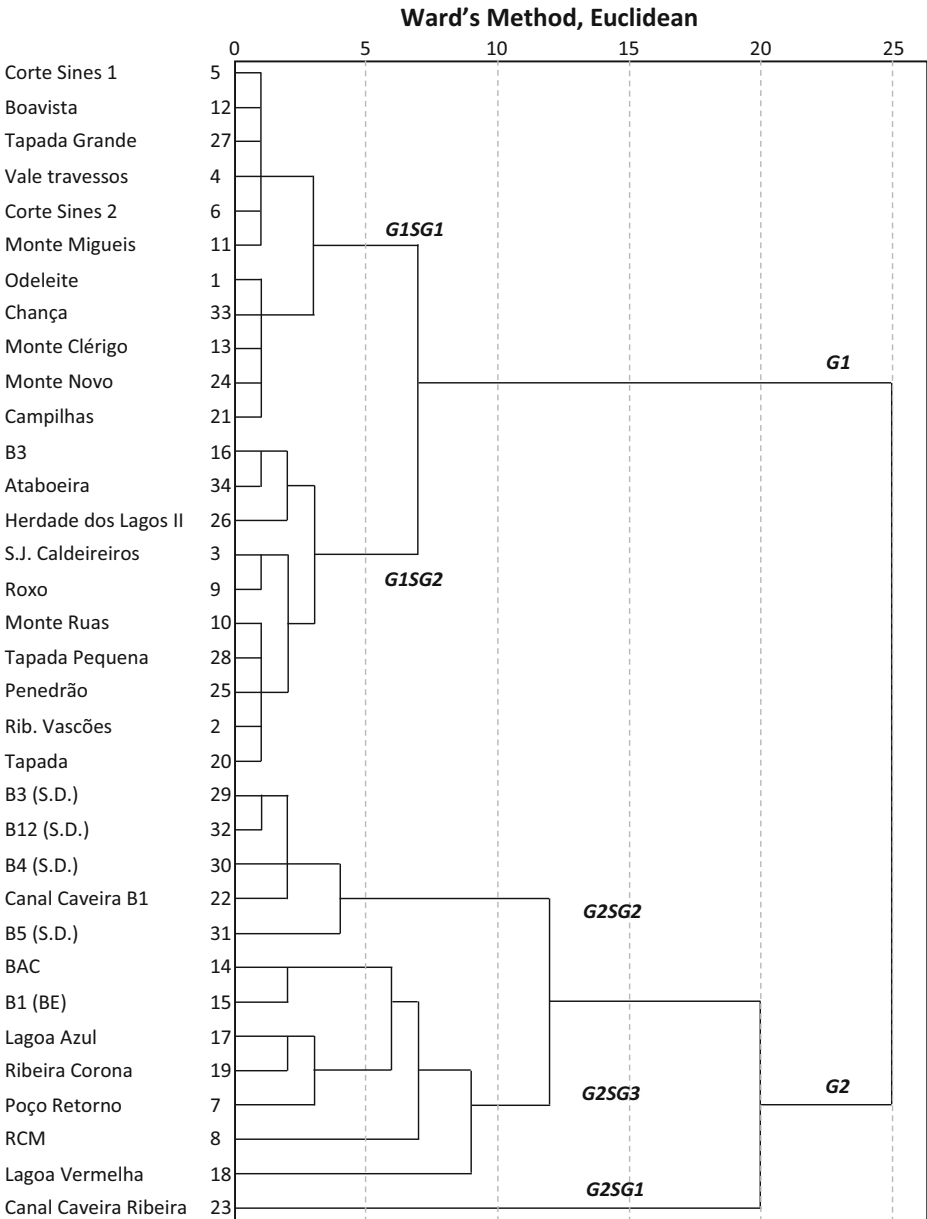
Ward's Method, Euclidean

| | | 0 | 5 | 10 | 15 | 20 | 25 |

Corte Sines 1 — 5
Boavista — 12
Tapada Grande — 27
Vale travessos — 4
Corte Sines 2 — 6
Monte Migueis — 11
Odeleite — 1
Chança — 33
Monte Clérigo — 13
Monte Novo — 24
Campilhas — 21
B3 — 16
Ataboeira — 34
Herdade dos Lagos II — 26
S.J. Caldeireiros — 3
Roxo — 9
Monte Ruas — 10
Tapada Pequena — 28
Penedrão — 25
Rib. Vascões — 2
Tapada — 20
B3 (S.D.) — 29
B12 (S.D.) — 32
B4 (S.D.) — 30
Canal Caveira B1 — 22
B5 (S.D.) — 31
BAC — 14
B1 (BE) — 15
Lagoa Azul — 17
Ribeira Corona — 19
Poço Retorno — 7
RCM — 8
Lagoa Vermelha — 18
Canal Caveira Ribeira — 23

G1SG1
G1SG2
G1
G2SG2
G2SG3
G2SG1
G2

Fig. 5 Dendrogram of water samples with p value between G1 and G2 of 10%

4.2.3 Radial Diagram Analysis

Figures 8 and 9 present the behaviour of the two major groups of water bodies (i.e., G1 and G2, respectively) for a set of selected parameters: EC, SO_4^{2-}, HCO_3^-, Al, Ca, Cu, Fe (total), Mg, Mn, Na, and Zn.
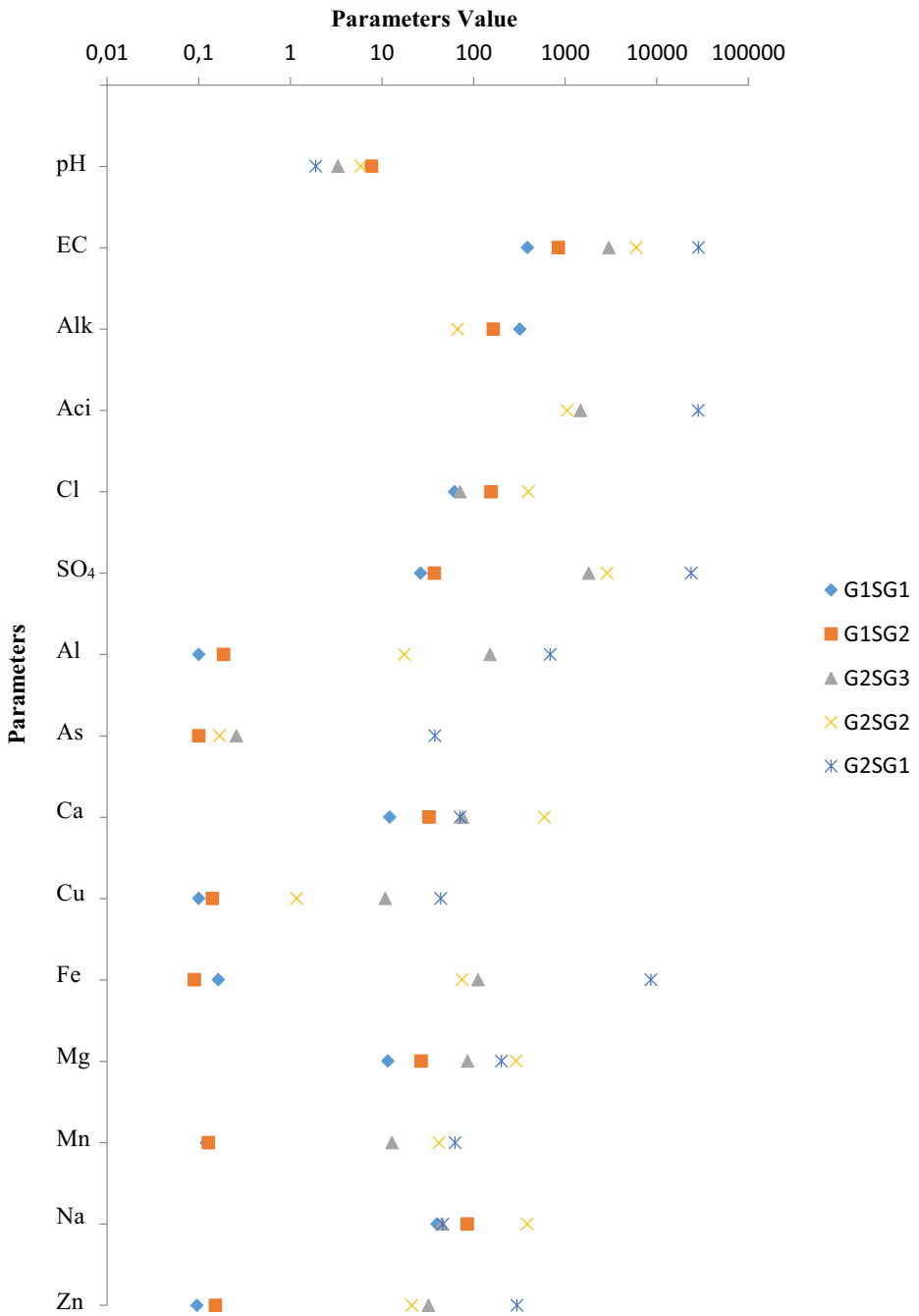
Fig. 6 Centroids of each cluster defined in the dendrogram (Fig. 5)

In Group I (Fig. 8), the samples of Herdade dos Lagos II, B3, Ataboeira, and Roxo exceeded 1000 μS/cm for EC. For all reservoirs, SO_4^{2-} was below the radius of 100 mg/L. In fact, B3 had the highest concentration of SO_4^{2-} and of trace elements in general, possibly as
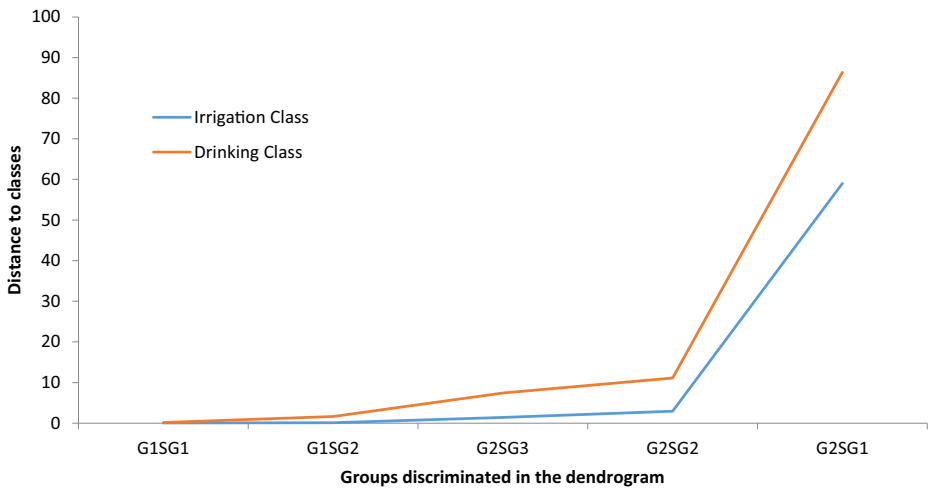
Fig. 7 Distance from the cluster centroids to the irrigation and drinking classes

a result of some AMD influence due to the proximity to the Aljustrel mine (Fig. 2). Regarding the anions, Ataboeira presented higher concentrations of Cl^-, NO_2^-, and NO_3^-, suggesting a possible source of organic contamination. In general, all samples had higher amounts of Ca, Na and Mg, and low concentrations of Al, Cu, Fe (total), Mn, and Zn. Reservoirs such as Monte Novo, Corte de Sines II, Chança, and Ataboeira had higher values of Fe (total). On the other hand, the Roxo reservoir presented higher concentrations of Cu, which can also suggest a slight AMD contribution. An important insight came from the Chança Reservoir, which is used for the production of drinking water. Although it is downstream of the São Domingos mine (Figs. 1 and 2) and receives drainage from this mining complex, this reservoir does not appear to be strongly contaminated by the mining effluents. However, the higher SO_4^{2-} and Fe (total) contents relative to other reservoirs shown in Fig. 8 may reflect some influence from the mining environment. As a conservative element, SO_4^{2-} persists in solution, supporting the higher concentrations that were observed.

Group II, shown in Fig. 9, shows a rather different behavioural pattern. The samples had the highest EC and the lowest concentration of HCO_3^-. The samples from BAC, B1, and Poço Retorno are exceptions, probably because they are located within active mining complexes (i.e., Aljustrel and Neves Corvo; Figs. 1 and 2); thus, the sites are subjected to environmental control measures that include the use of alkaline products for neutralization. Ribeira Corona represents stream water that was clearly affected by AMD, as was indicated by the sulphate and metallic patterns. In general, the diagrams in Fig. 9 show a metallic signature, with the exception of BAC, which had only Na, Mg, and Ca. This exception is explained by the water treatment procedures carried out for this dam.

The last sample, which is presented in Fig. 9, had the highest concentrations of the elements with toxicological concern, such as metals, as well as SO_4^{2-}, and EC. This sample, Canal Caveira Ribeira, is an AMD-affected stream because it directly receives drainage from the old exploitation of polymetallic sulphides (Canal Caveira; Figs. 1 and 2). It should be noted that this mine previously underwent environmental rehabilitation. However, the results show that there is still contamination of the surface water promoted by the leachates of the dumped waste.
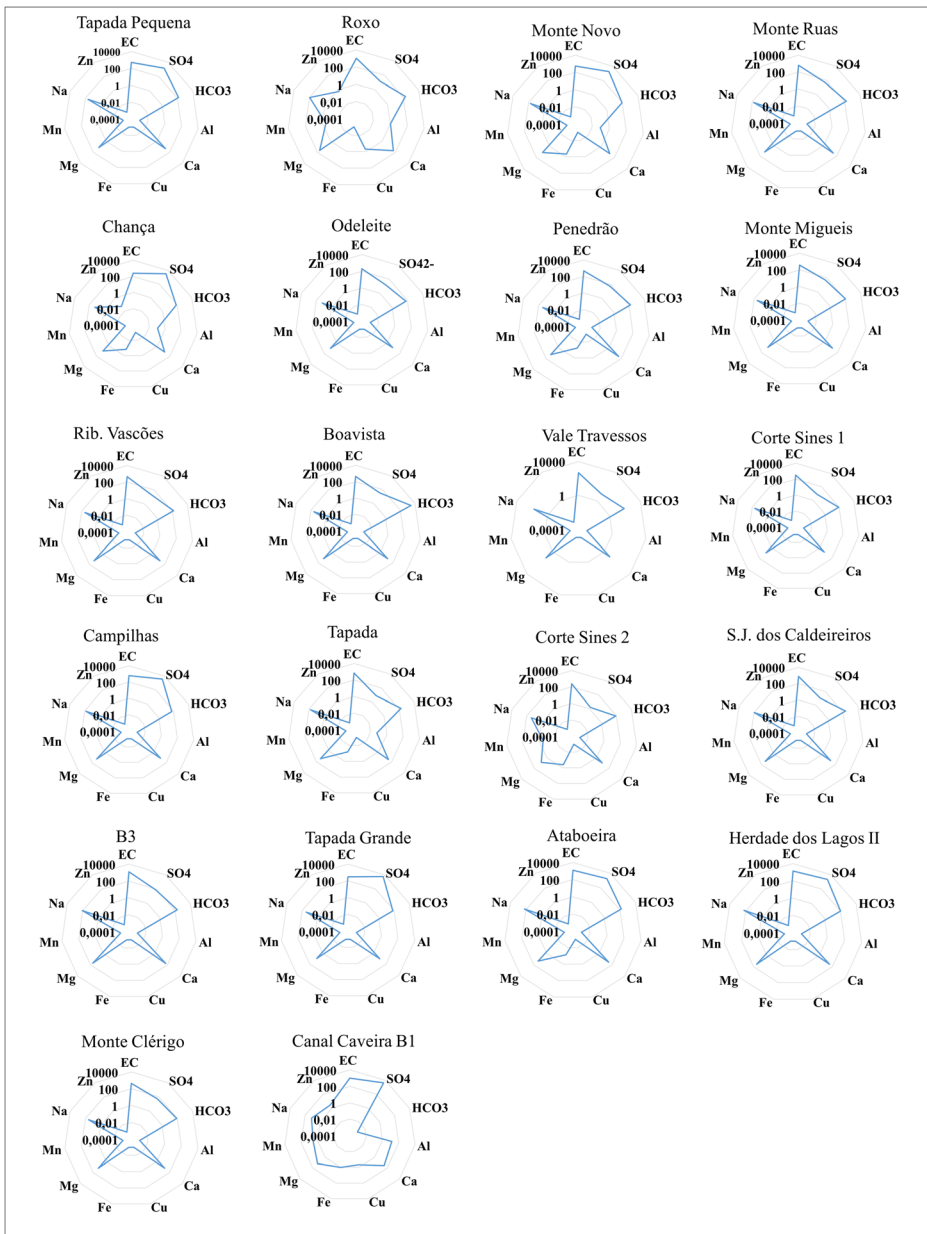
Fig. 8 Radial diagrams of Group 1 samples for a set of selected parameters

In general, the water quality and usability in the IPB are influenced by two main types of sources/activities. The impact of AMD is clear on mining water bodies, such as pit lakes and dams. Additionally, ephemeral streams show evidence of mining contamination (samples in Fig. 9). In the present conditions, the usability of these waterbodies is completely compromised, including the uses related to supporting ecological services.
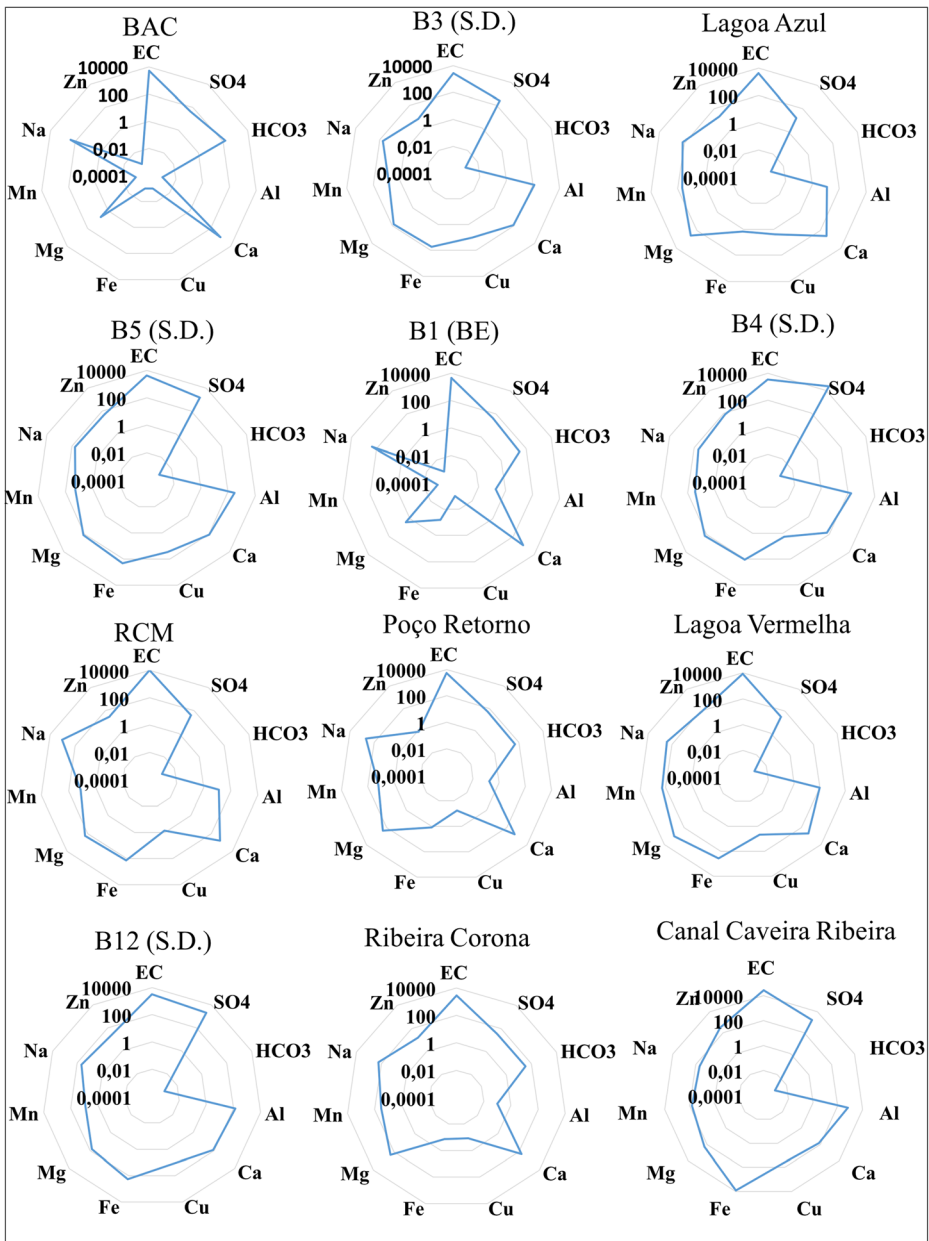
Fig. 9 Radial diagrams of Group 2 samples for a set of selected parameters

Pasture and wastewater discharges may affect the other constructed reservoirs (Fig. 8). This may explain the non-compliance for irrigation that was observed for chloride in more than 90% of the samples. Only two samples presented a low risk of salinization when used for irrigation (Fig. 4), which represents a critical limitation for actual use.

5 Conclusions

Water resources are critical for sustainable development, including agricultural and population growth as well as ecosystem conservation. With the decreasing precipitation levels observed in southwestern Europe, water shortages are increasingly common events. In some extreme cases, the population may have to use recycled water for public uses. Therefore, hydrochemical characterization and environmental assessments are crucial for a global perspective of the water quality in semi-arid regions with historic mining activity. The hydrochemical characterization of surface water bodies in the IPB revealed a dominant $HCO_3^--Cl^-$ or SO_4^{2-} pattern, depending on the AMD contributions. As a result, cluster analysis better reflects the discrimination of the waters exposed to mining contamination. Generally, waste dumps in abandoned mining areas still constitute a risk of contamination, even in cases that were subjected to environmental rehabilitation.

The obtained results suggest the need for remediation measures to protect the aquatic environment. The mitigation of organic pollution depends on agro-environmental measures and investments in controlling the discharge of wastewater. However, a greater challenge is posed by abandoned mining sites. The imperative investment in the data collection and treatment related to AMD is required. The passive systems that have already been implemented have proven to be inefficient. Greater effort may be required in terms of maintenance or even in the choice of treatment solutions. Furthermore, though completely different, the renewal of mining activity in the context of a circular economy may be possible. The current strategy to recover by-products in waste-dumps, and even in mine waters, may help control AMD and promote sustainable water management.

These types of research activities in the field of monitoring may contribute to the increased availability of water resources, which may benefit situations of water scarcity in semi-arid regions with mining traditions.

Compliance with Ethical Standards

Conflict of Interest None

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