Monitoring of a public water supply system: A case of groundwater contamination by acid rock drainage

Teresa Valente[1], Jorge Pamplona[1]

[1]*Institute of Earth Sciences, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal, teresav@dct.uminho.pt*

Abstract

The present study shows hydrochemistry of shallow groundwater from two wells planned to supply public fountains in the north of Portugal. One of the wells suffers higher impact by acid rock drainage due to mineral-water interaction in a host lithology richer in sulfides. Dissolution of sulfate efflorescences, infiltration and recharge, structural faults, and high porosity of the terrain control the evolution trends of water chemistry. The study concludes by noting the strong contamination, including by toxic elements (Al, Mn, Cd), making impossible to use the water for public supply as planned.

Keywords: ARD, volcanogenic affinity rocks, public supply

Introduction

The exposition of sulfide-rich rocks to weathering conditions results in acidic contamination, which often occurs as a consequence of the exploitation of coal and metals sulfide-rich mines. The leachates drained from waste dumps, piles and other mining structures result in acid mine drainage (AMD), creating one of the most problematic types of aquatic contamination worldwide. This acidic contamination may also develop under natural conditions, and in these cases the process takes the denomination of Acid Rock Drainage (ARD). When the geology is propitious to the appearance of ARD, the same effects that of AMD are expected to occur. So, the pH of runoff water is usually below 4 and newly formed minerals are commonly developed.

One of the most typical and problematic contexts of ARD arises from the rock excavation for constructions. For example, exposition of road cuts presents the appropriate conditions for the process, directly revealed by the presence of secondary minerals, as well as acid contamination of surface runoff. However, ARD may occur in other kind of scenarios, being only necessary appropriate conditions for sulfides oxidation as in the present case.

Sometimes water supply systems for small populations are implemented without the proper geological study. Moreover, excavation and terrain moving in the presence of sulfide-rich lithologies may result in development of ARD. In these conditions, ARD may affect the quality of the environment, namely by limiting the potential uses of water. The present study is focused on one of these cases, located in the north of Portugal, in which ARD compromises the usefulness of groundwater planned for public supply. The main objectives are (i) to describe the hydrochemical properties of shallow groundwater, assessing its quality as drinking water; (ii) to evaluate the seasonal response of the wells and respective water chemistry; (iii) to model the mineral-water interactions responsible for water properties in the sulfide-rich lithology.

Site description

The study site (Serro) is located in the north of Portugal; it is in one the rainiest regions of the country with average annual precipitation in the range of 1600-2000 mm. Figure 1 shows location and geological setting. The sector is located in the neighbouring of Serra de Arga (Dem, Caminha, NW Portugal) and it is mostly constituted by metamorphic rocks highly deformed, bounded by tectonic contacts belonging to the Arga Unit (Lower Allochthon). This unit is characterized by millimetric alternations of metapsammites and phyllites with abundant disseminated sulfides. It may contain intercalations of quartz-phyllites and volcanic to volcanoclastic rocks of different chemistry (Meireles et al., 2014). Surrounding this unit there is a monotonous sequence of metamorphic biotite micaschists (Meireles et al., 2014).

Two wells for obtaining water were installed in this site (SRn and SRs, in figure 1-B). A small reservoir receives and mixes the water from the two wells, which was then sent to the distribution network planned to supply some residences and a local system of public fountains. The dismantling and topographical regularization of the terrain for the installation of these wells promoted the exposure of the sulfide-rich rocks to weathering. From this works also resulted a small waste dump and some preferential channels for surface runoff (Oliveira et al., 2010). Before excavation, ferruginous colours were already observed on the exposed rocks as features of sulfide oxidation. Figure 2 illustrates the rock fragments that compose the waste dump and that are widespread in the area, reflecting the dominant lithologies.

The area shows evident manifestations of ARD, such as secondary minerals covering rock fragments (Figure 2 - right) and the typical ochre colours of the surface drainage (Figure 3 - left). Oliveira (2011) identified the salt efflorescences that cover rock fragments, revealing the dominance of Fe and Al-Mg-Ca sulfates.

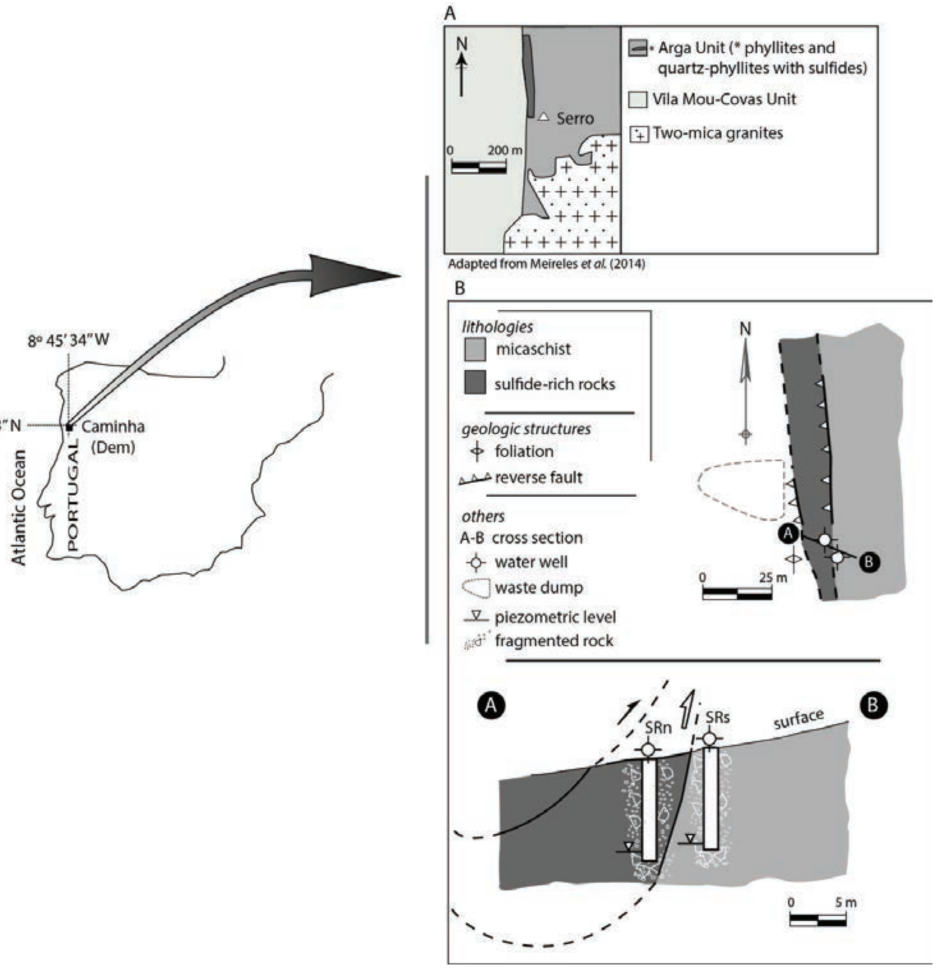

Figure 1 *Location and geology of the study area. SRn and SRs represent the two wells.*

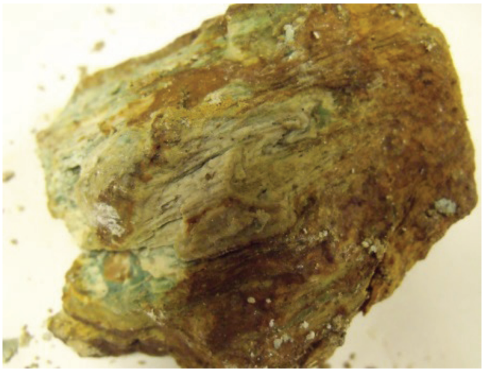


Figure 2 Images of rocks with volcanic affinity that typically have banded dissemination of sulfides (left), often covered by Fe-Al salt efflorescences (right).

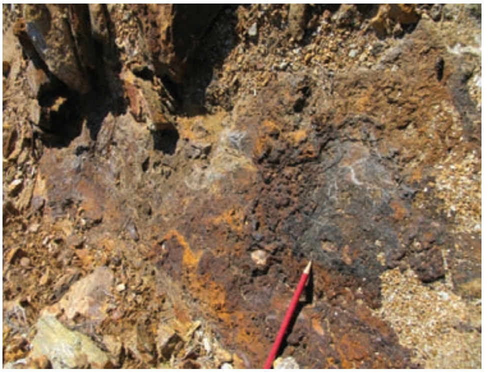


Figure 3 – Image of the ochre products in the study area. Crustification of surface drainage channels (left); Deposition of fluffy precipitates in the pipes, associated with the long term passage of the water (right).

Methods

The water wells were submitted to monitoring during 12 months for in situ parameters (pH, electric conductivity (EC), and temperature), anions, like sulfate, acidity, and alkalinity. Metals and arsenic were analysed in dry conditions (at the end of summer, September), before the first rains. Anions were obtained by ion chromatography, while acidity and alkalinity were determined by volumetric determination. Inductively coupled plasma mass spectrometry was used for metals and arsenic. Ochre products deposited in the pipes (Figure 3 – right) were also analysed by X-ray powder diffraction (XRD) (Philips PW 1710, APD), using CuKα radiation.

Results and discussion

The study performed by Oliveira et al (2010) pointed out, for the first time, the occurrence of ARD in the Serro site. This previous work indicated low pH (2.53) and high concentrations of acidity, sulfate and metals for the runoff water. Also, Oliveira (2011) presented preliminary results about the acid nature of the water supplied by the public system of fountains located in the village of Dem-Caminha (Figure 1).

Figure 4 shows the individual behaviour of the two wells, based on the results obtained for an entire year of monitoring. Seasonal trends of pH and EC (Figure 4-a) suggest higher stability for SRs (see figure 1-B for location). The influence of ARD is clear for SRn, with average values of pH and EC of 3.76 and 433 μS/cm, respectively. In accordance with this ARD conditions, the ochre product deposed in the pipe of SRn was identified as a mixture of schwertmannite and goethite, minerals typically found in AMD environments (e.g., Bigham et al., 1996, 1998; Dold, 2003).

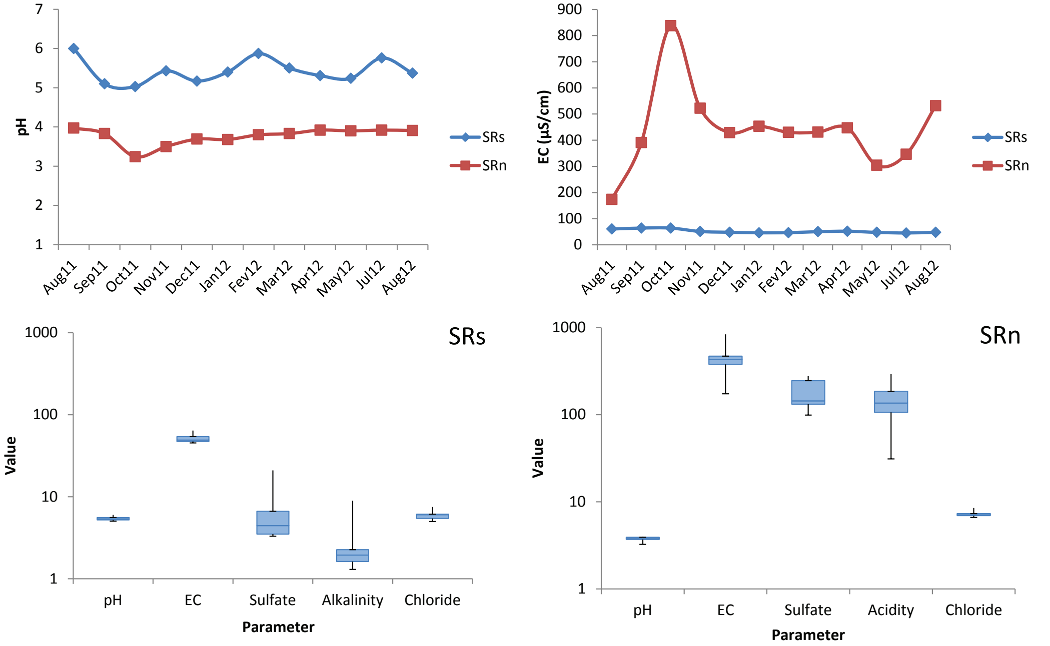

Figure 4 *Water properties. a) Seasonal behaviour of pH and Electric conductivity (EC); b) Box plots for SRs and SRn. Sulfate and chloride are expressed in mg/L; acidity and alkalinity are expressed in mg/L CaCO3.*

The worst conditions were detected in October, in the sequence of the first rain episode. This effect, plainly observed for EC, has been extensively referred in AMD scenarios, associated with salt efflorescences that are able to retain sulfates and metals during dry season (Alpers et al., 1994; Valente et al., 2013; Viers et al, 2018). Their dissolution by the first rains generates contaminant solutions, explaining the high EC. Figure 4-b confirms the strong ARD conditions for SRn, which behaves as acid sulfate water. On the contrary, SRs has alkalinity (although low values) and the sulfate signature is not so evident. Here chloride has similar expression (6-7 mg/L).

The metallic signature of groundwater in dry conditions is presented in figure 5, highlighting the distinctive chemistry of both wells. SRn has higher concentration for all elements, except the As, which presents the same low value for both wells (0.15 µg/L). Among the metals, Mn and Zn occur with relevant expression, reaching in SRn 2.4 and 1.8 mg/L, respectively. Concentrations in this well infringe the standards set by the European framework for water quality for most of the metals. The Al also deserves to be highlighted, since it surpasses the standard, even in SRs.

The different chemistry can be explained by the location of the two wells. Although both suffer the influence of sulfides, SRn is right in the middle of rocks with abundant sulfide disseminations, while SRs is hosted in the micaschists (Figure 1).

Major ion composition of the water depends on the host rocks composition and dissolution rates of minerals. Water-rock interaction causes the dissolution of sulfides, like pyrite and sphalerite (equation 1) and precipitation of secondary minerals, namely in fractured zones. Due to the low deep of the wells, the shallow groundwater is young and exposed to supply of metals and sulfate from surface acidic leachates, mainly under salt dissolution conditions. Equation 2 expresses this liberation process for halotrichite, one of the common secondary minerals at this site (Oliveira et al, 2010). The abundant chlorite and other Al-silicates also dissolve under these acidic conditions, releasing the highly toxic Al (equation 3). Thus, the high porosity of the terrain, enhanced by the mobilization and fragmentation facilitate the infiltration of these leachates. Furthermore, structural faults contribute to contamination by ARD.

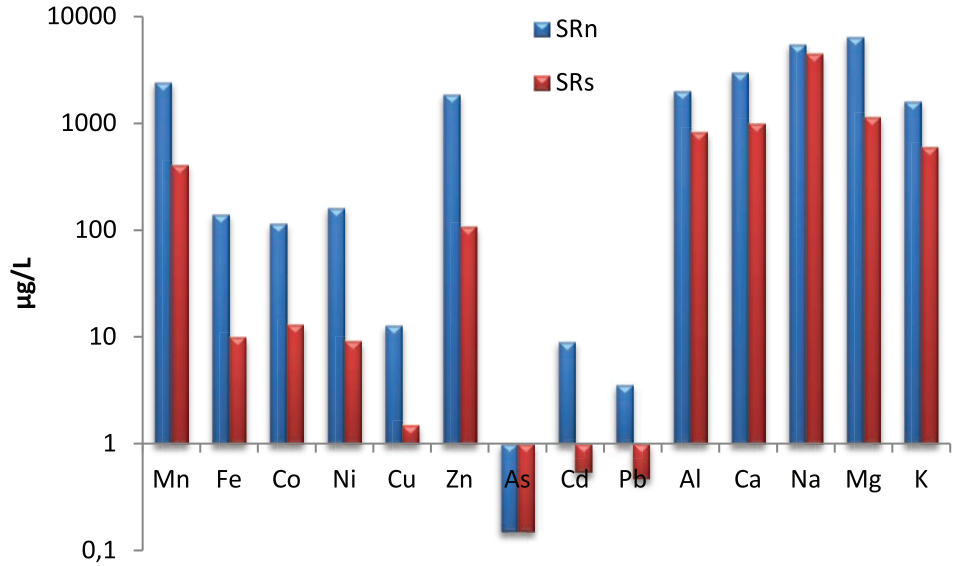

Figure 5 Metals and As concentrations for SRn and SRs. Data from a sampling campaign performed in September (dry conditions).

$(Zn,Fe)S + 3O_2 + H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + Zn^{2+} + 2H^+$ (equation 1)
$FeAl_2(SO_4)_4\ 22H_2O + O_2 \ \square\ 8Al(OH)_3 + 54H2O + 16SO_4^{2-} + 32H^+$ (equation 2)
$MeAlSiO_4 + H+ + 3H_2O \rightarrow Me^{n+} + Al^{3+} + H_4SiO_4 + 3OH^-$ (equation 3)

Conclusion

The obtained results indicated the presence of acid sulfate water, which emerged with high contents of toxic elements. The ochre product that forms on the borehole tap was identified as schwertmannite mixed with goethite, in accordance with the pH and sulfate values. The pH value, aluminium, zinc, and manganese contents are some of the most problematic parameters. Specifically, manganese concentrations are about 50 times higher than the limit allowed by the Portuguese legal framework. The water properties are directly controlled by seasonal variations, mainly promoted by rainfall and dissolution of secondary sulfates. Structural faults and high porosity of the terrain promote infiltration and recharge of these solutions, enhancing acidity and metal contents of the groundwater.

As a result of the presented monitoring procedure, the water supply system is now closed, avoiding the risk to the population. Nevertheless, mineralogical and physico-chemical indicators of ARD persist. The presence of sulfide-rich rock fragments at the surface together with fractures contributes to maintenance of water contamination.

Acknowledgements

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