

Assessment of sediments contamination caused by acid mine drainage: Stable isotopic and Sequential Extraction studies.

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This study investigated the use of Sulphur Isotopic Fractionation ($\delta^{34}\text{S}$), and Sequential Extraction to determine and quantify the occurrence of bacterial reduction and the availability of contaminants present in superficial sediments from a reservoir and a river at Poços de Caldas Plateau (MG – Brazil). The area comprises a former uranium mine and its surroundings located in Caldas Municipality (Figure 1).

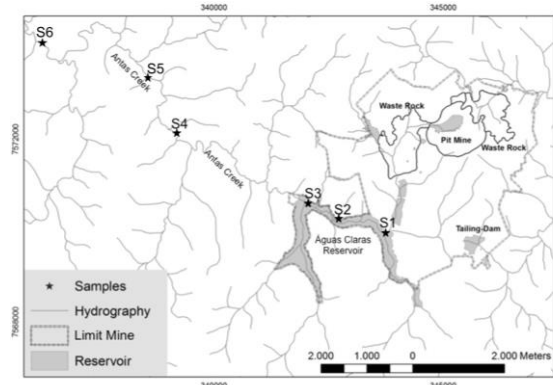


Figure 1. Overview of the study area showing the Águas Claras reservoir, the limits of the mining area, the Antas river and the sampling stations (indicated with stars).

Six sediment samples were taken along the Águas Claras reservoir and the Antas river (S1 to S6). The sequential extraction procedure was based on the modified BCR (Bureau Communautaire de Références) (Rauret et al. 1999) and Isotopic Fractionation analysis was according to Knöller et al., 2004. Sulphur isotopic fractionation is based on the fact that the sulphate from the Acid Mine Drainage can be reduced to sulphide due to bacterial action,

where the sulphate with lighter sulfur isotopes ($\delta^{32}\text{S}$) is more readily metabolized because their bonds are weaker. As a consequence of this microbiological process, a distinct sulfur isotopic signature in sulphide is produced by depletion in $\delta^{34}\text{S}$ of up to 46‰. The analyses were carried out in three distinct sulfur compounds present in the sediments: (i) the sulphur present in the AVS (Acid Volatile Sulphide), (ii) the elemental and pyritic sulphur (CRS – Chromium Reducible Sulphur) and the (iii) water soluble sulphate.

Figure 2 shows that the $\delta^{34}\text{S}$ signatures for the sulphate present slight variation throughout the reservoir and the river indicating that this anion derives from the same sulphur source in all sediments.

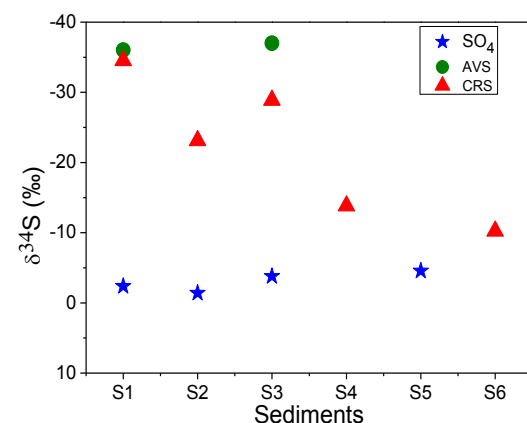


Figure 2. Isotope ratios in sulphate (SO_4), acid volatile sulphide (AVS) and chromium reducible sulphur for the surface sediments.

The average $\delta^{34}\text{S}$ value for the sulphate for all samples is -3.03‰, and it is within the values reported for the pyrite from the Poços de Caldas

Plateau region that ranges from +1.24 to -3.63‰. Thus, it may be concluded that the pyrite oxidation is the only source of sulphate. The AVS signatures were approx. - 37‰ for the sediments S1 and S3; the first and last sampling station inside the reservoir confirming the biological reduction. In addition, the lower $\delta^{34}\text{S}$ values for CRS inside the reservoir, ranging from -21‰ to -33‰, are lower than the values reported for the pyrite from the region and indicate the formation of neogenic pyrite originated from the FeS_2 which is depleted in $\delta^{34}\text{S}$ due to the bacterial reduction processes.

In contrast, the $\delta^{34}\text{S}$ value for CRS in the Antas river were more enriched and closer to the $\delta^{34}\text{S}$ value of -3.03‰ for the pyrite in the region. Therefore, bacterial sulphate reduction is a significant process inside Águas Claras reservoir and, consequently, the natural attenuation of contamination is expected, due to the precipitation of metallic sulphides followed by the formation of more stable phases such as neogenic pyrite.

Sequential Extraction (Figure 3) showed that the high amounts of Mn, around 28 to 81%, were extracted in the labile fraction by using acetic acid; most likely due to its association with the carbonate phase (dolomite and calcite). The highest content of U in the labile fraction, approx. 60% was presented by sample S1. Minor amounts of U were extracted in the labile fraction in the other sediments, ranging from 2 to 23%. For these samples, U can be non-specifically adsorbed on the surface of clays or on Fe and Mn oxyhydroxides. Despite the presence of the U in the labile fraction being extremely worrying, it is interesting to note that the U content in this fraction decreases downstream the reservoir from point S1 to S6, which indicated that the reservoir acts as a polishing pond. The mobility of Zn is evidenced by the high levels of extraction in the labile fraction (20 to 50%) indicating that it could be weakly adsorbed. Since metals in the labile fraction are considered readily and potentially bioavailable, the content of Zn associated to this fraction is especially concerning for the samples S1, S2 and S3, which contain high levels of zinc (5285 to 2417 mg/kg). Despite the evidences of natural attenuation, the presence of U, Zn and Mn in the labile fraction means that they can be easily available to the environment, and special monitoring should be carried out to detect changes in pH and/or reduction potential in the reservoir. Remediation proposals for the Águas Claras reservoir are being assessed and the determination of the types of contaminants, as well as the metals availability and the form in which they are present may support the final remediation project. One remediation strategy can be the enhancement of the bacterial sulphate reduction (e.g. by adding appropriate electron donors), favoring the formation of zinc

sulphide as well as the reduction of the highly soluble U(VI) to the less soluble and mobile U(IV).

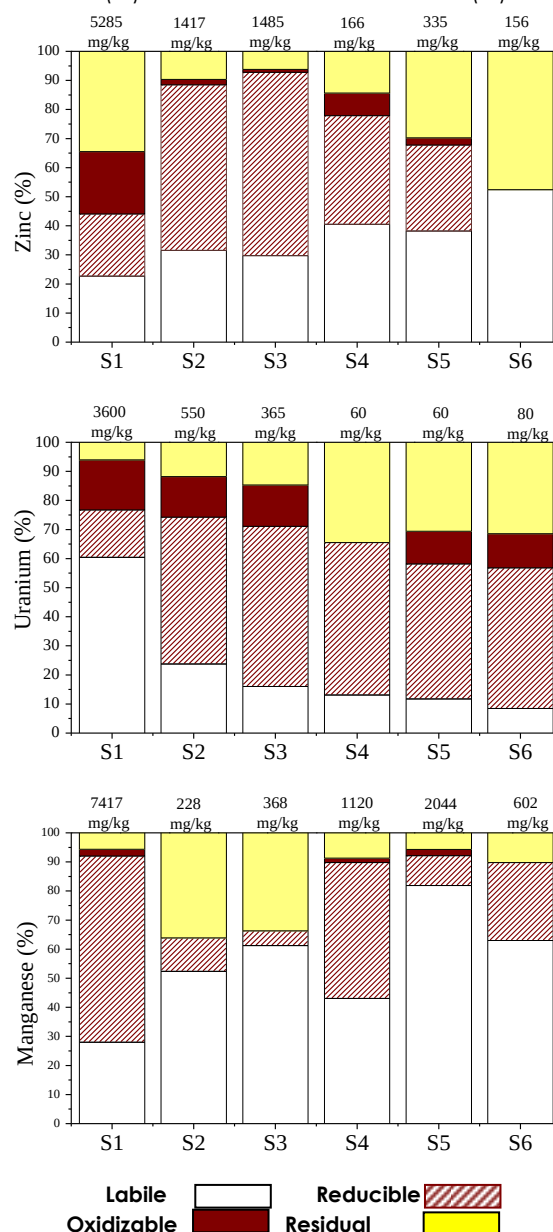


Figure 3 – Mn, Zn, U partitioning in the sediments, according to mBCR procedure. The metal concentrations in the original samples are displayed on the top of each column in mg/kg.

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References

- Rauret G, López-Sánchez JF, Sahuquillo A, Rubio R, Davidson C, Ure AM, Quevauviller P (1999). J Environ Monit 1:57–61.
- Knöller K, Fauville A, Mayer B, et al (2004). Chem Geol 204:303–323.