

Mining area disturbed by acid mine drainage – Acid Volatile Sulphur and Sequential Extraction studies

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Abstract This study investigated the sulfate bacterial reduction process in sediments from a water reservoir (Águas Claras) and the Antas creek contaminated by metals from acid mine drainage (AMD). The Acid Volatile Sulphur indicated that the bacterial reduction is a relevant process in the natural attenuation of the contamination in the reservoir. However, biological adverse effects are expected for sample S1 inside the reservoir, that is likely to be toxic whilst for the sediment S4 in the river, the toxicity is uncertain. The extraction procedure (mBCR) indicated that the predominance of the U (0.4%) in the labile fraction as well as the high concentrations of Zn (0.5%) and Mn (0.7%) inside the reservoir raise concerns regarding their availability to the environment. It was observed that the contamination is concentrated in Águas Claras reservoir.

Key words AVS, sulphate reduction, BCRm, sediments, uranium, zinc, manganese

Introduction

In Brazil, acid mine drainage (AMD) occurs in a former uranium mine at Poços de Caldas Plateau and contains radionuclides and other elements, which are precipitated from the acid water by liming. However, there are two important concerns related to the AMD treatment: i) the removal of contaminants by liming is not so effective and ii) significant amounts of precipitate escapes from the settling tanks from the Water Treatment Unit ending up at Águas Claras reservoir. The incorporation of this material into the sediments is a key issue to determine whether the contamination will reach the Antas creek and spread to the environment.

The bioavailability of contaminants in sediments can be predicted by understanding in which mineral phases they are incorporated and in which chemical form they are presented. The occurrence of the contaminants as a metal sulphides as well as their adsorption on iron and manganese oxides are important facts that leads to a more stable sediment. Therefore, the quantification of the sulphide phases simultaneously with sequential extraction methods are powerful to tools provide information about distribution, mobility and potential of migration of the contaminants to the environment (Morillo et al.. 2008; Charriau et al.. 2011; Larios et al.. 2012; Byrne et al.. 2010; Sarmiento et al.. 2009; Delgado et al.. 2011).

This study investigated the occurrence of bacterial reduction process in superficial sediments from Águas Claras reservoir and Antas Creek by determining the Acid Volatile Sulphur (AVS). In addition, the availability of the contaminants was assessed by sequential extraction tests. The sediments were characterized chemically and mineralogical and classified according to their toxicity based on international criteria. It is important to stress

that the presence of elements like uranium in addition to other metals requires a broad approach, so the association of different techniques to elucidate the bio-availability of the most hazardous contaminants is required. Additionally, the sediment's toxicity was predicted based upon the interactions of toxic metals with the sulphide and organic matter, and the availability of contaminants was assessed by sequential extraction procedure.

Methodology

Study Area and sampling

The area surrounds a former U mine at Minas Gerais State, Brazil, whose activity was ceased in 1996 leaving behind 44 tons of wastes containing pyrite and spharelite that generates acid mine water containing sulphate, F, U, Mn, and Zn at pH around 3.7. The acid waters are neutralized with CaOH_2 and the treated effluent is released into the Aguas Claras reservoir whose waters join the Antas Creek. Samples were taken in August 2011 along the reservoir and the Antas creek (Figure 1) by using a van Veen grab and a cylindrical collector. Samples were placed in plastic containers and stored at -4°C before analysis. The sampling stations were labelled S1, S2, S3, S4, S5, and S6.

Acid Volatile Sulphide (AVS) and Simultaneous Extracted Metals (SEM)

The AVS-SEM determination was in accordance to the EPA 821-R-91-100 (USEPA, 1991) procedures. The metals (Fe, Mn, Cu, Cd, Pb, Ni, Zn) were determined by flame atomic absorption spectrometry (Varian AA 240FS). Detection limits were 0.03 mg/L for Mn and 0.1 mg/L for all the other elements. Sulphide was determined by colorimetric method with methylene blue and the absorbance measured in a UV-VIS spectrophotometer (Varian Cary 50).

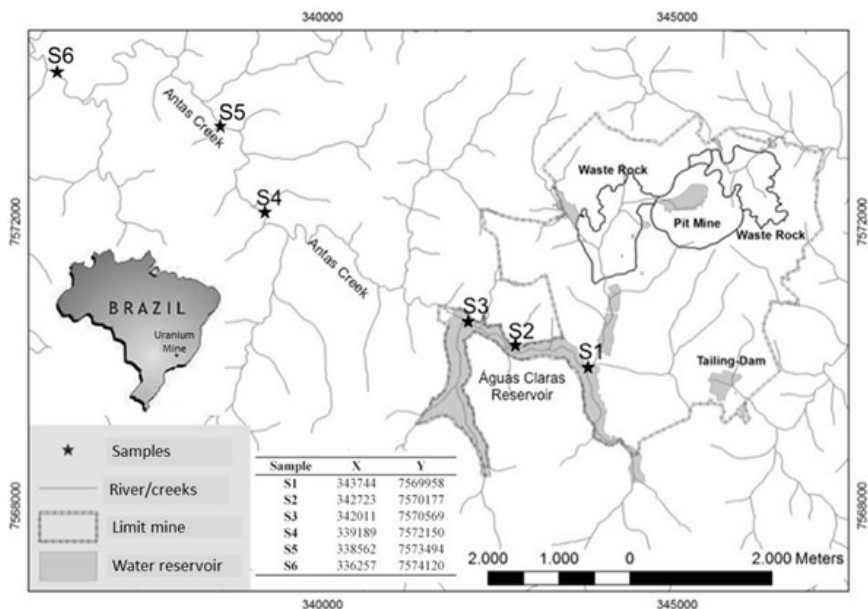


Figure 1 – Overview of the study area showing Águas Claras reservoir, the Antas creek, sampling stations (S1, S2, S3, S4, S5, and S6) and the UTM coordinates (southern hemisphere, zone 23).

Sequential Extraction

The sequential extraction procedure was based on the modified BCR (Bureau Communautaire de Références – Rauret et al., 1999) Measurements and Testing Programme (formerly BCR). The sequential fractions were named labile (E1); reducible (E2); oxidizable (E3); and residual (E4). The elements Fe, Mn, U and Zn were selected for being investigated. U analyses were carried out using a X-ray spectrometry (Kevex, model Sigma X9050) coupled with a radioactive source of americium (^{241}Am) and a Si(Li) detector with a detection limit of 10mg/L. Samples below this detection limit was determined by neutron activation in the Triga Marki IPR-R1 reactor and the detection limit was 0.1 mg/L. The other metals were analyzed by flame AA spectrometry (Varian AA 240FS) and the detection limits were 0.13, 0.03 and 0.08 mg/L for Fe, Mn and Zn.

Results and discussion

Acid volatile sulphide/Simultaneously extracted metals (AVS/SEM)

The AVS and SEM (U.S.EPA, 1991) were assessed in order to determine the extension of the reduction process by quantifying the sulphides and their bonded metals. The AVS fraction comprises the free sulphides (S^{2-}), iron sulphides such as FeS and Fe_3S_4 (Rickard and Morse 2005) a zone exists which releases H_2S if treated with acid. The materials that produce this sulfide are described as acid volatile sulfides or AVS and the sulfide which is evolved and collected by this treatment is called acid volatile sulfide (AVS-S and sulphides from bivalent metals such as Cu, Ni, Zn, Cd and Pb. The SEM fraction is composed of the metals, normally Cd, Cu, Pb, Ni, Hg, Ag and Zn, liberated from the sediment during the acidification. The results of AVS and SEM, as well as organic carbon (f_{oc}) and total sulfur (S_{Tot}) are in Table 1.

Table 1 – Organic carbon (f_{oc}), total sulphur (STot), AVS and metals extracted in the SEM procedure.

| | f_{oc} (g/kg) | S_{Tot} (g/kg) | AVS (mg/kg) | Fe (g/kg) | Mn (mg/kg) | Zn (mg/kg) | Pb (mg/kg) |
|----|---------------------------|-----------------------------------|----------------|--------------|---------------|---------------|---------------|
| S1 | 5.6 | 11.6 | 151 | 34.5 | 7184 | 5845 | 24 |
| S2 | 22.2 | 13.0 | 2665 | 42.5 | 184 | 1375 | 35 |
| S3 | 23.6 | 9.9 | 2969 | 31.7 | 300 | 1561 | 37 |
| S4 | 10.2 | 2.0 | 3 | 11.9 | 917 | 160 | 23 |
| S5 | 25.5 | 4.2 | 133 | 21.1 | 2058 | 188 | 23 |
| S6 | 21.4 | 3.2 | 58 | 17.9 | 789 | 101 | 30 |

As shown in Table 1, there is a significant variability in the content of AVS in the sediments, ranging from 3 to 2969 mg/kg. Sediments S1 and S4 present the lowest AVS con-

centration (150 and 3 mg/kg, respectively) along with the lowest concentration of organic carbon (5.584 e 10.214 mg/kg, respectively). Specific environmental conditions such as pH, redox potential and content of organic matter are necessary for the formation and precipitation of AVS phases. The other samples inside the reservoir (S2 and S3) present high AVS, around 3000 mg/kg, and the greatest amount of organic carbon. These results indicate that the sulphide production is prolific, leading to precipitation of metallic ions and reducing the availability of metals. Furthermore, the bacterial reduction could be one of the reasons behind the decreasing in the sulphate content in the waters of the reservoir, as reported in the Technical Report of the Water Committee (Comissão das Águas 2012). Despite the high concentrations of organic carbon in the sediments S5 and S6, the content of AVS is much lower, i.e., of 133 and 58 mg/kg, which implies that bacterial reduction processes are not pronounced. This fact is may be associated with the low content of sulphate in the waters of Antas creek (approx. 35 mg/L); much lower than the values in the reservoir. For sediment S1, the high content of total sulphur is associated with insoluble phases of sulphate (ettringite and gypsum) that overflows from the water treatment tanks (Gomes et al. 2012) formed by neutralization of acid mine drainage with lime, has been stored temporarily in the open pit of a uranium mine that floods periodically. The present study characterized samples of this sludge, named according to the time of placement as Fresh, Intermediate, and Old. Standard leaching and sequential extraction procedures assessed the associations and stabilities of U, Zn, Fe, Mn, and other contaminants in the solid phases. Corresponding mineralogical transformations associated with sludge weathering were modeled using PHREEQC. The main crystalline phases were ettringite, gypsum and calcite; the minor constituents were fluorite and gibbsite. This mineral assemblage could be attributed to the incongruent dissolution of ettringite to form gibbsite, calcite, and gypsum. Sequential extractions indicated high contents of U, Ca, SO₄. Table 1 also shows Fe, Mn, Zn and Pb, extracted during AVS-SEM procedure. The elements Ni, Cu and Cd were below the detection limit (0.1 mg/L) and considered not relevant for the assessment of the toxicity.

The toxicity in the sediments affect can be estimated by the difference ($\Sigma\text{SEM} - \text{AVS}$) (Di Toro et al. 2005). When there is an excess of sulphide, the metals precipitate as insoluble phases, such as NiS, ZnS, CdS, PbS, CuS and Ag₂S, which decreases their bioavailability. If $\Sigma\text{SEM} - \text{AVS} \leq 0$ the absence of toxicity can be assured, however, it cannot predict whether toxicity will occur if $\Sigma\text{SEM} - \text{AVS} > 0$. In this case, the organic carbon should be considered as additional bind phase as many dissolved metals bind to dissolved organic carbon forming complexes that do not appear to be bioavailable (Di Toro et al. 2005; U.S.EPA. 2005). Therefore, the difference of ($\Sigma\text{SEM} - \text{AVS}$) normalized by the fraction of organic carbon (f_{oc}), as shown in Table 2, was proposed to predict the biological effects.

The results for the assessment of toxicity based upon the difference ($\Sigma\text{SEM}-\text{AVS}$) and the normalized difference ($(\Sigma\text{SEM}-\text{AVS})/f_{oc}$) for all the sediments are shown in Table 3.

| Limit values in ($\mu\text{mol/g}_{\text{oc}}$) | Predicted biological effect |
|--|---|
| $\Sigma\text{SEM-AVS} \leq 0$ | Sediment is Non-toxic |
| $\left[\frac{\Sigma\text{SEM} - \text{AVS}}{f_{\text{oc}}} \right] < 130$ | Sediment Toxicity is not likely to be caused by Cd, Cu, Pb, Ni, Ag and Zn |
| $13 \frac{\Sigma\text{SEM} - \text{AVS}}{f_{\text{oc}}} < 100$ | Sediment Toxicity is uncertain due to Cd, Cu, Pb, Ni, Ag and Zn |
| $\frac{\Sigma\text{SEM} - \text{AVS}}{f_{\text{oc}}} > 3,000$ | Sediment Toxicity is likely to be caused by Cd, Cu, Pb, Ni, Ag and Zn |

Table 2 – Toxicity criteria for sediments based on AVS, SEM and fOC. (Adapted from USEPA, 2005).

Table 3 – Results of sediment toxicity based upon the difference ($\Sigma\text{SEM-AVS}$) and the normalized difference ($(\Sigma\text{SEM-AVS})/f_{\text{oc}}$).

| Sample | AVS $\mu\text{mol/g}$ | ΣSEM $\mu\text{mol/g}$ | f_{oc} $\text{g}_{\text{oc}}/\text{g}$ | $(\Sigma\text{SEM-AVS})$ $\mu\text{mol/g}$ | $(\Sigma\text{SEM-AVS})/f_{\text{oc}}$ $\mu\text{mol/g}_{\text{oc}}$ |
|--------|--------------------------|---|--|---|---|
| S1 | 4.70 | 89.40 | 0.006 | 84.70 | 15168 |
| S2 | 83.11 | 21.20 | 0.022 | - 61.91 | - 2785 |
| S3 | 92.58 | 24.05 | 0.024 | - 68.53 | - 2913 |
| S4 | 0.10 | 2.56 | 0.010 | 2.46 | 241 |
| S5 | 4.15 | 2.98 | 0.025 | - 1.17 | - 46 |
| S6 | 1.82 | 1.70 | 0.021 | - 0.13 | - 6 |

g_{oc} = gram of organic carbon

According to Table 3, the sediments S2 and S3, inside the Águas Claras reservoir, and the sediments S5 and S6 in the river were classified as non-toxic, since the difference of $\Sigma\text{SEM-AVS}$ were negative. On the other hand, the sediments S1 and S4 presented positive value, i.e. $(\Sigma\text{SEM-AVS}) > 0$, and were normalized by the fraction of organic carbon (f_{oc}). According to these criteria, the sample S4 presented uncertain toxicity once the value of $(\Sigma\text{SEM-AVS})/f_{\text{oc}}$ is between 130 and 3000 $\mu\text{mol g}_{\text{oc}}^{-1}$. The sediment S1 presented $(\Sigma\text{SEM-AVS})/f_{\text{oc}}$ greater than 3000 $\mu\text{mol g}_{\text{oc}}^{-1}$, which implies high risk of adverse biological effects mainly due to the high content of Zn. In general, the results show that the sulphate from the reservoir undergoes bacterial reduction producing highly insoluble sulphide, markedly the zinc, which decrease the metals availability to the environment. Therefore, despite the high levels of total metals in most sediments, samples S2, S3, S5 and S6 were assessed as non-toxic. However,

the redox potential needs to be monitored and controlled, once increased redox promotes the re-oxidization of the metal sulphides as well as the degradation of organic compounds. On the other hand, the low amounts of sulphide in the sediments S1 and S4 classified sample S1as likely to be toxic whereas biological adverse effects are uncertain for the sediment S4.

Sequential Extraction

The AVS procedure takes into account only the elements Cu, Zn, Pb, Ni, Cd, Ag in the estimation of the toxicity of the samples. Other toxic metals that may be present in sediments are not assessed by this method. As the study area presents other elements, such as U and Mn, and additional method should be used to identify their association with different mineralogical phases and their availability to the environment. Thus, sequential extraction tests were carried out for the selected metals: Fe and Mn (considered as a sink for contaminants) and Zn and U (considered hazardous and present in the sediments in high levels). Figure 2 shows the sequential extraction results as well as the total metal concentration in the original samples. It is noted that the sample station S1 presents the highest concentration of Mn, Zn and U (7417, 5285 and 3600 mg/kg) followed by samples S2 and S3 that are also enriched in U and Zn if compared to the sediments in the Antas Creek. This enrichment is caused by part of the precipitate that overflows from the Water Treatment Unit and sets at the bottom of the reservoir.

Iron: As shown in Figure 2, minor amounts of iron were associated with the labile and oxidizable fractions. In general, Fe was mainly extracted in the reducible and residual steps and these results are similar to those reported in the literature (Morillo et al., 2008; Charriau et al., 2011) but they are greatly affected by pollution from the Odjel River. Surface sediments from this area were analysed using the latest version of the BCR sequential extraction procedure to determine the fractionation of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn among four geochemical phases (acid-soluble, reducible, oxidisable and residual. The reducible fraction (E2) comprises 12 to 30% and consists of oxyhydroxides present in highly weathered environments (amorphous iron). In the sediments, these amorphous phases are important sinks for contaminants, since they have a high capacity of adsorbing other metals in their structure (Filgueiras et al., 2002)"} : {"article-journal", "volume" : "4" }, {"uris" : ["http://www.mendeley.com/documents/?uuiid=8fd1cccb-5dd6-4056-8a72-915e7a84694e"] }], "mendeley" : { "formattedCitation" : "(Filgueiras et al., 2002. A small portion of Fe was extracted in the oxidizable fraction, associated with the oxidation of reduced forms of iron, such as iron associated with organic matter and sulphides. In all sediments, Fe was preferentially associated with the residual fraction comprised of crystalline forms of hematite, goethite, in addition to aluminosilicates containing Fe (II and III) and pyrite.

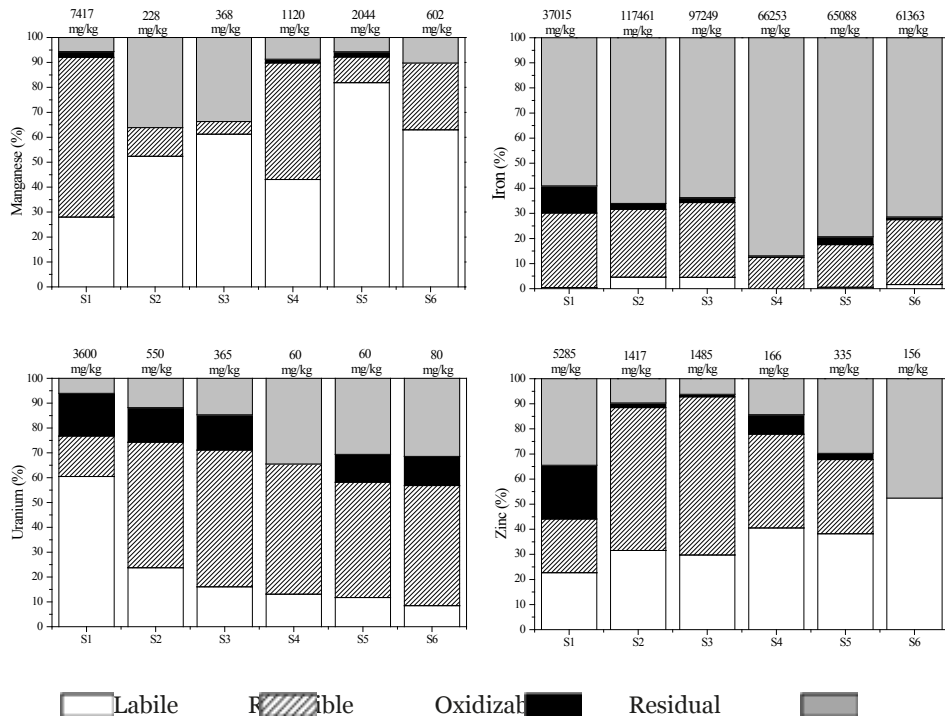


Figure 2 – Mn, Zn, U and Fe partitioning in the sediments, according to mBCR procedure. The original concentration is displayed on the top of each column.

Manganese: High percentage of Mn (28 to 81%) is present in the labile fraction (E1), most likely due to its association with the carbonate phases reported to be formed in the Water Treatment Unit (Gomes et al., 2012). The reducible fraction E2, i.e., amorphous Fe oxides and crystalline Mn oxides (Filgueiras et al. 2002) type: “article-journal”, “volume”: “4”}, “uris”: [“http://www.mendeley.com/documents/?uuid=8fd1cccb-5dd6-4056-8a72-915e7a84694e”]}, “mendeley”: {“formattedCitation”:“(Filgueiras et al. 2002, represents 5% to 64% of the Mn and the highest extraction is for sample S1 which also present the highest Mn content. The oxidizable fraction (E3) seems to be irrelevant as it represents at maximum 2% of the Mn. This is explained by the low content of Mn sulphides as well as the difficulty of Mn to form complexes with organic matter. Mn present in the residual fraction, which comprises the phases resistant to the weathering and bonded to lithogenic minerals, ranged from 6 to 36%.

Zinc: The mobility of Zn is evidenced by the high levels of extraction in the labile fraction E1 (20 to 50%). Since metals in the labile fraction are considered readily and potentially bioavailable, the 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). These results corroborate the findings in the AVS-SEM approach, in which sample S1 was classified as likely to be toxic due to the great amount of zinc highly bioavailable. Inside the reservoir, samples S2 and S3

have around 60% of total zinc extracted in the reducible fraction, mainly in the form of zinc oxide and/or adsorbed in Fe oxyhydroxides. The association of Zn in Fe–Mn oxides/hydroxides confirms the known ability of this phase to scavenge zinc from the aqueous phase, and these phases are completely extracted during the AVS/SEM procedure. The sediment S1 is the only one to present significant amount of Zn associated with the oxidizable fraction. Since this sediment presented low content of organic matter and sulphides, Zn is probably associated with other oxidizable phases such as CRS-Fe. Despite the elevated content of organic matter in the other samples, only 2% of total zinc was extracted in the oxidizable fraction, indicating that it is not significant as binding phase. Zinc extracted in the residual fraction indicate the presence of spharelite ZnS.

Uranium: The sample S1 presented the highest extraction of U in the labile fraction, approx. 60%, most likely due to the presence of calcium diuranate (CaU_2O_7) that overflowed from the Water Treatment Unit and settled down in the bottom of the lake (Gomes et al., 2012) formed by neutralization of acid mine drainage with lime, has been stored temporarily in the open pit of a uranium mine that floods periodically. The present study characterized samples of this sludge, named according to the time of placement as Fresh, Intermediate, and Old. Standard leaching and sequential extraction procedures assessed the associations and stabilities of U, Zn, Fe, Mn, and other contaminants in the solid phases. Corresponding mineralogical transformations associated with sludge weathering were modeled using PHREEQC. The main crystalline phases were ettringite, gypsum and calcite; the minor constituents were fluorite and gibbsite. This mineral assemblage could be attributed to the incongruent dissolution of ettringite to form gibbsite, calcite, and gypsum. Sequential extractions indicated high contents of U, Ca, SO₄. 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. The presence of the U in the labile fraction is particularly worrying as its high concentration – 3600 mg/kg in sample S1, for instance – can pose risks to the environment. However, it is interesting to note that the U content in the labile fraction decreases with distance from upstream to downstream the lake, i.e., from sample S1 to S6. In all samples except S1, most of the U is associated with the Mn and Fe oxyhydroxides (step E2), most likely due to the sorption or occlusion of U in hematite (Fe_2O_3) and goethite (Fe_3O_4) (Duff et al., 2002). The lower extraction of U in step E2 for sample S1, near 15%, is related to the low content of Fe in this sample. The U in the oxidizable fraction E3 is approx. 15%, and represents the U sorbed in the organic matter (Duff et al., 2002) and/or the U reduced into crystalline oxides (e.g., uraninite) in an effective mechanism of bioremediation. Sample S4, the only one without U in the oxidizable fraction, is also the one that presents the lowest level of total sulfur and organic matter. Significant contents of U in the residual fraction in sediments S4, S5 and S6; around 30% is probably due to its inclusion in the crystalline iron oxides, silicates and gibbsite or as uraninite; all of them typical minerals of the region.

Conclusion

According to the AVS-SEM analyses, the formation of sulphides result in the unlikely toxicity of the sediments S2 and S3 inside the reservoir, despite the high levels of Zn. Sequen-

tial extraction procedure indicates the presence of Zn mainly in the labile and reducible fractions. Similarly, the U was extracted mainly in the labile and reducible phases. The metals extracted in the labile fraction are the main cause of concern once they can be readily released in an acidic environment typical of AMD. In the light of these findings, we see that the precipitate that overflow from the Water Treatment Unit results in the enrichment of metals in the sediments of the Aguas Claras reservoir. Furthermore, the environmental impact is mostly restricted to the reservoir, where the concentration and bioavailability of metals in the sediments decreases downstream. However, although it was observed the decreases their bioavailability, in order to prevent later mobilization of the metals the sediments should remain in anoxic conditions, thus hindering the re-dissolution of the metal sulphides. The investigation of the bioremediation process as well as the definition of the chemical availability of the contaminants can support the decision making process on the best remediation plan for the reservoir, e.g., removing the sediments or improving/monitoring the bioremediation process.

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