



Geochemical speciation and dynamic of copper in tropical semi-arid soils exposed to metal-bearing mine wastes



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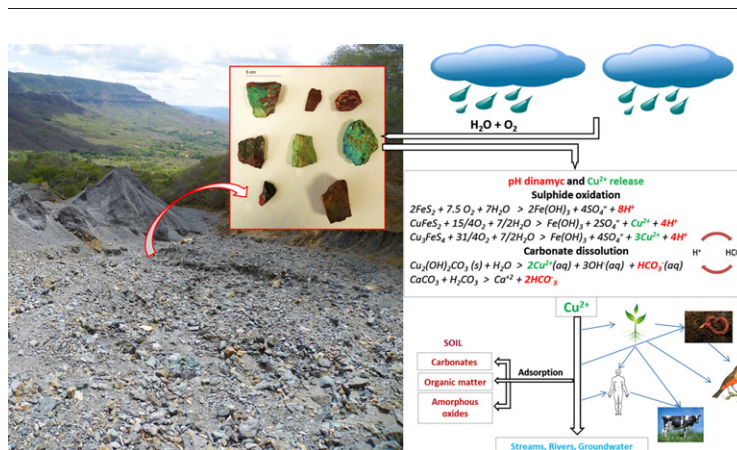
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HIGHLIGHTS

- The hazardous effects of mine waste rocks at environmental conditions were studied;
- Acid drainage, metal concentration and copper geochemical in soils were evaluated;
- The acidity generated by sulphides oxidation is buffered by carbonates dissolution;
- Copper are mainly associated with carbonates, amorphous Fe oxides and sulphides;
- Plants and organic compounds may enhance carbonates dissolution and Cu^{2+} in soils.

GRAPHICAL ABSTRACT



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ABSTRACT

The potentially hazardous effects of rock wastes disposed at open pit in three different areas (Pr: Ore processing; Wr: Waste rock and Bd: Border) of an abandoned copper mine were evaluated in this study, with emphasis on acid drainage generation, metal contamination and copper geochemical dynamics in soils. Samples of waste rock were analyzed by Energy dispersive X-ray fluorescence (XRF), scanning electron microscopy with microanalysis (SEM-EDS) and X-ray diffraction (XRD). Soil samples were analyzed to determine the total metal contents (XRF), mineralogy (XRD), pH (H_2O and H_2O_2), organic and inorganic carbon, % of total N, S and P, particle size, and a sequential extraction procedure was used to identify the different copper fractions. As a result of the prevalence of carbonates over sulphides in the wastes, the soil pH remained close to neutral, with absence of acid mine drainage. The geochemical interaction between these mineral phases seems to be the main mechanism to release Cu^{2+} ions. Total Cu in soils from the Pr area reached $11,180 \text{ mg.kg}^{-1}$, while in Wr and Bd areas the values reached, on average, 4683 and 1086 mg.kg^{-1} , respectively, indicating a very high level of soil contamination. In the Pr and Wr, the Cu was mainly associated with carbonates and amorphous iron oxides. In the Bd areas, the presence of vegetation has influenced the geochemical behavior of copper by increasing the dissolution of carbonates, affecting the buffer capacity of soils against sulphide oxidation, reducing the pH levels and enhancing the proportion of exchangeable and organic bound Cu. The present

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findings show that the use of plants or organic amendments in mine sites with high concentration of Cu carbonate-containing wastes should be viewed with caution, as the practice may enhance the mobilization of copper to the environment due to an increase in the rate of carbonates dissolution.

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1. Introduction

Nowadays, mining is safer and better regulated due to the application of stricter legislation and to advances made in the techniques used for environmental control. However, the lack of such control in the past has led to numerous abandoned mines around the world, without any kind of recovery measures being applied (Bradshaw, 1997; Abreu et al., 2008; Ersoy et al., 2008; Park et al., 2011; Otero et al., 2012). Waste rock containing metals, when disposed of in open pits, tend to react with water and oxygen and may be oxidized or dissolved, depending on the geochemical composition of the material, thereby transferring metals to the environment. This process therefore represents a serious risk to environmental and public health (Lottermoser, 2007).

Mining is one of the main anthropogenic activities that generates waste and water containing high levels of copper, especially when the aim is to extract ores such as chalcopyrite, chalcocite and malachite (Álvarez et al., 2003; Abreu et al., 2008; Guo et al., 2011; Wu et al., 2011; Li et al., 2014). Furthermore, the presence of high concentrations of sulphides generates acid mine drainage (AMD), thus increasing the risk of contamination via large decreases in soil and water pH, which increases copper mobility and bioavailability (Kimball et al., 2009).

Copper is a vital micronutrient for a wide range of metabolic processes and an essential constituent of the enzymes of various plants and (micro) organisms (Flemming and Trevors, 1989; Baker and Senft, 1995). Under natural conditions, and depending on the parent material, most soils contain Cu at concentrations ranging from 25–60 mg.kg⁻¹. However, at higher concentrations, Cu becomes a toxic element (Kabata-Pendias, 2010).

The ecotoxicological potential of Cu is directly related to its bioavailability in the soil, i.e. it depends on the geochemical forms of Cu that plants and (micro) organisms may have immediate access to and that can be consumed either by ingestion, absorption or direct contact (dermal, leaf, etc.) (Peijnenburg et al., 2007). The bioavailability of copper in soils depends on the soil composition and properties such as acid-base condition (pH), amount of organic matter (TOC), clay, carbonates and Fe oxyhydroxides (Graf et al., 2007; Sipos et al., 2008; Strawn and Baker, 2009; Fernandez-Calvino et al., 2009).

Because of the complexity of reactions between Cu ions and different soil components, the determination of total or pseudo-total concentrations may not always reflect the real risk that this element represents to ecosystems, as most Cu forms in natural environments will be scarcely accessible to plants and organisms (i.e. occluded Cu in crystalline forms of primary minerals or forming organometallic complexes) (Fernandez-Calvino et al., 2009).

To overcome this, the sequential extraction technique (SET) has been used to provide a more realistic estimate of actual environmental impacts by extracting metals from specific soil fractions, thus allowing a better understanding of the mechanisms controlling mobility and bioavailability of these elements in soils and sediments (Mossop and Davidson, 2003; Cuong and Obbard, 2006).

Despite the known intrinsic limitations, the SET provides a more complete and realistic diagnosis regarding the geochemical behavior of metals in soils than other techniques; it therefore enables more accurate interpretation of the potential damage that metals cause to ecosystems and the adoption of more efficient control and remediation techniques (Filgueiras et al., 2002).

In this study, we evaluated the mineralogical and geochemical composition of waste rocks and determine total Cu concentration and speciation in soils from three different areas of an abandoned copper mine.

The aims of the study were to assess geochemical transfer mechanisms of copper from waste rock to soil and its influence in the physical-chemical properties and in the bioavailability of copper, establishing the bases to predict the real ecotoxicological risks and to estimate the expected results for mine site restoration.

2. Study area

The study was conducted in Viçosa do Ceará (northeastern Brazil) (Fig. 1). The climate is classified as semi-arid warm tropical in the regions of lower altitude (where the mine is located – General Tibúrcio district) and sub-humid warm tropical in the regions at higher altitudes, with an average annual rainfall of 960 mm, mainly concentrated between January and May, and average annual temperatures ranging from 22 to 24 °C (FUNCEME, 2014). The regional vegetation consists of evergreen seasonal tropical forest on the top of the plateau and a dry tropical forest on the slopes (IBGE, 2012). The closest village to the mine is General Tibúrcio District, at a distance of about 5 km, and there are several other small villages, less than 1 km from the mine entrance. There are also many agricultural fields between the district and the mine, which serve as a source of food for subsistence of the local population (Fig. 1A).

The area is subdivided into three geological formations, from the base to the top: São Joaquim, Mambira and Ubari (Fig. 2).

The São Joaquim formation is mainly characterized by quartzite. The Mambira formation is subdivided into three parts: the basal portion is formed by mica-schists interbedded with quartzites, and the upper part, denominated Pedra Verde, is essentially composed of phyllites. The highest concentrations of Cu sulphide ores (chalcopyrite, chalcocite and bornite) occur in the upper formation. Superimposed on the Mambira, the Ubari formation comprises conglomerates of mudstone, sandstone, phyllite, quartzite and quartz, dispersed in a feldspathic matrix, which also contains Cu in oxidized ores (malachite and cuprite) (Korpershoek et al., 1979). The red iron oxide zone between the Pedra Verde phyllites and Ubari conglomerates contains, on average, 0.1% of Cu (Collins and Loureiro, 1971).

The Pedra Verde ore body (latitude 3°24'03" S, longitude 41°08'21" W) is of supergene origin and the Cu mineralized zone occurs in phyllites as sulphidic deposits, veins and irregular masses that fill associated fractures. The sulphide minerals include pyrite (FeS₂), chalcopyrite (CuFeS₂), chalcocite (Cu₂S), bornite (Cu₅FeS₄) and covellite (CuS), with arsenopyrite (FeAsS), galena (PbS) and sphalerite (ZnS) occurring in smaller proportions. In the upper portion of the mineralized horizon, between the phyllites and conglomerates, iron oxides predominate at levels reaching 0.1% Cu, with hematite (Fe₂O₃) as one of the main constituents, in addition to the occasional presence of cuprite (Cu₂O) (Collins and Loureiro, 1971).

An oxidized ore zone occurs in the superficial layers, mostly in the form of carbonates in malachite impregnations and streaks (Cu₂(CO₃)(OH)₂), which are concentrated along an area of more than 100 m in a fracture zone, at a depth not exceeding 15 meters. The gangue minerals are mainly composed of quartz, feldspar, carbonate, muscovite, sericite, chlorite and calcite (Collins and Loureiro, 1971).

The mine was exploited in the 1980s for the extraction and processing of Cu from sulphide (chalcopyrite and chalcocite) and carbonate (malachite) minerals. After the mine was closed in 1987, the processed minerals were dumped in piles on terraces constructed on the slope of the plateau. These waste piles are still 10 meters high. As a result of the large amount of waste involved and the lack of maintenance of the

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