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Fractionation and mobility of thallium in areas impacted by mining-metallurgical activities: Identification of a water-soluble Tl(I) fraction

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ABSTRACT

Mining and metallurgy generate residues that may contain thallium (Tl), a highly toxic metal, for which it is currently not feasible to determine its geochemical speciation through X-ray absorption spectroscopy due to a combination of very low contents and the interference of accompanying high arsenic contents. Therefore, fractionation studies in residues and soils are required to analyze the mobility and bioavailability of this metal, which in turn provide information to infer its speciation. For this purpose, in this work a modification of the BCR procedure was applied to residues and contaminated soils from three mining zones of Mexico and two mining zones of Spain, spanning samples with acidic to alkaline pH values.

The Tl extraction procedure consisted of the following fractions: (1) water-extractable, (2) easily exchangeable and associated to carbonates, associated to (3) poorly-crystalline and (4) crystalline Fe and Mn oxyhydroxides, and (5) associated to organic matter and sulfides; and finally a residual fraction as associated to refractory primary and other secondary minerals. The extracted contents were analyzed by Inductively-Coupled Plasma with Mass Spectrometry.

Surprisingly, water-soluble, in Tl(I) oxidation state, was detected in most areas, regardless of the pH, a fact that has not been reported before in these environments, and alerts to potential health risks not previously identified. Most of the samples from a metallurgy area showed high levels of Tl in non-residual fractions and a strong correlation was obtained between extracted Mn and Tl in the third fraction, suggesting its association to poorly crystalline manganese oxides. In the majority of samples from purely mining environments, most of the Tl was found in the residual fraction, most probably bound to alumino-silicate minerals. The remaining Tl fractions were extracted mainly associated to the reducible mineral fractions, and in one case also in the oxidizable fraction (presumably associated to sulfides).

Capsule: Soluble Tl(I) was found in all soil samples contaminated with either mining or metallurgical wastes. Additionally, in those affected by metallurgical wastes a very strong Tl-Mn correlation was found.

1. Introduction

The extraction and refining of natural resources from the subsoil through mining and metallurgical activities has produced much of the wealth of current day society. However, concurrently immense volumes of waste material have been and are continuously generated, deposited and exposed to environmental conditions from these activities worldwide, which are globally estimated to be larger than the movement of sediments by all the world rivers

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combined (Monastersky, 2015). Evidently, these large amounts of waste frequently cause large negative environmental and ecological impacts, making mining and metallurgy amongst the largest polluting activities of natural environments (inland and marine water bodies, soils, the atmosphere and their ecosystems). Their effects are present to a greater or lesser extent in all areas of the planet where deposits of solid minerals (metallic and non-metallic), liquid and gaseous materials are exploited.

Potentially toxic trace elements are usually concentrated through mining and metallurgy. Among them, thallium (Tl), although found in much lower contents than most other trace metals, is the most toxic regulated inorganic pollutant, more toxic than mercury, cadmium, lead and copper (Peter and Viraraghavan, 2005; Rodríguez-Mercado and Altamirano-Lozano, 2013). In addition, Tl may also be used in some pesticides or rodenticides, and thus it is one of the most dangerous elements in terrestrial environments (Nriagu, 1998).

Ionic thallium (I) shows chemical similarities to lead (II) (similar atomic weight) (Peter and Viraraghavan, 2005**)**, and to K^+ (similar charge/size ratio). Tl(I) shows high toxicity because it can replace K^+ in biological systems (Karbowska and Zembrzuski, 2016); however, the mechanism of thallium toxicity is not fully elucidated (Cvjetko et al., 2010). Tl(I) salts (acetate, carbonate and sulfate) are extremely poisonous and are rapidly absorbed into the skin or mucous membranes of the intestinal tract. Once ingested thallium is easily distributed and shows toxicity to various organ systems. It also results in abdominal pain, diarrhea and tingling of the extremities (Gómez-González et al., 2015).

The geochemical behavior of metals in general depends mainly on the chemical forms (species) in which they occur, and in turn this influences their mobility, toxicity and bioavailability, and in particular their binding mode to the soil matrix. Metals in uncontaminated soils are mainly present in primary minerals, such as silicates, resulting in relatively immobile forms (Karbowska and Zembrzuski, 2016), while those in contaminated soils tend to be more mobile due to their weaker binding to other soil components (Lukaszewski et al., 2003).

The two main geochemical sources of Tl in the environment are from weathering of rocks rich in potassium (Vaněk et al., 2009), and from sulfide minerals (Voegelin et al., 2015). The main anthropogenic source of thallium in the environment is through mining activities. Significant quantities of thallium have been found associated to sulfide minerals (ferrous and non-ferrous), mainly in gold, copper, lead, zinc and uranium mines (Peter and Viraraghavan, 2005; Lis et al., 2003; Campanella et al., 2017). Duchesne et al. (1983) reported total thallium values in a range of 30–6800 mg/kg in zinc and lead ores in Belgium, in this case the minerals analyzed were galena (PbS) and marcasite (FeS_2). In mining areas of Poland, thallium values ranging between 1.85 mg/kg and 2.05 mg/kg were reported, in this case the samples investigated were galena (PbS) and Zn blende or sphalerite (ZnS) minerals (Karbowska et al., 2014). Another source of Tl from mining activities has been reported associated to aluminosilicates in two areas near Madrid (0.67–2.43 mg/kg), in Spain, and the residues remaining on the site affect the soils and sediments of the natural water courses near the city (Gómez-González et al., 2015).

The proper estimation of the real threat caused by thallium to living organisms should be based on the assessment of the environmental availability of thallium, not only on measurements of total content (Yang et al., 2005), by analyzing the possible leaching of this toxic element from soils and sediments to water. A series of physicochemical parameters usually influence the availability of potentially toxic species in general. The techniques based on sequential chemical extractions are widely used to evaluate the mineral fractions to which they are associated, and in turn to better understand the processes that influence their mobility and availability (Gómez-González et al., 2015; Antić-Mladenović et al., 2017). Unfortunately, in the case of thallium, spectroscopic techniques, such as X-ray Absorption (XAS) are highly hindered for investigating its geochemical speciation in complex contaminated matrices, mainly because of the swamping interference on the Tl Lα signal caused by the K fluorescence from arsenic, a species which normally accompanies Tl but at much larger contents. Isotopic methods have been used in the past to trace Tl behavior and source (Vaněk et al., 2017).

The number of reports dedicated to Tl environmental geochemistry in mining scenarios is limited, and the scale of health risks associated with this element in these systems has not been widely studied. The objective of this work was to determine the content of Tl in different fractions of mining and metallurgical wastes and soil samples contaminated by them from different origins, in order to infer and further the understanding of its geochemical behavior. The samples chosen encompassed mining and metallurgical environments, with differences in climate regimes and pH values.

2. Materials and methods

2.1. Geological context and sampling

The areas studied in Mexico correspond to the Northwest and North-Center of the country “La Colorada” and “El Tecolote” mine tailings impoundments, both in Sonora; and the “San Luis Potosí” metallurgical District (Fig. 1 a, b and c respectively). Nine samples were analyzed from the old San Luis Potosí copper and arsenic plants, (SLP prefixes), five samples from the “La Colorada” mine (COL prefixes) and eleven samples from one tailings profile in “El Tecolote” (TJ prefixes). Table S1 summarizes the location and description coordinates of the selected samples.

The metallurgical District “San Luis Potosí” consisted of two production plants: one of copper and one of arsenic. Copper extraction was carried out through a pyrometallurgical process that used copper and iron concentrates, metallurgical byproducts of the plant, as well as copper, siliceous and limestone minerals from other foundries. In relation to the arsenic plant, its activity consisted in obtaining arsenic (arsenic trioxide) with 99% purity, starting mainly from the powders recovered in the Cu process (30% arsenious oxide), although concentrates of iron and byproducts generated in the same process were also used, such as powders and calcined materials from roasting. The main residues that were generated in both plants were vitreous slag and atmospheric emissions. Probably in each concentrate analyzed Tl was found as impurity, and due to the treatment at high temperatures it was released and therefore associated with the minerals that are its main destination in the environment: aluminosilicates and manganese oxides. Here, due to high temperatures, its presence in organic compounds and sulfides is unlikely.

“La Colorada” is an epithermal deposit, with veins containing Au and Ag. Thallium is an element associated with this type of deposit (Ochoa-Landín et al., 2011). The processing of materials in “La Colorada” occurred by leaching with cyanide. In this process the minerals were ground and disposed in piles. In these piles a continuous leaching process was carried out with a solution of sodium cyanide.

“El Tecolote” is a deposit of skarn type, with mineralization of Zn and Cu. This type of deposit is formed by a metasomatic process, related to contact metamorphism involving carbonate rocks. The skarn is generally characterized as containing minerals such as garnet and pyroxene. In this area mining was carried out underground and subsequently the material extracted by flotation was