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The redox processes in Hg-contaminated soils from Descoberto (Minas Gerais, Brazil): Implications for the mercury cycle

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ABSTRACT

Investigations of the redox process and chemical speciation of Hg(II) lead to a better understanding of biogeochemical processes controlling the transformation of Hg(II) into toxic and bioaccumulative monomethyl mercury, mainly in areas contaminated with Hg(0). This study investigates the speciation and redox processes of Hg in soil samples from a small area contaminated with Hg(0) as a result of gold mining activities in the rural municipality of Descoberto (Minas Gerais, Brazil). Soil samples were prepared by adding Hg(0) and $HgCl_2$ separately to dry soil, and the Hg redox process was monitored using thermodesorption coupled to atomic absorption spectrometry. A portion of the Hg(0) added was volatilized (up to $37.4 \pm 2.0\%$) or oxidized (from $36 \pm 7\%$ to $88 \pm 16\%$). A correlation with Mn suggests that this oxidation is favored, but many other factors must be evaluated, such as the presence of microorganisms and the types of organic matter present. The interaction of Hg with the matrix is suggested to involve Hg (II)-complexes formed with inorganic and organic sulfur ligands and/or nonspecific adsorption onto oxides of Fe, Al and/or Mn. The kinetics of the oxidation reaction was approximated for two first-order reactions; the faster reaction was attributed to the oxidation of Hg(0)/Hg(I), and the slower reaction corresponded to Hg(I)/Hg(II). The second stage was 43–139 times slower than the first. The samples spiked with Hg(II) showed low volatilization and a shifting of the signal of Hg(II) to lower temperatures. These results show that the extent, rate and type of redox process can be adverse in soils. Descoberto can serve as an example for areas contaminated with Hg(0).

1. Introduction

Hg contamination of soil and/or sediment occurs globally. The most toxic species are short-chain organomercury compounds, as they can cross cell membranes more easily. Hg is bioaccumulated and biomagnified, and it can be transported through the atmosphere over long distances. Therefore, the metal can be found in regions where no observed natural or anthropogenic sources exist (Andrade et al., 2012), and the metal cycle in the environment is a subject of study by many research groups.

Hg compounds are distributed in the environment as volatile species, for example, Hg(0) and dimethylmercury, reactive or soluble species in water, such as Hg(II), HgX_2, HgX_3^- and HgX_4^{2-} (where X=Br^-, Cl^- or OH^-), and less reactive species such as HgS and $Hg(CN)_2$ (Guedes, 2009). Compounds of organic and inorganic Hg are generated in various industrial activities, mainly the pharmaceutical, paper, electrochemical and pesticide industries and power plants (Mishra et al., 2005; Wang et al., 2012). In aqueous systems contaminated with Hg, a portion of the Hg may volatilize into the atmosphere. By way of rain, Hg may return to aqueous and terrestrial systems. Hg is easily transported in the atmosphere mainly in the form of Hg(0) and, to a lesser extent, as dimethylmercury. In the air or after deposition, Hg(0) can be converted into Hg(II) and organic forms and can bioaccumulate in various biotic and abiotic resources, such as fish, bryophytes, birds, soil, sediments and water (Palmieri et al., 2006). Physico-chemical soil parameters such as the pH, cation exchange capacity (CEC), particle size, organic matter content (OM) and types of clay minerals present play important roles in the variation of the oxidation state and the type of interaction with Hg soil components and, therefore, their mobility and availability (Rezende, 2009). The oxidation of metallic Hg, for example, can form soluble species (Hg (II)) and therefore make Hg more mobile in the environment because elemental Hg is barely soluble. In the case of the contamination of soil, sediment or other matrices, the choice of the

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type of intervention for decontamination also depends heavily on the species of the metal present (Raposo et al., 2003).

In addition to the well-known disaster in Minamata, Japan, in 1956, other cases of contamination have been reported, such as soil contamination in cinnabar extraction areas in Idrija, Slovenia (Biester et al., 2000; Gosar and Zibret, 2011; Gosar and Tersic, 2012; Tersic and Gosar, 2012; Tersic et al., 2011a, 2011b, 2014); San Joaquim, Mexico (Martinez-Trinidad et al., 2013); Almaden, Spain (Ruiz-Diez et al., 2012); Xunyang (Qiu et al., 2012) and Guizhou (Li et al., 2012), China; mining activities and/or gold mining for example, in the soils of Bolivia (Teran-Mita et al., 2013), Paracatu (Mulholland et al., 2012; Rezende et al., 2011), the Iron Quadrangle (Windmöller et al., 2007) and Descoberto (Durão Jr. et al., 2009) in Brazil, and industrial waste for example, the sludge from the petrochemical complex of Bandar Imam, Iran (Nik et al., 2013) and the industrial-waste landfills of Vale dos Sinos, Southern Brazil (Augustin and Viero, 2012).

In 2003, the presence of high concentrations of Hg in a small area located in the rural municipality of Descoberto in Minas Gerais/Brazil was discovered (CDTN/FEAM, 2005). The contaminated area consists of fairly steep terrain, and it is right next to the Rico stream. This stream is a tributary of the Ribeirão do Grama River that belongs to the Paraíba do Sul River basin. The Fundação Estadual do Meio Ambiente (FEAM) made a study of Hg concentrations in stream and rivers waters and mapped the area in terms of its metal concentration using a network and in-depth sampling (CDTN/FEAM, 2006). Several scientific studies have been conducted in the area to collect information about metal speciation (Durão Jr. et al., 2009; Varejão et al., 2009). The work of Durão Jr. et al. (2009) stated that “a large part of the metal, which had contaminated the environment as Hg(0), oxidized and is principally bound to Fe, Mn and Al oxyhydroxides” and up to 30% of it can be bound OM present in the soil. Fractionation studies in the same work showed that the Hg is only slightly available to the solubilization conditions that normally occur in the environment. The oxidation state of the metal is essentially important in his mobility and even the possibility of methylation reactions, which are key steps in the bioaccumulation and biomagnification of the metal process.

The objective of this work was to study the kinetics of oxidation, reduction and volatilization of Hg in the soils from the contaminated area of Descoberto (Minas Gerais/Brazil) by (1) spiking samples with various species of Hg and (2) monitoring the samples using thermo-desorption coupled atomic absorption spectrometry (TDAAS) and determining the total Hg (THg) using hydride-generation atomic absorption spectrometry (HGAAS).

2. Experimental

2.1. Study area, soil sampling and sample preparation

Fig. 1 shows the map of the studied area that was selected because of contamination by Hg. The darkest part of the plot indicates Hg concentrations higher than 2.5 mg kg^{-1} in samples collected at different depths (CDTN/FEAM, 2005, 2006). A rainwater containment barrier that drains the contaminated area was constructed, and boxes and sedimentation tanks of solid material were also installed, as shown in the figure.

The collection points selected were those likely to have low THg concentrations because the intention was to spike the samples with Hg. These collection points were surface samples (up to 30 cm) at D4, D6 and B7 shown in Fig. 1. Although the number of points was small, we can consider these to be representative of the area. The area is not large and is comprised of one type of soil with punctual variations in composition.

Using a manual, stainless-steel auger sampler, the soil samples (D4, D6 and B7) were collected, packed into polyethylene bags and refrigerated at 4 °C. In the laboratory, the soil samples were dried at room temperature and sieved to particle sizes < 2.0 mm. All analyses were conducted on this soil fraction.

2.2. Analytical procedures for determining the OM and Al, Fe and Mn content

The soil pH was measured using a glass electrode in suspensions of the soil samples in distilled water in the proportion of 1:2.5 (Embrapa, 1999).

The percentage (%) by weight of OM was determined by the Walkley–Black method according to Embrapa (1999). The method consists of the oxidation of an OM solution of potassium dichromate in the presence of sulfuric acid. The excess dichromate solution is then titrated with ferrous ammonium sulfate.

The contents of Al, Fe and Mn were determined by aqua-regia extraction (3:1; HCl:HNO_3). The mass of the samples was approximately 1 g, and the volume of aqua-regia used was 10 mL in a

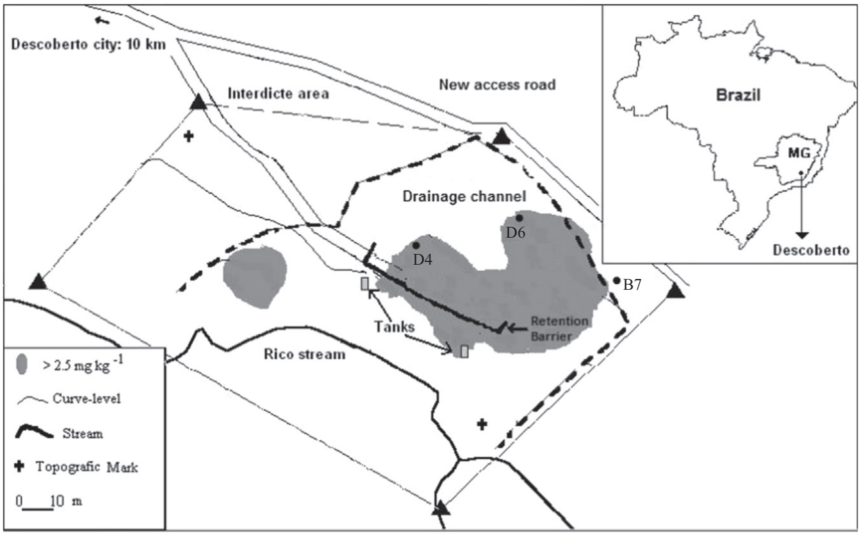

Fig. 1. Localization of the city of Descoberto, State of Minas Gerais, Brazil and a map of the contaminated area according to Hg contents displaying the sampling points (Durão Jr. et al., 2009).