



Accumulation and oxidation of elemental mercury in tropical soils



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HIGHLIGHTS

- Retention and oxidation of Hg⁰ in tropical soils depends on soil properties.
- Those processes vary greatly both quantitatively and qualitatively with soil type.
- Organic matter is the main soil characteristic in Hg adsorption and oxidation.
- pH and CEC also appear to be important soil characteristics in Hg adsorption.
- Hg⁰ oxidation occurred at the air/soil interface rather than only in the air.

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ABSTRACT

The role of chemical and mineralogical soil properties in the retention and oxidation of atmospheric mercury in tropical soils is discussed based on thermal desorption analysis. The retention of gaseous mercury by tropical soils varied greatly both quantitatively and qualitatively with soil type. The average natural mercury content of soils was $0.08 \pm 0.06 \mu\text{g g}^{-1}$ with a maximum of $0.215 \pm 0.009 \mu\text{g g}^{-1}$. After gaseous Hg⁰ incubation experiments, mercury content of investigated soils ranged from 0.6 ± 0.2 to $735 \pm 23 \mu\text{g g}^{-1}$, with a mean value of $44 \pm 146 \mu\text{g g}^{-1}$. Comparatively, A horizon of almost all soil types adsorbed more mercury than B horizon from the same soil, which demonstrates the key role of organic matter in mercury adsorption. In addition to organic matter, pH and CEC also appear to be important soil characteristics for the adsorption of mercury. All thermograms showed Hg²⁺ peaks, which were predominant in most of them, indicating that elemental mercury oxidized in tropical soils. After four months of incubation, the thermograms showed oxidation levels from 70% to 100%. As none of the samples presented only the Hg⁰ peak, and the soils retained varying amounts of mercury despite exposure under the same incubation conditions, it became clear that oxidation occurred on soil surface. Organic matter seemed to play a key role in mercury oxidation through complexation/stabilization of the oxidized forms. The lower percentages of available mercury (extracted with KNO₃) in A horizons when compared to B horizons support this idea.

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1. Introduction

Mercury and mercury-containing compounds are toxic to humans and the environment (Bernhoft, 2012). One significant aspect of the global biogeochemical cycling of mercury, which differs from those of other metals, is its volatility (Fergusson, 1990). Most mercury in the air is gaseous elemental mercury, which is deposited onto the ground and water in various ways and may be transformed into methylmercury through microbial action

(UNEP, 2008). Since gaseous elemental mercury has a long atmospheric lifetime (6–18 months) and can be transported around the globe, it is characterized as a global pollutant (UNEP, 2008). The behavior of the mercury remaining in soil is initially governed by physical and chemical processes that redistribute it within the soil and allow some of it to enter the soil solution (Renneberg and Dudas, 2001).

Abiotic oxidation of elemental mercury to Hg²⁺ occurs in the atmosphere, in water and in soil, but because so far research has focused on atmospheric transformations, little is known about the oxidation mechanisms of elemental mercury in water and soil (Barkay et al., 2003).

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Several studies have demonstrated that atmospheric deposition from nearby industries is the most likely source of mercury in soil (Wang et al., 2003; Hissler and Probst, 2006; Guédron et al., 2013; González-Fernández et al., 2014) and water (Hissler and Probst, 2006; González-Fernández et al., 2014). A comparison of vertical mercury profiles in soil from Grenoble, France, to those of other metals not emitted by the same plant suggested mercury enrichment in surface horizons due to atmospheric mercury input from the chlor-alkali plant (Guédron et al., 2013). A study conducted in Gijón, Spain (González-Fernández et al., 2014) showed that the recharge area of the springs exhibited mercury concentrations higher than the base level established for sandstone in the region and that the concentration of easily mobilized mercury was higher in the superficial soil horizon, suggesting mercury enrichment via atmospheric deposition. According to the authors, the source of mercury for atmospheric deposition on soil surface and its accumulation in soil was nearby industrial activity. The mining and roasting of Mercury-ore-containing rocks are also important sources of mercury release to the environment because of atmospheric mercury emissions (Li et al., 2009) and mercury leaching from contaminated soils to surface water and deeper into the soil (Tersic et al., 2014). Field investigation experiments showed a positive correlation between atmospheric mercury concentration and mercury content in a Cambisol (Wang et al., 2003). The same authors demonstrated in simulated experiments that a higher Hg^0 content in the air resulted in a higher mercury retention in a specific soil sample; however, they did not evaluate different soil classes.

In Brazil, gold mining is the major source of mercury in the atmosphere (UNEP, 2008). During the gold mining boom in the late 1980's, gold mining contributed about 110 t yr^{-1} mercury to the environment, with nearly 65% to the atmosphere. The most recent mercury release estimates show that gold mining has been greatly reduced due to the exhaustion of easy mining deposits, but that it still contributes about 31 t yr^{-1} of mercury, about 20 t yr^{-1} is released into the atmosphere (Lacerda et al., 1999).

According to the annual report by the Brazilian National Department of Mineral Production (DNPM), Brazil has gold reserves of 2592 tons, 582 tons (22% of total) of which are in Minas Gerais (DNPM, 2010). The scarce data available on atmospheric deposition due to mining are estimated for the Amazon region, where this activity is concentrated (Lacerda et al., 1999). Recent studies have also shown the importance of burning processes in the remobilization of mercury in the Amazonian ecosystem (Perez et al., 2014).

Most studies have been conducted on Northern hemisphere soils in addition to a few studies focused mostly on the Amazon region in the Southern hemisphere. Thermal desorption has been used to determine the total content of mercury in cinnabar since 1904. In this technique, solid samples are heated to high temperature and the vaporized mercury is swept by a gas flow to an atomic absorption spectrometer cell for quantification (Henry et al., 1972). Subsequently, Goleb also used this technique to differentiate mercury from natural and anthropogenic sources. They obtained mercury release profiles as a function of temperature for different rocks (Goleb, 1971).

Many other studies have shown the potential of this technique for the speciation and/or determination of different mercury interactions in contaminated area soils (Windmüller et al., 1996; Biester and Scholz, 1997; Biester et al., 2000; Biester et al., 2002; Valle et al., 2005).

Recently, in a study of fifteen commercial mercury compounds, researchers analyzed their use as fingerprints and showed that the identification of mercury species by thermal desorption is possible (Rumayor et al., 2013). Thermal desorption has also been used

even in the development of an innovative technology for the remediation of contaminated soils (Navarro et al., 2009).

Therefore, in order to evaluate mercury retention and oxidation in tropical soils, we analyzed several types of tropical soils exposed to an atmosphere saturated with gaseous mercury using thermal desorption coupled to atomic absorption spectrometry (TDAAS), a technique that allows the qualitative speciation of mercury (Valle et al., 2005).

Studies have demonstrated that soil characteristics affect the mercury exchange flux between the soil and the atmosphere (Hissler and Probst, 2006; Liu et al., 2014).

In this work, the role of chemical and mineralogical soil properties in the retention and oxidation of atmospheric mercury in tropical soils is discussed based on laboratory experiments and thermal desorption analysis.

Therefore, this study goes beyond the simulation of soil contamination by gaseous mercury to distinguish possible processes of gaseous mercury retention and oxidation in tropical soils and in two of their horizons (A and B) as well.

2. Material and methods

2.1. Sampling area and geological setting

One of the study areas is located in Southeast Brazil and covers most of Minas Gerais state and the other, Itaperuna town, is in Rio de Janeiro state. The soil sampling points, sample horizon and identification, geographical location, soil classification and chemical and textural characteristics are given in Table 1.

Minas Gerais is a large state, with an area of $586,522.122 \text{ km}^2$, comparable to the size of Ukraine. It has a great geological variability, with two outstanding regions: Triângulo Mineiro, a region of volcanism, with mafic rocks, and the Quadrilátero Ferrífero, with geochemical anomalies and mineral deposits (Mello and Abrahão, 2013). Most samples were collected in and around the Quadrilátero Ferrífero. Quadrilátero Ferrífero is the greatest Brazilian iron mining region. It also presents deposits of manganese, gold, bauxite and gems like topaz and emerald (Roeser and Roeser, 2010). Two of the most important hydrographic basins are located in Minas Gerais state, the Doce River basin and the Velhas River basin.

2.2. Soil sampling

Samples of typical tropical soils (ultisol, oxisols, inceptisols, alfisols and entisol) were collected at three points at two depths (horizons A and B) from areas not affected either by agricultural or industrial activities. The samples were disaggregated, sieved with a 2-mm sieve and air dried (air-dried fine earth). These samples were submitted to textural analysis. For chemical analysis, the samples were also ground and sieved with a mesh 80 (0.177 mm) sieve.

2.3. Characterization

The following soil parameters were determined: pH, cation exchange capacity (CEC) and carbon, clay, silt, sand and iron and aluminum oxide contents were determined. pH, CEC and granulometry values were determined following EMBRAPA (1997). Crystalline iron oxides were extracted using a dithionite-citrate-bicarbonate (DCB) and amorphous iron oxides were extracted using ammonium oxalate, following Mehra and Jackson (1960) and McKeague (1966), respectively. Iron and aluminum analysis was performed in a Perkin Elmer atomic absorption spectrometer,

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