Geoderma 213 (2014) 255–260

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Extraction of mercury water-soluble fraction from soils: An optimization study

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ARTICLE INFO

Article history:
Received 28 December 2012
Received in revised form 26 July 2013
Accepted 12 August 2013
Available online 12 September 2013

Keywords:
Water-soluble fraction
Soil
Mercury
Extraction

ABSTRACT

The procedure for extraction of water-soluble mercury species from soil was studied and optimized. Aspects studied included the soil:water ratio, time of extraction, separation technique (centrifugation vs. filtration) and analytical technique used to analyze the extract (pyrolysis-atomic absorption spectrometry vs. atomic fluorescence spectrometry). Results indicated that the process of extraction is not influenced by the soil:water ratio in the range studied (1.5:100 to 20:100). The kinetic study performed showed that it takes 24 h for extraction to reach equilibrium, and that the mercury removal reaction takes place in two stages, a faster one ($0 < t < 6$ h), followed by a slower stage ($t > 6$ h). Hence, a two first-order reaction model was tested and proved to fit the experimental data. The particle size distribution seemed to have an influence on this process. Results also showed that filtration is preferable to centrifugation, as it avoids the presence of colloidal material in the leachate. Concerning the analytical technique used for quantification, atomic fluorescence spectrometry offers a lower limit of quantification; therefore it is more appropriate due to the low mercury concentrations often found in this fraction.

The conclusions of this study contribute to the refinement of an important step of sequential extraction procedures and soil toxicity assessment methods, and, ultimately, constitute a helpful tool for the prediction of long-term risks to the environment.

1. Introduction

Soil is recognized as one of the environment's most important but also most vulnerable resources (Blum, 2005). There is growing awareness that soil contamination represents an important issue with significant impact on the environment. Soil mercury contamination, in particular, is a problem found at many active and inactive industrial and mining sites (Biester and Scholz, 1997; Fernández-Martínez et al., 2005; Inácio et al., 1998). Concentrations of a few to several thousand mg of mercury per kg of soil have been found in the vicinity of industrial facilities where mercury and its compounds are or were used (Biester and Scholz, 1997; Reis et al., 2009). In soils, mercury can undergo a wide array of chemical and biological transformations, such as Hg^0 oxidation and Hg^{2+} reduction or methylation (Weber, 1993), that can increase its mobility and bioavailability to organisms. If high contents of organic matter are present in the soil, the formation of organic Hg^{2+} complexes will be the dominant process (Gabriel and Williamson, 2004; Schuster, 1991). If, in contrast, organic matter content is low, mercury will be present in ionic and more reactive species that, in turn, can be transformed into more toxic, bioavailable forms, such as methylated mercury species or Hg^0. Nevertheless, organic Hg^{2+} complexes and even HgS also can be methylated, although to a lesser degree and depending on the methylation potential of the matrix (Bloom et al., 2003).

Ions present in soil solution, such as chloride and hydroxide, have the ability to increase mercury's solubility and mobility (Schuster, 1991; Skyllberg et al., 2006).

Therefore, meaningful risk assessment of contaminated soils strongly depends on understanding and predicting the fate of contaminants in the soil and the availability of these chemicals, as the consequences of soil contamination can be observed not only in terrestrial communities, but also in aquatic ecosystems owing to drainage and run-off processes of toxic substances present in soils (Dolores Fernández et al., 2006; Rolston et al., 2003). The transport of contaminants through soil depends on physical–chemical characteristics both of the contaminants and of the site, such as soil type, soil heterogeneity, geochemical environment, and moisture content (Charbeneau et al., 2003).

Measurement of the water-soluble fraction of mercury in soil is a particularly important tool for the assessment of the potential risk of groundwater contamination and the potential biological uptake and toxicity for aquatic organisms when leaching, runoff, and erosion occur in polluted soils (Wahle and Kördel, 1997). In the literature there are several procedures reported for the extraction of mercury's water-soluble fraction, usually constituting the first step of a sequential extraction procedure. These procedures differ in soil:water ratio and/or

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http://dx.doi.org/10.1016/j.geoderma.2013.08.010

Table 1
Soil:water ratio, time of extraction and percentage of Hg extracted in different extraction procedures for the water-soluble fraction found in literature. Procedures considered in this study (P1, P2, P3 and P4) are shown in bold.

Author(s)	Soil (g):water (mL) ratio	Time of extraction	Hg extracted (%)
(P1) Panyametheekul (2004)	**3:100**	**60 min**	**0%**
(P2) Renneberg and Dudas (2001)	**1.5:100**	**30 min**	**<10%**
(P3) Biester and Scholz (1997)	**20:100**	**60 min**	**Chlor-alkali plant soil — 0.15%** **Mine soil (Idrija, Slovenia) — 0.12%**
(P4) Bloom et al. (2003)	**1:100**	**18 ± 4 h**	**0.4–1.3%**
Bloom and Katon (2000)	1:100	18 ± 3 h	Gold mine tailings — 1.3% HgS mine soil — 0.01% Chlor-alkali plant soil — 0.18%
Neculita et al. (2005)	10:100	2 h	<1.1%
Boszke et al. (2006)	17:100	3 h	1.0%

time of extraction. Table 1 shows some examples of different water-soluble fraction extraction procedures used by different authors. Considering the environmental significance of this fraction, it is important that extractions are optimized to provide the most accurate estimation of the water-soluble Hg fraction and, hence, the most appropriate interpretation of the behavior of water-soluble Hg species in soil. The optimization of the extraction procedure for estimation of water-soluble mercury species in soil may aid in providing an indication of the maximum potential metal extractability in water drainage and runoff, a helpful tool for the prediction of long-term risks to the environment. Therefore, in this work, experiments were conducted to establish optimal procedural conditions for extraction of the water-soluble fraction of mercury in soils. Parameters such as the soil:water ratio and the time of extraction were studied. The kinetic aspect is crucial to correctly predict the behavior of the metal in soil, and although the study of the kinetic behavior has been evaluated for other elements (Fangueiro et al., 2002, 2005; Manouchehri et al., 2006), it was only applied to mercury by Issaro et al. (2010), using sodium-thiosulfate as extractant. The influence of the separation technique (filtration vs. centrifugation) and the quantification methodology chosen to perform analysis (atomic fluorescence spectroscopy vs. direct mercury analyzer) were also considered. This way, this study intends to contribute to the refinement of a crucial step of mercury sequential extraction procedures and soil toxicity assessment methods and, ultimately, improve the characterization of risk for terrestrial and aquatic systems, providing useful information to decision makers in terms of focusing site cleanup and remedial efforts.

2. Materials and methods

2.1. Sampling sites and methodology

Three soil samples (Industrial 1, Industrial2, and Industrial 3) were collected from fields within a radius of <1 km from an industrial complex located in Estarreja, northern Portugal, close to a former effluent stream. For many years this complex was home to a large chlor-alkali plant which formerly produced chlorine and caustic soda by the mercury cell process, where liquid elemental mercury was utilized as a cathode in the electrolysis of a saturated brine solution (Ullrich et al., 2007). As other studies show (Lacerda and Salomons, 1998; Ullrich et al., 2007) mercury-cell chlor-alkali plants have been identified as major sources of mercury to the environment. Even though the plant completely ceased the use of mercury in 2002 (Ospar Commission, 2006), mercury that was emitted from the plant still remains significant in the surrounding environment nowadays (Reis et al., 2009), which can constitute a problem, considering that these fields are used mainly for agricultural and cattle grazing purposes.

Samples Mine 4, Mine 5, and Mine 6 were collected in the surroundings of the Caveira mine, Portugal. More specifically, Mine 4 was collected from a tailing deposit, while samples Mine 5 and Mine 6 were collected at an agricultural field located approximately 1.7 km from the mine pit. The Caveira sulfide mine is located in Grândola, in the North-West region of the Iberian Pyrite Belt (IPB). The IPB is a well-known mining district of worldwide significance, due to its unusual concentration of large and medium sized mineral deposits, including ores of copper, iron, lead, sulfur and zinc. Antimony, arsenic, cadmium, cobalt, gold, mercury, selenium and silver can also be found in soils from the IPB (Barriga, 1990). Large volumes of waste were produced by the mining activities and various types of tailings deposited in the area (the amount of waste stored on the site is estimated to be larger than 2 Mt) (Cardoso Fonseca and Ferreira da Silva, 2000). Rainwater circulates and percolates easily over and through these tailing materials causing significant erosion and transport of tailings debris to areas nearby and downstream.

A seventh sample collected at a non-contaminated area (Gandra 7) was used as reference site.

Sampling was performed using a plastic spatula and samples were placed in plastic bags during transport to the laboratory, where they were pre-treated within 1 h. The soil sampling depth was 0–15 cm. Once in the laboratory, soil samples were air dried at room temperature to constant weight. Stones were removed and soil clumps were crushed and homogenized during the drying stage. The dried samples were sieved to <2 mm using a nylon sieve. The air-dry soil, <2 mm fraction, was used for the extraction procedures.

2.2. Soil sample characterization

The soil pH ($CaCl_2$) was determined using a WTW pH meter-538, according to the ISO 10390:1994 method. Total carbon (TotC) was measured on an elemental analysis instrument (LECO CNH-2000), according to ISO 10694:1995. For the determination of organic carbon content (OrgC), an excess of 4 mol L^{-1} of hydrochloric acid was added to a crucible containing a weighed quantity of soil. The crucibles were left to stand for 4 h and then were digested for 16 h at 60–70 °C to remove the organic carbon. The residue was then analyzed to give the inorganic carbon content, and organic carbon was calculated by difference.

The particle size distribution and clay contents of the soil samples were determined using a Coulter LS230 laser diffraction particle size analyzer. The classification of soils followed the USDA Texture Classes: sand fraction ($0.050 < \% < 2$ mm), silt fraction ($0.002 < \% < 0.050$ mm), and clay fraction ($\% < 0.002$ mm). Classification of samples was achieved by using the *Talwin 42®* classification software program.

2.3. Extraction of water-soluble fraction from soils

Four water-soluble fraction extraction procedures were considered in this work: those of Panyametheekul (2004) (procedure 1 — P1); (Renneberg and Dudas, 2001) (procedure 2 — P2); (Biester and Scholz, 1997) (procedure 3 — P3); and (Bloom et al., 2003) (procedure 4 — P4). The operational conditions associated with each extraction procedure are presented in Table 1, in bold. These procedures were chosen based on their differences in soil:water ratio and time of extraction. Procedures P1 and P3 have the same time of extraction, albeit very different soil:water ratio, therefore allowing studying the effect of time of extraction. Procedure P4 has a longer extraction time. Soil samples (weight indicated in Table 1) were shaken with 100 mL of distilled water in an end-over-end shaker. After shaking, the samples were centrifuged (3000 rpm) and the supernatant was acidified with concentrated HNO_3 and stored at 4 °C until analysis. In all extractions distilled water (conductivity = 2 μS cm^{-1}) was used. Extractions were performed in triplicate for each sample.