Environmental Pollution 228 (2017) 425–432

Contents lists available at ScienceDirect

Environmental Pollution

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

# Effect of soil organic matter on antimony bioavailability after the remediation process[☆]

Yasuo Mitsui Nakamaru [a, *], Francisco José Martín Peinado [b]

[a] Laboratory of Integrated Crop Management Science, Faculty of Bioindustry, Tokyo University of Agriculture, 196 Yasaka, Abashiri, Hokkaido 099-2493, Japan

[b] Departamento de Edafologia y Quimica Agricola, Facultad de Ciencias, Universidad de Granada, Campus Fuentenueva s/n, 18002 Granada, Spain

ARTICLE INFO

*Article history:*
Received 24 February 2017
Received in revised form
11 May 2017
Accepted 17 May 2017
Available online 27 May 2017

*Keywords:*
Antimony
Soil organic matter
Remediation
Aznalcóllar
Bioavailability

## ABSTRACT

We evaluated the long-term (18 year) and short-term (4 weeks) changes of Sb in contaminated soil with SOM increase under remediation process. In the Aznalcollar mine accident (1998) contaminated area, the remediation measurement implemented the Guadiamar Green Corridor, where residual pollution is still detected. Soils of the re-vegetated area (O2) with high pH and high SOM content, moderately re-vegetated area (O1) and unvegetated area (C) were sampled. Soil pH, CEC, SOM amount and soil Sb forms were evaluated. Soil Sb was measured as total, soluble, exchangeable, EDTA extractable, acid oxalate extractable, and pyro-phosphate extractable fractions. Further, the short-term effect of artificial organic matter addition was also evaluated with incubation study by adding compost to the sampled soil from C, O1 and O2 areas. After 4 weeks of incubation, soil chemical properties and Sb forms were evaluated. In re-vegetated area (O2), soil total Sb was two times lower than in unvegetated area (C); however, soluble, exchangeable, and EDTA extractable Sb were 2–8 times higher. The mobile/bioavailable Sb increase was also observed after 4 weeks of incubation with the addition of compost. Soluble, exchangeable, and EDTA extractable Sb was increased 2–4 times by compost addition. By the linear regression analysis, the significantly related factors for soluble, exchangeable, and EDTA extractable Sb values were pH, CEC, and SOM, respectively. Soluble Sb increase was mainly related to pH rise. Exchangeable Sb should be bound by SOM-metal complex and increased with CEC. EDTA extractable fraction should be increased with increase of SOM as SOM-Fe associated Sb complex. From these results, it was shown that increase of SOM under natural conditions or application of organic amendment under remediation process should increase availability of Sb to plants.

## 1. Introduction

Antimony (Sb) is a toxic metalloid and often emitted from metal ore mining and smelting sites (Crecelius et al., 1974; Ragaini et al., 1977), the US Environmental Protection Agency (US EPA, 2014) has long listed it as priority pollutant. In this study, we focused on the effect of soil organic matter (SOM) and related soil chemical properties on Sb behaviour in the heavy metal contaminated soil of Aznalcollar, Spain. In 1998, acidic waters and toxic tailings from a breach in the dam of the holding pond of tailings of Aznalcollar pyrite mine, caused severe contamination of heavy metals into the Agrio and Guadiamar river basins, affecting some 43 km$^2$ (Grimalt et al., 1999). Soils were highly polluted with high concentrations of zinc (Zn), copper (Cu), cadmium (Cd), arsenic (As), lead (Pb), thallium (Tl) and antimony (Sb) (Simón et al., 2001). A few years later a very important soil remediation program was applied to restore the affected area, concluding with the establishment of the Guadiamar Green Corridor (GGC) (CMA, 2003).

Fifteen years after the accident, the main soil properties (pH, SOM, CEC) and most of the soil-vegetation system of the contaminated area successfully recovered except highly contaminated and heterogeneously dispersed sites representing 7% of total affected area (Romero-Freire et al., 2015). In the contaminated land, the mean values of total and soluble concentration of Cu, Zn, As, and Pb decreased with time, however, soluble As increase with time was also observed (Martin Peinado et al., 2015). The rise in pH values could be attributed to ageing and higher crystallinity of iron oxy-

---

[☆] This paper has been recommended for acceptance by Prof. W. Wen-Xiong.

[*] Corresponding author.

*E-mail addresses:* y3nakama@bioindustry.nodai.ac.jp (Y.M. Nakamaru), fjmartin@ugr.es (F.J. Martín Peinado).

http://dx.doi.org/10.1016/j.envpol.2017.05.042

hydroxides that led to the partial desorption of the As immobilized by these iron compounds as reported by Pedersen et al. (2006). Among contaminants, Sb also can be solubilised due to rise of pH (Nakamaru et al., 2006). In soil, it was known that only few percent of Sb is usually in a mobile form (Wilson et al., 2010; Nakamaru et al., 2014), most Sb is the immobile fraction sorbed by amorphous Fe, Al oxy-hydroxides, Mn oxides (Crecelius et al., 1975; Thanabalasingam and Pickering, 1990; Meima and Comans, 1998; Takahashi et al., 2010) and SOM (Pilarski et al., 1995; Steely et al., 2007). However, the change of the “small mobile, labile or available Sb fraction” and “large oxy-hydroxides bound or SOM bound Sb fraction” in relation to plant or human activity was not clarified.

The effect of SOM on soil Sb mobility is controversial. SOM should decrease Sb availability to plants by making stable complexes of Sb-humic acid (Steely et al., 2007). Ahmad et al. (2014) tested the effect of organic amendments on Sb and Pb contaminated soil, indicating that biochar addition decreased Sb availability to plant. On the other hand, Clemente et al. (2010) reported that application of compost to heavy metal contaminated soil increased As and Sb in soil pore water, and As plant uptake was boosted while Sb uptake was not increased. Iron-rich amendments can also immobilize Sb under field conditions (Okkenhaug et al., 2016), although a rise in soil pH can decrease the positive surface charge of iron oxides reducing the sorption capacity of Sb in soil (Johnson et al., 2005). The recovery of the area affected by the Aznalcóllar spill involved different types of amendments (organic and inorganic), creating an ideal situation for studying the behaviour of Sb under natural conditions over time.

In the present study, long-term (18 year) and short-term (4 week) changes of contaminated soil with SOM addition (vermicompost) were evaluated. The studied soils were collected from the Guadiamar Green Corridor in sectors where the effects of residual pollution were evidenced by the presence of irregular patches without vegetation dispersed within re-vegetated areas. Soil chemical properties and soil Sb concentrations for the major Sb fractions were evaluated after 18 years of evolution. Further, the short-term effect of artificial organic matter addition was also evaluated in a soil incubation study. The aim of this work is to study the Sb mobility and bioavailability in remediated soils of the Guadiamar Green Corridor, to assess the effect of soil properties over time and to evaluate the influence of SOM on Sb behaviour under re-vegetation process.

## 2. Materials and methods

### 2.1. Soil samples

Soil samples were collected in the area affected by the Aznalcóllar mine spill, today transformed into the Guadiamar Green Corridor, in a sector close to the holding pond of tailings (Fig. 1). Between 1998 and 2001, soils were recovered by the removal of tailings and intensively amended with inorganic (mainly calcium carbonate-rich materials) and organic (manure). Anyway, fine particles of tailings remained intimately mixed within the soil matrix, producing residual contamination over time (Martin Peinado et al., 2015). This contamination was evidenced by the presence of soil patches (few square meters) without vegetation heterogeneously dispersed among re-vegetated areas. Soils were sampled from the center of the unvegetated patches (C area), from the moderately re-vegetated stripes surrounding the patches without vegetation (O1 area) and from densely re-vegetated area (O2 area) surrounding O1 areas. This sampling design was repeated in four different plots from the same sector (Fig. 1).

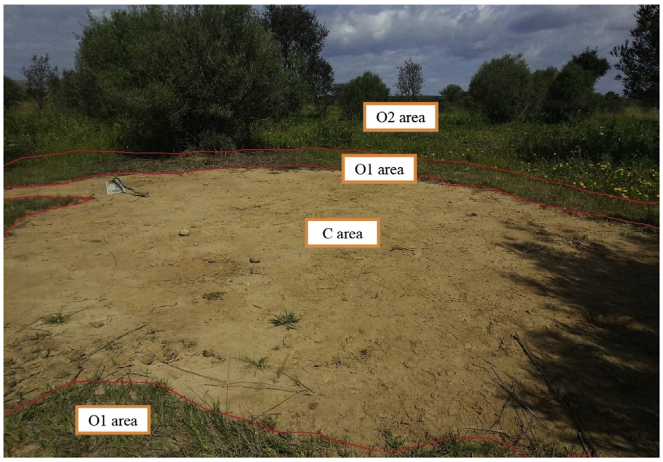

**Fig. 1.** Example of soil sampling site in this study. Soils were sampled from the center of the unvegetated patches (C area), from the moderately re-vegetated strips surrounding the patches without vegetation (O1 area) and from densely re-vegetated area (O2 area) surrounding O1 areas.

For the short-term study, sampled soils from C, O1 and O2 of the different plots, were amended in laboratory with different amount of compost made from horse manure and produced by *Eisenia andrei* (vermicompost). Soil chemical properties and Sb fractions in treated soils were evaluated after 4 weeks of incubation.

### 2.2. Incubation study

Soil samples from C, O1, and O2 areas with different levels of re-vegetation were treated with compost in different application rates. Chemical characteristics of compost used for this study was shown in Table 1. Four treatments (T0-T3) were conducted with 0 g (T0), 1.67 g (T1), 3.33 g (T2), 6.67 g (T3) of compost added to 100 g of air-dried soils (corresponding to 0, 25, 50, and 100 Mg ha$^{-1}$, respectively, assuming a soil bulk density of 1.5 g cm$^{-1}$ and a soil depth of 10 cm). The organic amendment and range in application rates were based on previous treatments in the area (Martin Peinado et al., 2015bib_citation_to_be_resolved) and designed to determine practical application of this treatment for the recovery of the residual contaminated areas. The compost selected was applied to improve the properties of acidic contaminated soil encouraging soil quality by the increase in SOM, CEC, macronutrients and pH and to promote the re-vegetation in the area. Soils amended with composts were thoroughly mixed, incubated for 4 weeks at room temperature (25 °C, 12 h of light per day), maintaining soil water content to 60% of water holding capacity (297 g $H_2O$ kg$^{-1}$ dry soil) and monitored weekly to maintain moisture content. After the incubation period, soil was dried and used for following analysis.

### 2.3. Soil analysis

#### 2.3.1. Soil chemical properties

For all soil samples, pH ($H_2O$), electrical conductivity (EC), cation exchange capacity (CEC), $CaCO_3$ content, total and organic carbon (T-C, O-C, respectively) and total nitrogen (T-N) contents were measured as soil general properties following standard methods (MAPA, 1994). Total concentration of Sb was analyzed in the laboratory, after fine grinding and acid digestion ($HNO_3 + HF + HCl$), by