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ScienceDirect
Geoderma 136 (2006) 75–86
GEODERMA
www.elsevier.com/locate/geoderma

Amount of amorphous materials in relationship to arsenic, antimony, and bismuth concentrations in a brown forest soil

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Received 7 March 2005; received in revised form 12 January 2006; accepted 22 February 2006
Available online 19 April 2006

Abstract

The objective of this study was to examine the relationship between the amounts and chemical compositions of total amorphous materials and elements in the soil. Total amorphous materials in a brown forest soil were quantified by an X-ray powder diffraction method, chemical compositions of total amorphous materials were determined by a balance sheet method, and arsenic (As), antimony (Sb), and bismuth (Bi) concentrations in the soil were analyzed. The soil samples were collected in 10-cm increments from the surface to 100 cm depth in central Ibaraki Prefecture, Japan. After separating each sample into fractions by grain size, the amorphous ratio of each fraction was determined. Total amorphous materials decreased from 360 g kg^{-1} at 0–10 cm depth to 210 g kg^{-1} at 90–100 cm. The chemical compositions of the total amorphous materials were different in different size fractions of soil. Finer fractions had much Fe_2O_3, and coarser fractions much SiO_2. As, Sb, and Bi concentrations were generally higher in the finer fractions but decreased with depth. As, Sb, and Bi were positively correlated with the Fe_2O_3 component in total amorphous materials. These findings can be explained by the affinity of each element to solid phases.

Keywords: Soil; Amorphous materials; Arsenic; Antimony; Bismuth

1. Introduction

Solid organic and mineral phases in soils and sediments have various surface chemical properties (Sposito, 1984; Davis and Kent, 1990). Inorganic materials in soils and sediments are found in both crystalline and amorphous phases. The amorphous minerals are environmentally important (Cornell and Schwertmann, 2003; Sherman and Randall, 2003), because they are ubiquitous in soils (e.g., Jones et al., 2000; Ryan et al., 2002), thermodynamically unstable, and have large reaction surfaces, which increase their adsorption capacity for various elements.

As an amorphous material, hydrous ferric oxides are known to be the most important adsorbents of trace elements (e.g., Sposito, 1984; Davis and Kent, 1990; Dzombak and Morel, 1990; Stumm, 1992; Smedley and Kinniburgh, 2002; Sherman and Randall, 2003). A positive relation between the amounts of iron and trace elements is observed in both contaminated and uncontaminated areas; for example, Terashima et al. (2001a,b) found that concentrations of trace elements were positively related to the amount of Fe_2O_3 in uncontaminated soils in their investigation of the background levels of trace element concentrations in soils. However, they did not determine the identity of the Fe_2O_3 component, which was probably hydrous ferric oxide because hydrous ferric oxide is one of the most important

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doi:10.1016/j.geoderma.2006.02.002

sorbing minerals at low temperature under oxidizing conditions. In addition, the question remains as to what components in amorphous materials affect trace element concentrations and what amounts of amorphous materials affect trace element concentrations.

The main objective of the present study was to examine the relations between the amounts and chemical compositions of amorphous materials and trace elements in soil. Thus, we quantified the total amorphous materials in soil samples by an X-ray powder diffraction method (Alexander and Klug, 1948; Chung, 1974; Popović and Gržeta-Plenković, 1979; Hiller, 2003), determined the chemical compositions of total amorphous materials by a balance sheet method (Jones et al., 2000), and determined trace element concentrations. The soil sample was a brown forest soil from an uncontaminated area in Japan. This study focused on three trace elements: arsenic (As), antimony (Sb), and bismuth (Bi).

Arsenic concentrations in soils are on the order of 5–10 mg kg^{-1} (for review, see Smedley and Kinniburgh, 2002). Higher concentrations are related to industrial sources such as smelting and fossil-fuel combustion products (Li and Thornton, 1993) and to agricultural sources such as pesticides and phosphate fertilizers (Ure and Berrow, 1982). Arsenic mobility in soils depends on processes that affect iron redox chemistry. Ferrous ions dissolved from minerals are oxidized forms of hydrous ferric oxide, and hydrous ferric oxide binds As. On the other hand, reductive dissolution of hydrous ferric oxide releases adsorbed or combined As.

Antimony concentrations in sediments and soils are on the order of 0.2–10 mg kg^{-1} (for review, see Filella et al., 2002). Higher concentrations are directly related to anthropogenic sources, mainly proximity to smelting plants (Crecelius et al., 1974; Ragaini et al., 1977; Ainsworth et al., 1990; Asami et al., 1992; Li and Thornton, 1993). However, not much is known about Sb mobility in soils. Antimony appears to accumulate near the soil surface and decrease in concentration with depth (Ragaini et al., 1977; Ainsworth et al., 1990). This pattern indicates that Sb is rather unreactive in soils.

Bowen (1979) showed that Bi concentrations in soils are on the order of 0.1–13 mg kg^{-1}, whereas Asami et al. (1988) reported concentrations in soils on the order of 0.12–0.91 mg kg^{-1}. Higher concentrations are related to anthropogenic sources such as smelting plants (Asami and Kubota, 1993; Li and Thornton, 1993). Bismuth mobility may be related to iron chemistry, since Reimann et al. (2001) and Sterckeman et al. (2004) indicated that Bi concentrations were positively correlated with Fe concentrations in soils.

2. Materials and methods

2.1. Natural soil samples

Samples were obtained from a brown forest soil from the Kasama area of central Ibaraki Prefecture, which is 100 km northeast of Tokyo, Japan. The soil at this site is a typical temperate forest soil above granitic rocks and classified as Regosols according to FAO (1998). The top layer of fallen leaves (about 1 cm) is an O horizon. The second layer (from the soil surface to 10 cm depth) is an A horizon. The third layer (10–70 cm) is a B horizon. The fourth layer (70–100 cm) is a C horizon.

The soil samples were collected in 10-cm increments from the surface to 100 cm depth. The moisture soil samples were first oven-dried at 303 K until constant weight was reached. The relative amounts of organic and inorganic materials in each sample were determined as follows. After removing the organic matter in 6% hydrogen peroxide solution with heating (~333 K) for 1 week, the sample was dried at 303 K, and the amount of inorganic material was determined as the mass of dry sample remaining. The amount of organic matter was obtained from the difference of sample weight before and after removing.

The samples from which moisture and organic matter had been removed were separated into >2000, 2000–1001, 1000–251, 250–64, 63–17, 16–4, and <4 μm fractions by a combination of dry sieving (>16 μm) and gravity settling (<16 μm) according to Stokes' law; deionized water was used throughout. The weight of each fraction was determined after drying in an incubator at 303 K. Except for the 63–17, 16–4, and <4 μm fractions (in which the grains were too fine), each fraction was subdivided into several mineral groups. The >2000 and 2000–1001 μm fractions were subdivided into quartz fractions and orthoclase fractions by hand picking. The 1000–251 and 250–64 μm fractions were subdivided into quartz fractions, orthoclase and plagioclase fractions, weathered biotite fractions, magnetite fractions, and pyroxene and hornblende fractions with an isodynamic separator and by hand picking. After subdivision, the weight of each subfraction was determined.

2.2. Standard samples

The internal standard used for quantitative X-ray analysis of minerals was MgO powder (Kanto Chemical Co., Tokyo, Japan). MgO powder has a small number of reflections that do not overlap any large reflections of major rock-forming minerals. Although MgO powder may contain amorphous materials, the quantitative