



# The associations of heavy metals with crystalline iron oxides in the polluted soils around the mining areas in Guangdong Province, China



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## H I G H L I G H T S

- Soil Cd, Cu, Pb and Zn fractions were analyzed using a modified SSE method.
- Soil Fe oxides are mainly Al-substituted goethites and hematites.
- Crystalline Fe oxides have affinity for metals in the order Cd > Pb > Zn > Cu.
- Metals associated with crystalline Fe oxides have potential environmental risks.
- The modified SSE can be used for weathered soils enrich in crystalline Fe oxides.

## A R T I C L E I N F O

### Article history:

Received 16 April 2016

Received in revised form

27 June 2016

Accepted 6 July 2016

Available online 17 July 2016

Handling Editor: X. Cao

### Keywords:

Soil pollution

Iron oxyhydroxides

Selective sequential extraction procedures

Metal fraction

Mobility

## A B S T R A C T

In current selective sequential extraction (SSE) methods, heavy metals associated well-crystallized iron oxyhydroxides are not well defined and considered, and usually fall into residual forms, which actually make their mobility and environmental risk underestimated. This study compared various fractions of heavy metals in samples of mining tailings and nearby soils under different land uses in Guangdong Province of China. Iron oxides in these soils were mainly Al-substituted goethites and/or hematites. Independent of the land uses, the percentages of various Cd fractions in the soils decrease in the order of well-crystallized iron oxyhydroxides-associated (27.2–91.2%) > residual (2.1–37.0%) > reducible Fe–Mn oxides (3.2–45.7%) > exchangeable (1.0–28.2%) > organic-associated form (0–5.1%). Pb mainly exists in the residual fraction (25.9–74.5%), followed by crystalline iron oxyhydroxides-associated (0.4–69.0%) and reducible fractions (2.4–40.4%). Zn mainly exists in the residual fraction (25.4–85.9%), followed by the well-crystallized iron oxyhydroxides-associated fraction (6.4–55.0%). However, Cu mainly exists in the residual form and the fractionation of Cu varies obviously between samples. The association of these metals with crystalline iron oxyhydroxides in the soils decreases in the sequence of Cd > Pb > Zn > Cu. These results suggest that in heavy-metal-polluted weathered soils in tropical and subtropical areas enriched with iron oxides, it is essential to assess potential bioavailability and toxicity of heavy metals bound to well-crystallized iron oxyhydroxides with appropriate procedures in the fractionation measurement. The modified Tessier method present here can be used to quantify the fractions of heavy metals in such areas.

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## 1. Introduction

Anthropogenic activities such as mining, smelting of metal ores and agricultural practices have promoted the accumulation of heavy metals in soils. These pollutants will undergo a series of

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physical, chemical and biological reactions with soil active components, including adsorption, complexation, precipitation and substitution. Thus the mobility and toxicity of heavy metals in soils depend not only on their total concentration, but also strongly on their specific chemical forms, metal types, environmental factors and soil properties like pH, organic matter content and type and redox conditions (Gleyzes et al., 2002; Nyamangara, 1998). Analysis of the fractionation of heavy metals is fundamental for evaluating their toxicity in ecosystems and understanding their geochemical behaviors (Adriano, 2001; Keller and Hammer, 2004; Kot and Namiesnik, 2000; Lamy et al., 1993; Rodríguez et al., 2009).

In order to assess mobility of heavy metals in soils, sediments and waste materials and hence to estimate the actual environmental impact, selective sequential extraction (SSE) procedures have been widely used to fractionate heavy metals; these procedures are based on the rational use of a series of selective reagents to successively dissolve the different mineralogical fractions (Dang et al., 2002; Gleyzes et al., 2002; Guevara-Riba et al., 2004; Hass and Fine, 2010; Rauret, 1998; Zimmerman and Weindorf, 2010).

Commonly used SSE procedures include the Tessier method and its modifications (Ferreira et al., 2007; Huynh et al., 2003; Peltier et al., 2005; Salomons and Forstner, 1984; Tessier et al., 1979; van Hullebusch et al., 2005) and the BCR method (Basta et al., 2005; Cuong and Obbard, 2006; Kartal et al., 2006; Petit and Rucandio, 1999; Quevauviller, 1998; Quevauviller et al., 1994; Rauret et al., 1999; Ure et al., 1993; van Hullebusch et al., 2005). In these methods, heavy metals associated with Mn and Fe oxyhydroxides are usually specifically and selectively extracted using  $\text{NH}_2\text{OH}\text{--HCl}$  solutions based on the assumption of reductive dissolution of these minerals. Iron and Mn oxyhydroxides in soils include Mn oxyhydroxides, amorphous Fe oxyhydroxides and well-crystallized Fe oxyhydroxides. Mn oxides can be readily mobilized by changes in environmental conditions, such as soil flooding (Patrick and Jugsujinda, 1992), soil drying (Makino et al., 2000) and soil sterilization (Suda et al., 2009), whereas well-crystallized Fe oxides have to be reduced under strong reducing conditions (Patrick and Jugsujinda, 1992). The  $\text{NH}_2\text{OH}\text{--HCl}$  solution was found to have low dissolution efficiency for well-crystallized Fe oxides (Fortin et al., 1993; La Force and Fendorf, 2000). Furthermore, natural Fe oxides (i.e. goethite and hematite) in the weathered soils of tropical and subtropical areas usually contain a certain amount of  $\text{Al}^{3+}$  and other cations (Cornell and Schwertmann, 2003). The substitution of these cations also affects the dissolution of these Fe oxides under reducible reagents (Silveira et al., 2006). Thus many modifications have been attempted to overcome the low dissolution efficiency of  $\text{NH}_2\text{OH}\text{--HCl}$  solutions for the extraction of Fe and Mn oxide-associated metals, such as the increase of the concentration of  $\text{NH}_2\text{OH}\text{--HCl}$  solution from 0.1 M to 0.5 M and the adjustment of the pH to 1.5 (Mossop and Davidson, 2003; Rauret et al., 1999); the substitution with other reagents like the mixtures of 0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , 0.2 M  $\text{H}_2\text{C}_2\text{O}_4$  and 0.1 M ascorbic acid (Leleyter and Probst, 1999; Shuman, 1982) or 6 M HCl solutions (Silveira et al., 2006). However, the reducibility of these reagents is not sufficient for the specific and selective extraction of the metals associated with well-crystallized Fe oxyhydroxides. In these SSE schemes, metals associated with Fe–Mn oxyhydroxides are extracted in one step, with a large portion of metals associated with the last part included in the residual component, i.e. aluminosilicates.

In polluted soils around mining areas in tropical and subtropical areas, Fe oxides along with other active components retain in various amounts of metals. With environmental changes such as alternation of wetting and drying, various farming practices and application of organic fertilizer, Fe oxides can be activated, aged and transformed, resulting in adsorption, lattice substitution and

coprecipitation of heavy metals. It is noteworthy that association with Fe oxides does not permanently immobilize these heavy metals, which are still volatile and may be released upon decomposition of the oxides under reduced conditions, leading to a significant impact on soil environments (Chlopecka, 1996; Rodríguez et al., 2009). This part of heavy metals have higher potential mobility than those held in the crystal structures of primary and secondary minerals. Current SSE schemes may not be appropriate for the fractionation analysis of heavy metals in the polluted soils in the weathered areas with a high content of Al-substituted Fe oxyhydroxides, and underestimate the content and potential mobility of these heavy metals, and result in the misleading recognition and evaluation of the bioavailability and toxicity of metal pollutants in these soils.

This study used a modified method from the Tessier procedure to compare fractions of heavy metals in polluted subtropical red soils under different land uses around an old mining area. The objectives were (i) to analyze the total concentration and fractionation of Pb, Zn, Cu and Cd in soil, (ii) to associate the types and contents of these heavy metals with well-crystallized Fe oxyhydroxides, and (iii) to propose a more rational SSE method for evaluation of heavy metal toxicity in polluted soils in subtropical and tropical soils.

## 2. Materials and methods

### 2.1. Sampling and pre-treatment of samples

The study site is located around in Shaoguan city, Guangdong Province, China. Sixteen samples were collected from two mine areas, among which twelve were from Dabaoshan mine and the other four were from Fankou mine (Fig. 1). Dabaoshan Mine, a well-known Pb–Zn polymetallic massive sulfide deposit, is located at the boundary between Qujiang and Wengyuan counties in the southern part of the city. The mine is one of the most important production regions of Fe, Cu, Pb, Zn and S. The Dabaoshan deposit is characterized by varied mineral suites and multiple types of mineralization, which include centrally-located (weathering-

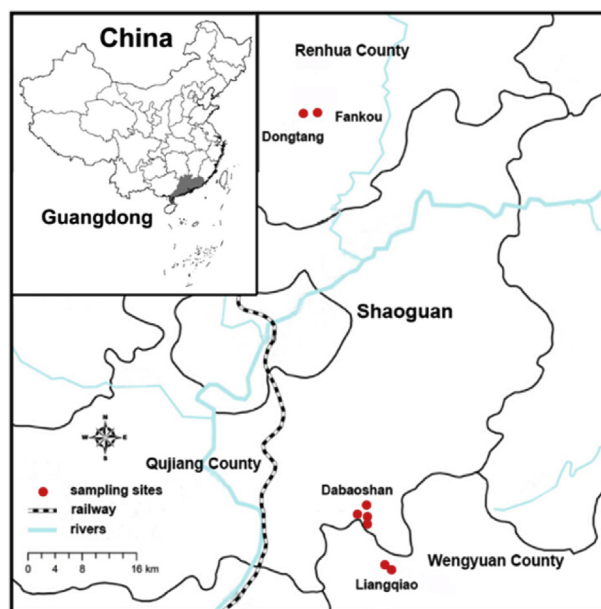


Fig. 1. Locations of the sampling sites in vicinity of the Dabaoshan mine area in Guangdong Province, China.

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