Geoderma Regional 7 (2016) 300–310

Contents lists available at ScienceDirect

Geoderma Regional

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

Metals and arsenic concentrations of Ultisols adjacent to mine sites on limestone in Western Thailand

Pichamon Intamo [a], Anchalee Suddhiprakarn [a,*], Irb Kheoruenromne [a], Saowanuch Tawornpruek [a], Robert J. Gilkes [b]

[a] Department of Soil Science, Faculty of Agriculture, Kasetsart University, Bangkok 10900, Thailand
[b] School of Earth and Environment, Faculty of Natural and Agricultural Sciences, University of Western Australia, Crawley, WA 6009, Australia

ARTICLE INFO

Article history:
Received 27 August 2015
Received in revised form 3 June 2016
Accepted 8 June 2016
Available online 9 June 2016

Keywords:
Mineralized limestone
Ultisols
Pb/Zn mine
Fractionation
Mine sites
Heavy metals
Arsenic
SEM/EDS

ABSTRACT

Soil samples collected from Ultisols at various distances from mine sites were analyzed to map metals and arsenic (As) concentrations in a Pb/Zn mineralized limestone area, Western Thailand. Total metals and As in soil samples (<2 mm) were determined by acid digestion (*aqua regia*). Chemical forms of metals and As were investigated using sequential extraction and SEM/EDS. High median concentrations in soils at mine sites were 76 mg/kg As and 835 mg/kg Pb, which are higher than the limits for agricultural and residential uses. The high Cd, Pb and Zn concentrations in the surface soil horizon at sites throughout the area indicate that contamination of soils by dust from mining activities has occurred. Arsenic and Cu are present at uniform concentrations to one meter depth in soils indicating that these elements have been derived by weathering of underlying mineralized limestone. Some As and Pb are associated with the NH_4-oxalate fraction being bound to poorly crystalline Fe/Mn oxides. SEM/EDS results confirm that Pb is associated with clay minerals and Fe/Mn oxides. The results suggest that the abandoned Pb—Zn mining sites are "hot spots" of soil contamination and that contamination also affects soils distant from mines so metals and As contamination of soils poses a pervasive environmental problem for local land uses.

1. Introduction

Mining may be a major cause of environmental pollution by heavy metals (Leblanc et al., 2000; Gosar, 2004; Ezeh and Chukwu, 2011) and metalloids (Duker et al., 2005; Paktunc, 2013). The mobility and bioavailability of contaminant metal/metalloids in soils are determined by their concentration and chemical forms (Wenzel et al., 2001; Kierczak et al., 2008). Heavy metals and metalloids may be involved in complex chemical and biological interactions (Violante et al., 2010). These factors affect the short- and long-term environmental impacts on land contaminated with metals/metalloids (McBride, 1994). Heavy metals in soils can be present in a number of chemical forms, exhibiting different behaviors with respect to chemical interactions, mobility, bioavailability and toxicity (Pueyo et al., 2008; Giacomino et al., 2010; Kim et al., 2014). Metal fractionation may be investigated by extraction with "selective extractants" (Tessier et al., 1979; Wenzel et al., 2001) and by various spectroscopic and electron optical techniques (Jerzykowska et al., 2014). The determination of metal/metalloid fractions will provide information about the likely mobility of metals/metalloids and their bioavailability (Cetiner and Xiong, 2008; Kim et al., 2014). Bioavailability and the mobility of metals and metalloids are related to the higher concentrations of mobile toxic metals and metalloids in the soil which increases the potential for plant uptake, and animal/human consumption (Roussel et al., 2010; Sheoran et al., 2011). For example, Anju and Banerjee (2011) reported that the Pb and Zn in soil samples from a mining and smelting area in Zawar, India were present mainly in the reducible fraction and it was assumed that mobility and bioavailability are related to the solubility of various geochemical forms of metals.

The western part of Thailand is a traditional mining region with Ag, Au, Sn, Pb, Zn and W mines (Holdstock and Mlot, 2008). Between 1978 and 2002, a total of 5,237,800 tonnes of Pb/Zn ore was produced from the region. The area is extensively mineralized with Pb/Zn deposits existing within Ordovician carbonates (Diehl and Kern, 1981). The carbonates are part of a belt that extends from the Gulf of Thailand to China. The mineralization mainly consists of quite finely intergrown sphalerite (ZnS) and galena (PbS) with a Pb:Zn ratio of approximately 2.5:1 (Kuchelka, 1981).

The mines closed in 2002 due to economic constraints and subsequently orange and other plantations have been developed in and adjacent to the mined areas. However after closure of the mines and processing facilities the mine-spoil, ore processing wastes and contaminated soils were not adequately remediated and they represent a

* Corresponding author.
E-mail address: agrals@ku.ac.th (A. Suddhiprakarn).

http://dx.doi.org/10.1016/j.geodrs.2016.06.002
2352-0094/

potential source of toxic metals (Miler and Gosar, 2012; Monterroso et al., 2014). Sittiwilai (2011) has reported that soil at the former processing plant of a mine in the study areas contains 18,543 mg/kg Pb and the tailing dam contains 1686 mg/kg Pb. These elevated concentrations can cause severe contamination of water, soil and plants in the vicinity of mines. The mines in Western Thailand are located in a mountainous area and in periods of high rainfall, there is offsite transport of heavy metals (Panichayapichet et al., 2008). During the dry season dust from mine sites and tailings ponds is eroded by wind. Moreover, ore was transported in trucks on public roads along a north to south axis and some contamination of adjacent soils may have occurred. Previous studies at Thong Pha Phum District, Kanchanaburi Province showed that soils of mineralized areas were contaminated with Pb with concentrations up to 7473 mg/kg as compared to a background level of 55 mg/kg (Zarcinas et al., 2004). Nobuntou et al. (2010) also reported on the potential risk to the environment of abandoned mines in Thong Pha Phum District due to Pb contamination of the surface soil.

This paper reports on the concentration of metals (Cd, Cu, Pb and Zn) and As in soils in a mined area in Western Thailand including sites adjacent to and distant from the actual mine sites that are used for agriculture. The research has determined forms of elements in the soils to provide an indication of the potential bioavailability of metals and As.

2. Materials and methods

2.1. Description of the study area

The mineralized area is situated in the Meklong Highlands, a jungle covered region in Kanchanaburi Province between the deeply incised valleys of Khwae Yai and Khwae Noi rivers, approximately 300 km northwest of Bangkok and 186 km from Kanchanaburi. The area is underlain by limestone with a typical karst topography of steep sided hills covered by thick tropical vegetation including bamboo jungle and rain forest (Holdstock and Mlot, 2008). The area has plantations of cassava, para rubber, citrus, bamboo, teak and corn. The annual average temperature and rainfall are 26–27 °C and 1972–2335 mm, respectively with the rainy season from May to September representing over 80% of the total annual precipitation. Soils are Ultisols and have silty clay loam, clay loam, silty clay and clay textures. This study was carried out in a Pb/Zn mineralized area in the Thong Pha Phum district, Kanchanaburi province, Thailand (UTM N 1645000/UTM S 1624000) where mines were in operation from 1986 to 2002 (KEMCO, 1984). Waste materials from mining activities include finely ground ore tailings from a froth flotation plant have been exposed to erosion by wind and water. The processing plant for the mines is at the northern mine with a tailing area and tailing dam located at the lowest position. Ore was transported by truck to the northern plant. Substantial contamination of soil and water courses has caused Pb toxicity of individuals in this region (Rotkittikhun et al., 2006; Pusapukdepob et al., 2007; Nobuntou et al., 2010; Sittiwilai, 2011).

2.2. Field work and sampling

Soils were sampled at ninety five locations along traverses across geomorphically contrasting sites including crest, shoulder, upper midslope, lower midslope, upper footslope, lower footslope, spur and valley floor positions. This strategy was adopted on the expectation that surficial process may have distributed metals and As into particular geomorphic sites.

Sampling sites are located along but not closely adjacent to roads and at various distances from mines, and are separated in to three groups: (at the mine sites, near (<1 km) and far (>1 km)). Soil samples were taken from three depths (Ap, Ap-60 and 60–100 cm) as it was anticipated that the soil profiles would consist of colluvium over residuum. The sampling locations and topography of the study area are shown in Fig. 1.

2.3. Some soil properties and total elements concentrations by aqua regia extraction

Air-dried samples were gently crushed, to completely pass through a 2-mm stainless steel sieve. Analysis was undertaken using this fine earth. Particle size distribution was determined by the pipette method (Gee and Bauder, 1986). Soil pH was measured in 1:1 soil:solution using H_2O (National Soil Survey Center, 1996; Fieldes and Perrott, 1966).

Aqua regia extraction was used to estimate the total concentration of metals and As in soils. In this procedure 0.5 g soil was placed in a 50 ml Pyrex digestion tube. Pre-digestion was at 110 °C for 15 min with 1 ml of 37% HCl. Then, the suspension was digested at 140 °C for 1 h with 3 ml of 70% HNO_3 in a reflux condenser. The digest was diluted to 30 ml with deionized water and stored in a polyethylene bottle at 4 °C. Analyses were by inductively coupled plasma optical emission spectrometry (ICP-OES) (Vega et al., 2006). The accuracy of the method was assessed by analyzing certified standard reference material (ASPAC 54).

2.4. Fractionation of metals (Cd, Cu, Pb and Zn) and As

Sequential extraction procedures have recently been developed to determine the speciation of trace metals in soil matrices. Partitioning of soil metals and As into fractions used the sequential extraction procedure of McKeague et al. (1971). Extractants were Na-pyrophosphate (metals and As bound to organic matter), NH_4 oxalate (metals and As bound to poorly crystalline Fe/Mn oxides) and dithionite-citrate-bicarbonate (DCB) (metals and As bound to crystalline Fe/Mn oxides). Metals and As not dissolved in these extractants comprise the residual fraction that is calculated as total (*aqua regia*) metals and As minus the sum of extractable metals and As. The extractions were carried out in a 50 ml polyethylene centrifuge tube. Following each extraction step, the suspensions were centrifuged at 3000 rpm for 15 min, the solution was removed and analyzed by ICP-OES (Perkin Elmer Optima 5300 DV) after suitable dilution.

2.5. Micro-characterization

Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) was used to analyze soil particles on a Tescan VEGA3 SEM at an accelerating voltage of 20 Kv and working distance of 15 mm. Soil samples were sieved <2 mm and sprinkled on to carbon tape, the excess soil was blown off with compressed air and the sample was sputter-coated with carbon to achieve conductivity. Samples were scanned in electron back scattering mode. The elemental composition of particles was then determined using EDS.

This instrument was used for semi-quantitative point analysis, for microphotographs in backscattered and secondary electron modes, and for elemental mapping.

2.6. Statistical analyses

The basic population statistics of the data were calculated by STATISTICA (StatSoft, Inc. (2003). Data did not have normal distributions so some common statistical procedures are inappropriate. It was decided to present median concentrations in this paper rather than mean concentrations and to use standardized data for statistical calculations. The spatial distribution of metals and As was mapped using a MapInfo geographic information system (GIS) software. Samples were divided in to five equally populated groups on the basis of their metal and As concentrations and these groups are the mapping units shown in the figures.