Geoderma 164 (2011) 73–84

Contents lists available at ScienceDirect

Geoderma

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

Tracing the spatial distribution and mobility of metal/metalloid contaminants in Oxisols in the vicinity of the Nkana copper smelter, Copperbelt province, Zambia

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ARTICLE INFO

Article history:
Received 30 November 2010
Received in revised form 12 April 2011
Accepted 21 May 2011
Available online 12 June 2011

Keywords:
Oxisols
Metals and metalloids
Pb isotopes
Cu smelting
Mobility
Zambia

ABSTRACT

The copper mining and smelting activities in the Copperbelt province (Zambia) left enormous pollution related to the disposal sites for mining/smelting waste (tailings, slags) and to the continuous deposition of smelter stack particulates in the soil systems. Topsoils in the vicinity of the Nkana copper smelter were studied in order to assess the spatial distribution of metal/metalloid contaminants (As, Co, Cu, Pb, Zn) in a 32-km^2 zone around the smelter ($n = 196$ soil samples). The bulk concentrations of metal/metalloid contaminants were determined by ICP techniques, supplemented by the determination of the Pb isotopic composition of selected samples measured by quadrupole-based ICP-MS. The spatial distribution of the major contaminants indicated the highest contamination NW of the smelter stack, corresponding to the prevailing wind direction in the area. The highest metal/metalloid concentrations in the topsoils were: 255 mg As kg^{-1}, 27,410 mg Cu kg^{-1}, 606 mg Co kg^{-1}, 480 mg Pb kg^{-1} and 450 mg Zn kg^{-1}. Lead isotopes helped to differentiate the extent of metallic pollution and indicated the mixing of three major pollution sources (given as ^{206}Pb/^{207}Pb ratios): smelting activities (1.19–1.28), petrol combustion (1.07–1.09) and regional background (deep soil horizons, ca. 1.35) To assess the vertical mobility of these inorganic contaminants, a 110-cm-deep profile in Oxisol in a highly polluted zone in the near vicinity of the Nkana smelter was sampled and studied by combination of bulk chemical analysis, sequential extraction procedure (SEP) and Pb isotopic tracing. Investigation of the soil profile indicated that the contamination is mostly located in the uppermost soil horizons enriched in organic matter (<10 cm). Based on SEP, the isotopic composition and knowledge of smelter activities in the area, it was predicted that anthropogenic Pb (corresponding to a concentration of 1 mg kg^{-1}, i.e., approx. 1.5% of total Pb) exhibited downward migration in the soil profile with estimated penetration rate of 1.36 cm year^{-1}. Copper, being substantially bound in the exchangeable fraction, also showed significant mobility in the profile. As a result, the sources of anthropogenic emissions in the Kitwe smelting area represent an important source of mobile (and potentially bioavailable) metals.

1. Introduction

Non-ferrous metals smelting activities represent one of the most important point sources of metal/metalloid pollution of soils via atmospheric deposition (Rieuwerts et al., 1999; Sterckeman et al., 2000; Burt et al., 2003; Udachin et al., 2003; Martley et al., 2004; Williamson et al., 2004; Ettler et al., 2005; Douay et al., 2008; Ettler et al., 2010). So far, relatively few studies have been focused on ecosystems (soils, water, air, biota) polluted by mining/smelting industries in developing countries in Africa (e.g., Meter et al., 1999; Kříbek et al., 2010). Environmental and ecotoxicological research is mainly conducted in developed countries where risks for the population are efficiently reduced by legislation and technical measures (Banza et al., 2009). Another aspect is that a number of models have been developed in recent years to predict mobile/bioavailable concentrations of potentially toxic elements in soils, but these models are based on data for temperate soils and could not be successfully applied to tropical soils (Rieuwerts, 2007). In this context, the binding and mobility in highly contaminated soil systems in the tropics is still not fully understood (Rieuwerts, 2007).

The Copperbelt is a well known district of base metal mining and processing (mainly Cu and Co). On the Zambian side of the Copperbelt, it is estimated that 30 million tonnes of Cu metal have been produced since mining began on a full scale in 1930. The average ore grade is 30 g Cu kg^{-1} and 1.8 g Co kg^{-1} (Kamona and Nyambe, 2002). According to the US Geological Survey (USGS, 2010), Zambia was the 8th largest global producer of Cu and 7th largest global producer of Co in 2009. The Copperbelt province, including Zambia and the Democratic Republic of Congo, is the richest Co mining district in the world, with a total 27,500 tonnes mined in 2009 and reserves

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doi:10.1016/j.geoderma.2011.05.014

estimated at 3,670,000 tonnes (USGS, 2010). More than 90 years of intense Cu and Co mining and ore processing have left enormous pollution related to the disposal sites for mining/smelting waste (mine tailings, slags) and to the continuous deposition of smelter stack particulates in the soil systems. Detailed environmental studies are still rare in this area (Meter et al., 1999; Tembo et al., 2006; Banza et al., 2009; Křříbek et al., 2010; Šráček et al., 2010; Mihaljevič et al., 2011).

Based on a previous screening study focusing on the central-northern part of the Zambian Copperbelt (Kříbek et al., 2010), we investigated in detail the soil contamination around the Nkana smelter at Kitwe, one of the hot spots of metal/metalloid contamination in this region. This paper is focused on the spatial distribution of As, Co, Cu, Pb and Zn in topsoils around the Nkana smelter coupled to Pb isotopic tracing of the degree of contamination and detailed investigation of the vertical mobility of inorganic contaminants in these highly polluted soils using chemical fractionation and Pb isotopic methods.

2. Materials and methods

2.1. Site description

The Zambian Copperbelt forms the south-eastern part of the Neoproterozoic Lufilian Arc, a Pan-African orogenic belt consisting of metasedimentary rocks of the Katanga Supergroup, and represents one of the world's most important sediment-hosted stratiform Cu- and Co-bearing sulphide deposits (more detailed information about the geology of the Zambian Copperbelt is given in Kříbek et al. (2010) and references therein).

The Cu smelter at Nkana near Kitwe is the oldest metallurgical factory in the Zambian Copperbelt (commissioned in 1931, closed in 2009). It consisted of reverbatory furnaces, Peirce–Smith converters and blister casting facilities. The blister copper production was 6000 tonnes during the first year of operation. At the production apogee in 1971, 330,000 tonnes of Cu were produced; between 1993 and 2006, the production was between 100,000 and 125,000 tonnes of Cu per year. In 1994, an El Teniente converter (CT) was installed to upgrade the reverbatory furnace matte to white metal (S-poor Cu_2S, with composition Cu_2S_{1-x}), prior to its refinement in conventional PS converters (Cutler et al., 2006).

The climatic seasons in the Copperbelt are (i) a hot rainy season with tropical thunderstorms (November–April), (ii) a cool dry season (May–August) and (iii) a hot season with practically no rain (September–November). The average annual rainfall in Kitwe is 1320 mm (Kříbek et al., 2010). From March until October, strong winds from the south-easterly quadrant are predominant, whereas the season from November to February is dominated by light north-easterly winds (Kříbek et al., 2010).

The majority of the land is covered with grass and bamboo, with sparse forested areas mainly consisting of *Brachystegia* and *Isoberlinia* species (Kříbek et al., 2007). The Kitwe area in the vicinity of industrial complexes is partly covered with waste deposits, dumps and tailing ponds (Fig. 1). Agricultural activities are located close to the urban areas, rivers and small streams. Cassava (*Manihot esculenta*), sweet potatoes (*Ipomoea batatas*) and, to a lesser extent, maize (*Zea mays*) are the main crops cultivated in the area (Kříbek et al., 2007).

2.2. Sampling and sample processing

The field work was carried out in May 2008. Based on a previous regional study (Kříbek et al., 2010), a total of 196 topsoil samples (A horizon, depth 0–5 cm) were collected to cover the 32-km^2-large zone in the vicinity of the Nkana copper smelter (see Figs. 1 and 2 for the location of the sampling points). In addition, a 110-cm-deep soil profile was sampled in a 1 × 1-m-wide pit within the highly polluted zone close to the smelter stack (Fig. 1, GPS position: S 12°50′09.8″, E 28°11′43.0″) to investigate in detail the vertical mobility of the contaminants ($n = 13$ samples). According to the Soil Taxonomy (Soil Survey Staff, 2010), the soil was characterised as Oxisol, subgroup Rhodic Haplustox. The samples were stored in polyethylene (PE) bags and treated immediately on returning to the laboratory. Slag samples ($n = 7$) were sampled on the slag dumps in the vicinity of the Nkana smelter. As it was not possible to obtain any dust from the filtering units in the smelter; as a proxy material we sampled the dust deposited on the surface of tyres forming the barriers along the road, 200 m away from the smelter ($n = 2$).

Topsoils and soils from the contaminated profile were air-dried in the laboratory to constant weight. All the soil samples were sieved through a clean 2-mm stainless steel sieve (Retsch, Germany). The fraction below 2-mm was used directly for the sequential extraction procedure (SEP) and measurements of the pH, particle size distribution and cation-exchange capacity (CEC). An aliquot part of each sample was finely ground in an agate mortar (Fritsch Pulverisette, Germany) and used for subsequent bulk chemical and isotopic analyses. Slag and fly ash samples were dried at ambient temperature and finely ground in an agate mortar before subsequent digestion in mineral acids and bulk chemical analyses.

2.3. Analytical procedures

2.3.1. Determination of soil properties and mineralogy

The soil colour was determined on the moist samples using the Munsell soil colour chart tables. The description of the soil samples from the contaminated profile was carried out directly in the field. The soil pH was measured by a Schott Handylab pH metre equipped with a Schott BlueLine 28 pH electrode (Schott, Germany) in a 1:5 (w/v) soil-deionised water suspension after 1-h agitation (Pansu and Gautheyroux, 2006). The particle size distribution was measured by the hydrometer method. The cation exchange capacity (CEC) was determined as the sum of the basic cations and Al extracted with the unbuffered 0.1 mol l^{-1} $BaCl_2$ solution and the extractable acidity (0.05 mol l^{-1} NaOH titration) (Pansu and Gautheyroux, 2006). Basic cations and Al were measured by flame atomic absorption spectrometry (FAAS; Varian SpectrAA 280 FS, Australia).

About 0.5 g of the pulverised samples was used for identification of the bulk mineralogical composition of the soils from the contaminated profile. We used X-ray diffraction analysis (XRD; PANalytical X'Pert Pro diffractometer with X'Celerator detector) with CuKα radiation at 40 kV and 30 mA over the range 2–80° 2theta with a step of 0.02° and counting time of 150 s per step. X'Pert HighScore 1.0 software equipped with the JCPDS PDF-2 database (ICDD, 2002) was used for the qualitative analysis. In addition, the heavy mineral fraction was separated from the topmost soil horizon in 1,1,2,2-tetrabromethane (density 2.96 g cm^{-3}) in a centrifuge (Janetzki S70D, Germany) at 1800 r.p.m. for 30 min. The heavy mineral fraction was then washed in ethanol and analysed by XRD using the same analytical conditions as for the bulk samples.

2.3.2. Determination of bulk concentrations

Total organic carbon (C_{org}) and total sulphur (S_{tot}) were determined on an Eltra CS 530 analyzer (Eltra, Germany). Determination of the total inorganic carbon was carried out using an Eltra CS 500 analyzer (Eltra, Germany), but its concentrations were below the detection limit (0.1 g kg^{-1}) for all the studied samples.

A mass of 0.2 g of dry soil sample was dissolved in a Pt dish in 10 ml of hot HF and 0.5 ml $HClO_4$ and evaporated to dryness. The procedure was repeated with 5 ml HF and 0.5 ml $HClO_4$ in order to remove all the silica from the sample. Subsequently, the residue was dissolved in 2 ml HNO_3 and diluted to 100 ml. All the acids used in the dissolution procedure were of reagent grade (Merck, Germany and Lach-ner, Czech Republic) and MilliQ+ (Millipore, USA) deionised water was used for all the digestions. The total digestions were