Ecotoxicology and Environmental Safety 113 (2015) 391–399

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China

Peizhong Li [a,c], Chunye Lin [a,*], Hongguang Cheng [a], Xiaoli Duan [b], Kai Lei [a]

[a] *State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Beijing Normal University, Beijing, China*
[b] *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, China*
[c] *Beijing Key Laboratory of Industrial Land Contamination and Remediation, Environmental Protection Research Institute of Light Industry, Beijing, China*

ARTICLE INFO

Article history:
Received 29 September 2014
Received in revised form
8 December 2014
Accepted 14 December 2014
Available online 23 December 2014

Keywords:
Soil
Lead
Zinc
Heavy metal
Contamination
Health risk

ABSTRACT

Anthropogenic emissions of toxic metals from smelters are a global problem. The objective of this study was to investigate the distribution of toxic metals in soils around a 60 year-old Pb/Zn smelter in a town in Yunnan Province of China. Topsoil and soil core samples were collected and analyzed to determine the concentrations of various forms of toxic metals. The results indicated that approximately 60 years of Pb/Zn smelting has led to significant contamination of the local soil by Zn, Pb, Cd, As, Sb, and Hg, which exhibited maximum concentrations of 8078, 2485, 75.4, 71.7, 25.3, and 2.58 mg kg^{-1}, dry wet, respectively. Other metals, including Co, Cr, Cu, Mn, Ni, Sc, and V, were found to originate from geogenic sources. The concentrations of smelter driven metals in topsoil decreased with increasing distance from the smelter. The main contamination by Pb, Zn, and Cd was found in the upper 40 cm of soil around the Pb/Zn smelter, but traces of Pb, Zn, and Cd contamination were found below 100 cm. Geogenic Ni in the topsoil was mostly bound in the residual fraction (RES), whereas anthropogenic Cd, Pb, and Zn were mostly associated with non-RES fractions. Therefore, the smelting emissions increased not only the concentrations of Cd, Pb, and Zn in the topsoil but also their mobility and bioavailability. The hazard quotient and hazard index showed that the topsoil may pose a health risk to children, primarily due to the high Pb and As contents of the soil.

1. Introduction

Heavy metals are one of the most troublesome types of pollutants due to their widely distribution, persistent toxicity, and bioaccumulation in the food chain (Nriagu, 1996; Dudka and Adriano, 1997; Kabata-Pendias and Mukherjee, 2007; Zhang et al., 2012; Douay et al., 2013). Nonferrous metal smelting is one of the most important anthropogenic sources of heavy metal pollution (Nriagu, 1996). Smelting-emitted metals are transferred to environmental compartments, such as water, soil and plants, and they can eventually enter human bodies through food or direct ingestion, creating a threat to human health (Kabata-Pendias and Mukherjee, 2007; Douay et al., 2007; Pelfrêne et al., 2013).

In general, trace metals emitted from nonferrous smelting tend to initially accumulate in nearby soils (Nriagu, 1996; Dudka and Adriano, 1997; Sun et al., 2010). However, the trace metals in soils may be transported by water, air, and organisms. Their specific chemical forms largely determine their mobility, bioavailability, and bioaccessibility (Pelfrêne et al., 2013; Tessier et al., 1979; Waterlot et al., 2013). Selective sequential dissolution (SSD) methods have been widely used to determine the quantities and proportions of metals present in soils and sediments (Tessier et al., 1979; Usero et al., 1998; Han and Banin, 1995, 1999). Many studies have also used the enrichment factor to quantitatively assess the degree of contamination and to distinguish between natural and anthropogenic pollution sources (Sterckeman et al., 2006; Bourennane et al., 2010).

China is the world's largest nonferrous metal producer and consumer (Zhang et al., 2011; Li et al., 2012; Shao et al., 2013). Yunnan Province is extremely rich in nonferrous sources. The nonferrous output of Yunnan Province was approximately 2.1×10^9 kg in 2010, the second highest in China (ECYNMIC, 2010). The Pb/Zn smelter in the small town of Zhehai (Huize County of Yunnan Province) was established in 1951, and its Pb/Zn output gradually increased to 100×10^6 kg per year in 2010 (approximately 40×10^6 kg for Pb and 60×10^6 kg for Zn). However, the contamination of the soil by Pb and other toxic trace elements has not yet been investigated.

In this paper, an attempt was launched to investigate the horizontal and vertical distributions of toxic trace elements in the soil

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* Corresponding author.
E-mail address: c.lin@bnu.edu.cn (C. Lin).

http://dx.doi.org/10.1016/j.ecoenv.2014.12.025
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around the smelter, to identify their geochemical fractions and to assess the contamination in this area.

2. Materials and methods

2.1. Study area

Huize County (103°03′–103°55′E and 25°48′–27°04′N) is located in the northeastern part of Yunnan Province, at the junction of the East Yunnan and West Guizhou plateaus in southwestern China. Huize County is characterized by a mountainous topography and mild climate. The average annual temperature, annual precipitation, and altitude are 12.7 °C, 784 mm, and 2120 m above sea level, respectively. The soil in Huize County is generally classified as Alfisols. Zhehai is a small town in Huize County, located at the bottom of a valley (Fig. 1).

2.2. Sampling procedure

Using a soil driller (Eijkelkamp, Netherland), 24 topsoil (approximately 0–20 cm depth) samples and three soil profiles (0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm depths) were collected in Zhehai to investigate the spatial distributions of elemental concentrations (Fig. 1). In addition, two topsoil samples and one soil profile were collected as controls in Huize City, approximately 10 km southwest from Zhehai. To minimize the heterogeneity and uncertainty, topsoil was sampled from five locations at each site, and the samples were mixed together. The detailed sampling sites are shown in Fig. 1. Some sites are in agricultural fields and others are in native vegetation fields. Soil profiles were collected from the agricultural fields. The main crops are wheat and maize. The soil samples were transferred to acid-washed dark-colored polyethylene bags and transported to the laboratory, where they were air-dried, slightly crushed, passed through a 2-mm sieve, and stored in glass bottles.

2.3. Chemical analysis

The pH of each soil sample was analyzed in a 1:10 soil/water suspension using a combination pH electrode (Orion). Soil organic matter (SOM) concentrations were measured based on the weight loss upon combustion at 400 °C (Ben-Dor and Banin, 1989). The carbonate content was measured by the manometric method following the addition of dilute HCl to dissolve the carbonates (Loeppert and Suarez, 1996). The granularity of the soil samples was measured by an LS 230 laser diffraction particle analyzer (Beckman Coulter), and the proportions of clay (< 2 µm), silt (2–20 µm), and sand (20 µm – 2 mm) were calculated.

Portions of the soil samples were further ground (< 0.149 mm in particle diameter) and digested with HNO_3–HF–$HClO_4$ (Lin et al., 2008a). The Cr, V, Mn, Al, and Fe in the extracts were measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II, Thermo Electron), and Cd, Co, Cu, Ni, Pb, Sc, and Zn were measured with an inductively coupled plasma mass spectrometer (ICP-MS) (X Series II, Thermo Electron). In addition, portions of the soil samples were digested with aqua regia, 1% $KMnO_4$ solution, and 1% oxalic acid. The concentrations of As and Sb in the supernatant were determined by hydride generation atomic fluorescence spectrometry (HGAFS), and cold vapor atomic fluorescence spectrometry (CVAFS) was used to determine the concentration of Hg. The accuracy of each method was assessed by replicate analyses of the elements in the certified

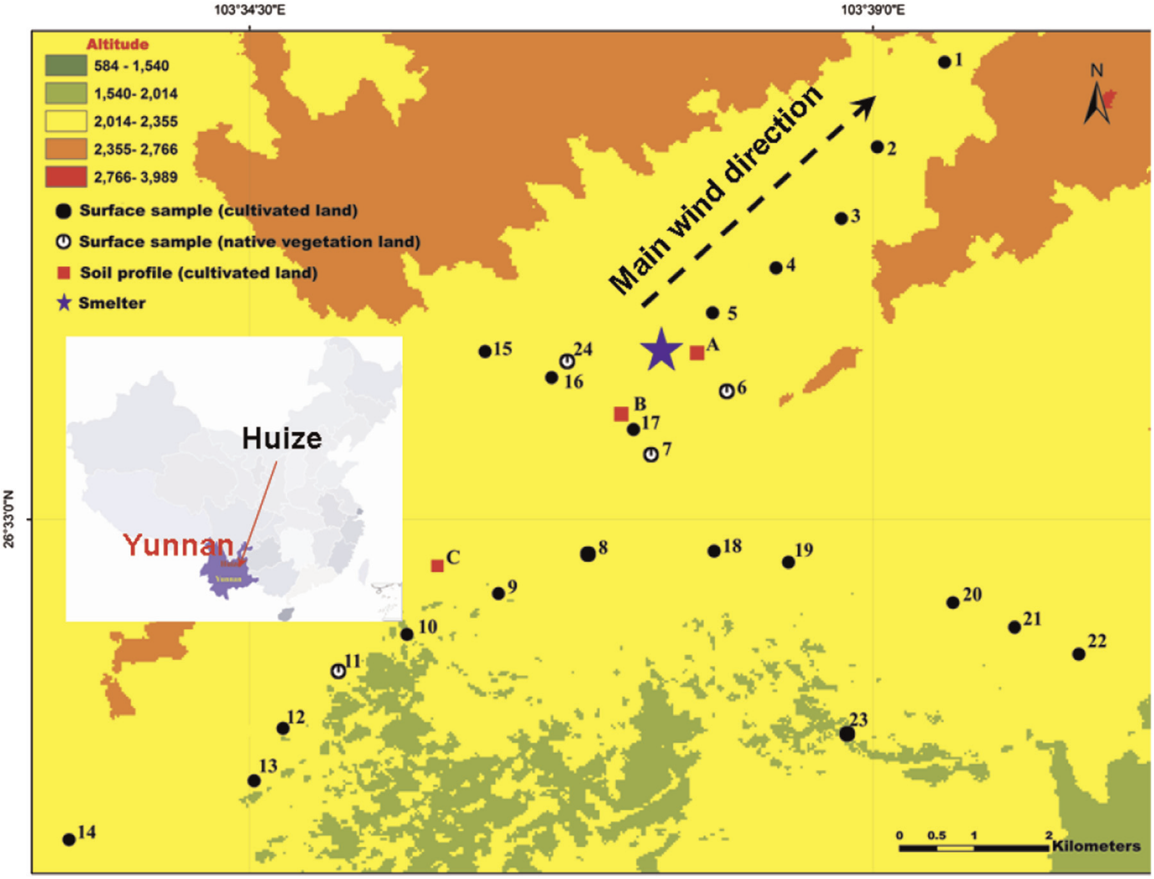

Fig. 1. Map of sampling locations in Zhehai town, Huize county, Yunnan Province of China.