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Contamination of heavy metals and isotopic tracing of Pb in surface and profile soils in a polluted farmland from a typical karst area in southern China

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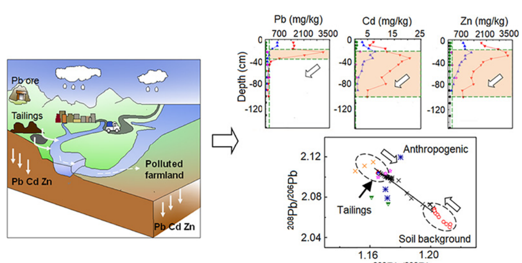
HIGHLIGHTS

- Cd and Zn are easier to migrate to the deep soil than Pb and Cu.
- Pb isotope ratios point out tailings is the major source to the polluted soil.
- Atmospheric contribution to soil Pb budget is limited.
- Anthropogenic Pb is mostly bound in organic fraction because of the soil moisture in karst region.

GRAPHICAL ABSTRACT



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ABSTRACT

Farmland top soils and soil profiles situated in the karst area of Guilin, Guangxi Zhuang Autonomous Region, southern China, reveal different degrees of heavy metal pollution, both in respect to the lateral as well as the vertical dimension. Pb isotope ratios clearly identify that heavy metal contributions to the soil represent the legacy of former Pb-Zn mining and smelting in the area. Depending upon soil properties, differences in the intensity of the vertical penetration of heavy metal pollution are discernible. Top soil coverage by local farmers provides little remediation. Consequently, hazardous conditions for the regional ecology, for agricultural usage and ultimately for human health remain in place. Based on chemical and isotopic results obtained, more effective remediation strategies need to be developed.

1. Introduction

China is one of the largest producers and consumers of metals such as iron, lead, manganese, zinc, and others (Li et al., 2014), and exploitation

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of the national mineral resources contributed greatly to the development of China's economy. Yet, improper treatment of abandoned mines and tailings continues to cause severe environmental pollution to surrounding areas, in particular in respect to heavy metals (Simate and Ndlovu, 2014). These can enter into the soil from fly ash, wastewater and slag through migration, retention and deposition, subsequently threatening the health of humans and the ecology of local/regional environments (Acost et al., 2011).

Mine tailings resulting from the mechanical and chemical separation of minerals during mining and smelting (Sternal et al., 2017) contain a mixture of milled ore, gangue material, country rock, beneficiation wastewater and residual process chemicals (Ignatkina et al., 2010; Gutiérrez et al., 2016). Frequently, tailings are piled on land without any prior/subsequent treatment, resulting in severe metal pollution to the adjacent agricultural soil as well as the surface and ground water (Rodríguez et al., 2009; Bohdalkova et al., 2014; Rodríguez et al., 2018). Consequences include the degeneration of typical soil functions, poor plant growth, and a serious threat to human health (Bhopal et al., 1998; Siciliano et al., 2009; Zhang et al., 2016). Therefore, urgent action is essential in order to reduce the environmental risks, to improve the health of the ecosystems, and to secure safe agricultural production. In that respect, it is crucial to study the spatial distribution of heavy metals for obtaining a detailed understanding about the origin and fate of heavy metals in soils.

Metal isotopes have been utilized as an effective tool for tracing the source(s) and fate (degradation, migration and transformation) of heavy metals and for providing constraints for modeling pertinent migration and transformation processes. In recent years, continuous improvements in analytical techniques and instrumentation enhanced the application potential of metal isotopes, such as Pb (Rosman et al., 1997; Michael, 2005; Mackay et al., 2013), Zn (Bigalke et al., 2010; Fekiacova et al., 2015), Cd (Cloquet et al., 2006), and Cu (Fekiacova et al., 2015). Among them, Pb isotopes have been utilized most successfully in environmental studies due to the fact, that different potential Pb sources have characteristically different isotopic compositions. Such diagnostic Pb isotope fingerprints have a high potential for being preserved in various environments (Wen et al., 2015). Consequently, Pb isotope ratios in combination with concentration data, have been successfully applied in tracing the origin of a contamination and apportion individual contributions from different source(s) in top soils and soil profiles (Walraven et al., 2014; Wen et al., 2015), in sediments (Hu et al., 2013; Yu et al., 2016), in plants (Li et al., 2012; Wang et al., 2013), in the atmosphere (Díaz-Somoano et al., 2009; Zhao et al., 2015), and in seawater (Zurbrick et al., 2017).

In southern China, where nonferrous mineral resources are quite abundant, thousands of sites with mine tailings exist. Due to the subtropical climate and the underlying karst lithology, the mobility of heavy metals is quite substantial. Contamination of the nearby farmland is a serious environmental and agricultural problem, ultimately also affecting human health (Chen et al., 2015).

For the past 40 years, soils in the area around the former Guilin Pb-Zn mine have been heavily polluted by heavy metals due to mining, smelting, and the collapse of a mine tailings dam. Despite this situation, the area has witnessed little research attention until the suspected emergence of “itai-itai disease”, a severe cadmium poisoning, among the resident population. Thus, there is obvious and urgent need for studying the spatial distribution and migration of heavy metals in the impacted soil.

Guilin is a tourist area, famous for its beautiful karst landscape. The former Guilin Pb-Zn mine started its operation in the 1950's, with sphalerite and galena being the principal ore minerals. In the 1970's, the collapse of a tailing dam flooded the farmland along the river with tailing material, leading to severe heavy metal pollution of agricultural soils. Subsequently, local farmers covered the tailings with soil and planted crops, which severely endangered the ecology of the local environment and threatened the health of the local residents.

The aim of this research is (1) to ascertain the spatial distribution of heavy metals in the regional farmland soil (topsoil and profile soil), (2) to quantitatively identify sources of Pb using Pb isotopes, and (3) to explore the migration and transformation processes of Pb using Pb isotopes in a typical karst region of southern China.

2. Materials and methods

2.1. Study area and sampling

The study area is located in Guilin, Guangxi Zhuang Autonomous Region, southern China (Fig. 1). Topsoil and end member samples were collected in December 2015 and soil profiles were sampled in June 2016. The study area comprises approximately 0.93 km^2. A 200 × 200 m grid for topsoil sampling was established and 100 samples were collected (Fig. 1). Based on the spatial distribution of heavy metals in the top soil, the study area was divided into four parts (Fig. 2) using the Nemero Index (Nemerow, 1974): non-polluted area (NP, $0 < P_N < 1$); slightly polluted area (SP, $1 < P_N < 3$), moderately polluted area (MP, $3 < P_N < 10$), heavily polluted area (HP, $P_N > 10$):

$$P_N = \sqrt{\frac{\left(1/n\sum_{i=1}^{n} P_i\right)^2 + {P_{i\,\max}}^2}{2}}$$

$$P_i = C_i/S_i$$

where P_N is the Nemero Index; P_i refers to the single index of each heavy metal in the soil samples; P_{imax} identifies the maximum single index of each soil sample; C_i represents the concentration of each heavy metal in the soil samples; and S_i refers to the soil quality standard of each heavy metal (Table 1) in the soil samples.

Three soil profiles were excavated, representing these different pollution stages (SP, 24°58′34.42″, 110°33′11.25″; MP, 24°58′53.23″, 110°23′23.44″; HP, 24°59′16.52″, 110°33′14.31″). In addition, a soil profile was collected from the non-polluted area (NP: 24°57′59.45″, 110°33′36.57″) and one from the abandoned mining zone (AM: 25°00′01.67″, 110°36′43.67″). For each vertical profile, soil samples were collected every 5 cm for the 0–40 cm depth interval, every 10 cm in the 40–80 cm depth range, and every 20 cm in the 100–140 cm depth interval, respectively. For the AM profile, soil samples were collected at a 20 cm depth interval within the 0–60 cm depth range. Material from mine tailings, rainwater, aerosol (TSP), vehicle exhaust, and coal was collected as end member samples.

2.2. Elemental and isotopic analyses

2.2.1. Total metal concentrations, pH, total organic carbon and Pb extraction

Soil samples were digested in a mixture of HF, HNO_3 and $HClO_4$ (Chenery et al., 2012). Reference materials were GBW07404 and GBW07405. Arsenic concentration was analyzed by Atomic Fluorescence Spectrometry (AFS), and all other elemental concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

Soil pH was measured in a 1:2.5 mixture of soil and water. The soil organic carbon content was determined by Elemental Analyzer after eliminating the soil carbonate (Midwood and Boutton, 1998).

The chemical partitioning of Pb in the different soil profiles (SP, MP, HP) was performed using a modified Tessier's 5-step sequential chemical extraction method (Wong and Li, 2004). Total extracted Pb was divided into five chemically different fractions: (1) exchangeable, i.e. soluble and exchangeable Pb; (2) carbonate, i.e. Pb bound to carbonate and adsorbed to weak organic and inorganic complexes; (3) Fe–Mn oxide, i.e. Pb bound to iron and manganese oxides in soil; (4) organic, i.e. Pb bound to stable complexes of organic and sulphide; and