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Origin and spatial distribution of heavy metals and carcinogenic risk assessment in mining areas at *You'xi* County southeast China

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ABSTRACT

An extensive study on the spatial distribution and source apportionment of heavy metals in soils and so by risk assessment at *You'xi* County, a major Pb–Zn mining area southeast China, was conducted in this contribution. A total of 93 soil samples were examined with the concentration of heavy metals (As, Cd, Cr, Cu, Hg, Pb, and Zn), pH, and soil organic matter (SOM) contents by using geostatistical approaches combined with geographic information system (GIS) analysis. The mean values of heavy metals were determined to be 7.9 ± 5.8, 12.8 ± 14.1, 80.4 ± 42.0, 34.4 ± 45.0, 0.12 ± 0.13 368.5 ± 873.6, and 369.6 ± 505.5 mg kg^{-1} (mean ± SD) for As, Cd, Cr, Cu, Hg, Pb, and Zn, respectively. Contents of all heavy metals present in the study area were considerably higher than their background values of provincial and national standards except for As. A principle component analysis revealed the main origin of heavy metals: soil parent materials for Cu, Pb, and Zn; atmospheric deposition during mining processes for Cr, and Hg; and human farming activities for Cd. Carcinogenic risk was assessed with an average value of 69.3×10^{-6} mg kg^{-1}, suggesting an average of 69 individuals per million people being predisposed to cancer. Meanwhile, the identification of heavy metal sources in agricultural soils might be beneficial to local soil protection and soil quality improvement.

1. Introduction

Soil plays a role of scavenger agent for heavy metals and adsorptive sink for environmental contamination in nature (Post, 1999; Okoro et al., 2012). Once heavy metals enter soil, they are difficult to be extracted or diluted out of the system, and become hazardous to organisms and soil ecosystem structure and function (Zhou and Song, 2004; Lambers et al., 2009). Since the late 20th century, soil pollution related to heavy metals has attracted increasing attention all over the world (Nriagu and Pacyna, 1998; Vermeulen et al., 2012), though it normally turns out not to be as intuitively visible as that of air or water pollution.

The spatial variability of soil properties includes variations in soil moisture, physical and chemical properties etc. Moreover, temporal and spatial variations of heavy metals relate to both natural variability of soils and human activities, thus to be considered as powerful tracers for monitoring the impact of human activity (Deng et al., 2012; Li et al., 2012). Indeed, heavy metal accumulation in soils from both natural and anthropogenic sources occurs in a same manner, which makes it somewhat difficult to identify and determine the origin of heavy metals in soil.

Heavy metals can be readily transferred into human body as a consequence of dermal contact, absorption, inhalation, and ingestion (Ferreira-Baptista and de Miguel, 2005; Chary et al., 2008). Moreover, heavy metals typically accumulate in human body due to their non–-biodegradable nature and long biological half–lives for elimination. For example, low–level of Pb exposure has been known to be harmful to enzyme systems involved in blood production, while high–level of Pb exposure affects the intelligence of humans (Babula et al., 2008). Due to the fact that soil pollution influences human health, a proper assessment of the potential hazard of heavy metals in a study area can be essentially vital. The study on soil pollution has been mainly concentrated in the total contents of various heavy metals and the contamination degree of soils, which are likely related to the biological absorption/uptake of heavy metals through food chain into the human, animals, and plants, and result in potential toxicity. In theory, there are no acceptable levels of exposure to carcinogenic substances. Heavy

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metals are ubiquitous in the environment and thus present in the diet and in the natural products. Generally, heavy metals flow into the human body through the following pathways: (a) feeding on crops with enriched heavy metals, (b) breathing contaminated soil dust in the air, (c) direct contact between contaminated soil and human skin, and (d) drinking (indirect). Among the seven heavy metals investigated in this study, carcinogenic elements As and Cd, with particularly important focus, have been analyzed to evaluate the health risk in the study area.

On the other hand, the rapid growth of mining industry in China, in the interest of satisfying the needs of economic growth, has produced significant environmental concerns including air, water, and soil pollution (Chen et al., 2008; Bian et al., 2012), which seriously influences food safety and the health of animals and humans. In this study, we investigate the mapping of heavy metal distribution and evaluate the carcinogenic risk at *You'xi* County, southeast China, where rich mineral resources are observed and a large number of Pb–Zn mines are developed. Several research targets has been successfully achieved in this study: (i) to reveal the physical and chemical characteristics of soils at *You'xi* County; (ii) to determine the concentration of seven heavy metals (As, Cd, Cr, Cu, Hg, Pb, and Zn) in soils; (iii) to analyze the interrelationships among heavy metals thus highlighting their anthropogenic origin; and (iv) to evaluate the carcinogenic risk in the study area.

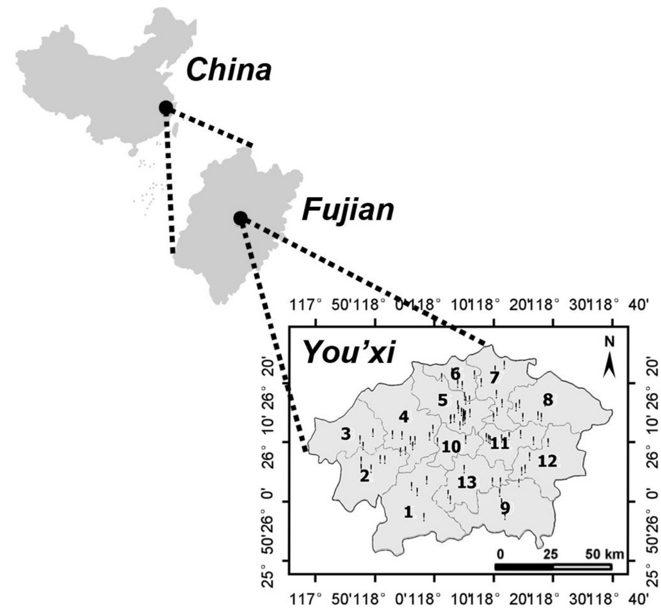

Fig. 1. Sketch maps of the study area with sampling spots. **1**, *Banmian*; **2**, *Xinyang*; **3**, *Guanqian*; **4**, *Xicheng*; **5**, *Meixian*; **6**, *Lainhe*; **7**, *Xibin*; **8**, *Yangzhong*; **9**, *Zhongxian*; **10**, *Chengguan*; **11**, *Xiwei*; **12**, *Tangchuan*; **13**, *Taixi*.

2. Materials and methods

2.1. Description of the study area

You'xi County (117°48′E–118°39′E, 25°50′N–26°26′N) is the second largest county of Fujian province, SE China with a north–south length of 72 km, west–east length of 88 km and a total area of 3463 km^2, among which 689.5 thousand acres of mountains, 56 thousand acres of cultivated land, and 110 thousand acres of water and other areas (Lü et al., 2016). Geologic structures of *You'xi* County are formed by repeated tectonic superposition with developed folds and faults in different periods. There are four main geomorphologic types including mountains and hills (northwest and southeast *You'xi*), intermountain basins, and valley plains, showing a subtropical monsoon climate with an annual mean temperature of 19.2 °C and average rainfall of 1620.6 mm. Main soil types in the study area are dominated by red soils with deep and moist layers, supplemented by yellow soils, paddy soils, fluvo aquic soils and lime soils. These favorable environmental conditions are suitable for agricultural farming and planting. The main profile system of *You'xi* County is controlled under Cathaysian and new Cathaysian structures, showing a north–to–east distribution, which brings *You'xi* rich mineral resources. A total of thirty–one kinds of minerals have been detected, including non–metallic minerals (limestone, marble, dolomite, granite, tonbarthite, pyrite, diorite, diabase, rhyolite, quartzite, sandstone, wollastonite, silica, kaolin, fluorite, pyrophyllite, coal, clay, etc.) and metallic minerals (sphalerite, galena, pyrrhotite, copper pyrite, iron pyrite, specularite, limonite, scheelite, chessylite, green schist, permeable epidote schist, diopside, hedenbergite, galenite etc.), with especially abundant Pb and Zn, having a proved reserves of more than two million tons that ranks the first in eastern China region.

2.2. Soil sampling

In order to study the spatial distribution of heavy metals at *You'xi* County, as well as their potential influences on the health of local residents, a total of 93 surface soil samples (0–20 cm) were collected, based on the distribution of Pb–Zn mining areas, different cultivate types, and congested population (Fig. 1). According to the regulation and norms promulgated by Ministry of Geology and Mineral Resources and the State Environmental Protection Administration (Evangelou et al., 2004), the samples were positioned through a mixed–points sampling method. Samples from five serpentine points were mixed and then chosen by inquartation, removing the debris and surface layer of grass, in order to take exactly equal amounts at each point. After mixing, ca. 1.0 kg of each soil sample was taken by using a stainless steel spade and stored in a self–sealing plastic bag. Cylindrical soil sampling depth was 0–40 cm, covering plough layer and subsurface with 5 cm of hierarchy. Among all soil samples, 24 were from sand and silt (25.8%), 26 from silt (28.0%), 23 from silty loam (24.7%), and 20 from clay loam (21.5%), primarily relating to farmland types. Soil samples were stored in clean glass bottles and sent to the laboratory for analysis. Sampling locations were positioned accurately by using the Global Positioning System (GPS). GIS software was used to produce spatial distribution maps and identify the potential sources of heavy metals in this study (Croner, 2003).

2.3. Physical and chemical analysis

Soil pH (± 0.1) was measured in a 1:5 soil–to–water suspension after stirring for 2 h. The soil organic matter (SOM) content of soils was determined by loss on ignition at 600 °C. The Cr, Cu, Pb, and Zn concentrations were determined by X–ray fluorescence spectrometry using pressed boric–acid–backed pellets of bulk samples. X–ray counts were converted into concentrations using a computer program based on a matrix correction method. The accuracy of determinations was checked based on certified internal reference material. The analytical precision, measured as relative standard deviations (RSDs), was below 5%. 1.0 g of soil was placed in a Teflon autoclave and treated in turn with 3.0 mL of HCl, 9.0 mL of HNO_3, 2.0 mL of HF, and 8.0 mL of $HClO_4$. Cd concentration was measured using a graphite furnace. As and Hg concentrations were determined using cold vapor atomic absorption spectrometry. Calibration was performed on each 10 sets of samples using prepared internal standards via the standard curve approach. Special care was taken into preparing and analyzing samples to minimize contamination from air, glassware, and reagents. Controlled measurements on internal reference material, reagent blanks, and duplicated soil samples selected randomly from the set of available samples were applied to ensure quality assurance/quality control (QA/QC). The average deviation between duplicate samples was ca. 6.7%.

The sequential extraction method was applied according to the reported procedure (Tessier et al., 1997), by which heavy metals in soils