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Sources of heavy metal pollution in agricultural soils of a rapidly industrializing area in the Yangtze Delta of China

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ABSTRACT

The rapid industrialization and urbanization in developing countries have increased pollution by heavy metals, which is a concern for human health and the environment. In this study, 230 surface soil samples (0–20 cm) were collected from agricultural areas of Jiaxing, a rapidly industrializing area in the Yangtze Delta of China. Sequential Gaussian simulation (SGS) and multivariate factorial kriging analysis (FKA) were used to identify and explore the sources of heavy metal pollution for eight metals (Cu, Zn, Pb, Cr, Ni, Cd, Hg and As). Localized hot-spots of pollution were identified for Cu, Zn, Pb, Cr, Ni and Cd with area percentages of 0.48 percent, 0.58 percent, 2.84 percent, 2.41 percent, 0.74 percent, and 0.68 percent, respectively. The areas with Hg pollution covered approximately 38 percent whereas no potential pollution risk was found for As. The soil parent material and point sources of pollution had significant influences on Cr, Ni, Cu, Zn and Cd levels, except for the influence of agricultural management practices also accounted for micro-scale variations (nugget effect) for Cu and Zn pollution. Short-range (4 km) diffusion processes had a significant influence on Cu levels, although they did not appear to be the dominant sources of Zn and Cd variation. The short-range diffusion pollution arising from current and historic industrial emissions and urbanization, and long-range (33 km) variations in soil parent materials and/or diffusion jointly determined the current concentrations of soil Pb. The sources of Hg pollution risk may be attributed to the atmosphere deposition of industrial emission and historical use of Hg-containing pesticides.

1. Introduction

Heavy metal pollution in soils is a growing risk that is of great concern due to the potential negative impacts of heavy metals on human health and the environment (Yanez et al., 2002). Consequently, areas that are polluted by heavy metals and possible heavy metal sources must be identified to develop pollution control policies, effective soil remediation and management recommendations.

In soils, heavy metals mainly originate from the weathering of soil parent material and from external inputs resulting from human activities, such as industrial activities, the application of agricultural chemicals, and the improper disposal of waste (Gil et al., 2004; Romic and Romic, 2003; Zhao et al., 2008). Heavy metals are natural components of the Earth's crust, and the natural concentrations of soil heavy metals tend to remain low (Rodríguez Martín et al., 2013). However, over the last few decades, the anthropogenic inputs of several heavy metals into soils have exceeded the natural heavy metal inputs from pedogenesis, even at a regional scale (Facchinelli et al., 2001). Facchinelli et al. (2001) analyzed the effects of anthropogenic and natural influences on the heavy metal concentrations of cultivated soils in the Piedmont (northwest Italy) using multivariate statistics and geostatistical approaches. They found that the Cr, Co and Ni concentrations were mainly controlled by the parent rocks, whereas Cu together with Zn, and Pb alone were controlled by anthropogenic activities. The As, Ni and Hg concentrations in the topsoil from the Pearl River Delta of China mainly originated from the soil parent materials, but the Cd, Zn, Cu, Pb and Cr concentrations largely originated from anthropogenic sources (Hu and Cheng, 2013). Among the various anthropogenic sources, soil heavy metal pollution is often correlated with the degree of current and/or historical industrialization, or urbanization and the intensity of chemical use

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in agriculture. For example, in the Duero basin of Spain, Hg inputs from human activities associated with airborne emissions and deposition from industrial plants are observable at local scale. However, agricultural practices have not altered the natural content of Cd, Cr, Ni, Pb, Zn and Cu in the agricultural soils in this basin (Nanos and Rodríguez Martín, 2012). In addition, an analysis of heavy metals in the agricultural lands surrounding an abandoned Pb–Zn mine in a karst area of the Guangxi Zhuang Autonomous Region in Southwest China demonstrated higher Cd, Cu, Pb, Zn and Hg pollution risks due to the Pb–Zn mining operations, in particular when the mine operated in the karst environment (Huang et al., 2012). The source identification of heavy metals in the urban soils of Changchun (northeast China) indicated that the enrichments of soil Cu, Zn, and Pb mainly resulted from vehicle emissions, with Zn primarily resulting from vehicle tires, Hg and As primarily resulting from coal combustion, and Cd primarily resulting from industrial sources (Yang et al., 2011). The sources of Ni, Cu, Pb and Zn in urban soils from Kowloon (Hong Kong) were closely linked to road junctions, major roads, and industrial buildings, and to areas with concentrated heavy metal pollution, which mainly occurred in old industrial and residential areas (Li et al., 2004). In the highly urbanized and commercialized Hong Kong Island area, hot-spots of Cd, Co, Cr, Cu, Ni, Pb and Zn were closely related to areas with high traffic volumes (Lee et al., 2006). A comparison of the heavy metal concentrations in arable soils from the western areas of the Andalusian Autonomous Community (southeast Spain) and greenhouse soils from the Almería province suggested that heavy metal hazards were particularly evident in greenhouse soils due to the widespread use of agrochemicals in greenhouse farming (Rodríguez Martín et al., 2013). In addition, a study regarding heavy metal concentrations in vegetable fields revealed that the intensity of agricultural chemical use influenced the heavy metal concentrations in agricultural soils (Chen et al., 2009).

Jiaxing is located in the northeastern region of Zhejiang Province in the central part of the Yangtze Delta of China. With the rapid increases in industrialization, urbanization and intensive agriculture in the last three decades, Jiaxing has become one of the most developed areas in the Yangtze Delta. However, the soil quality in Jiaxing has been impacted by the rapid transformation from an agricultural to industrial economy since the implementation of economic reform and open policy in the 1980s. Therefore, it is important to identify areas of soil heavy metal pollution and potential pollution sources in Jiaxing because this knowledge can be used to plan management strategies for achieving better environmental quality in similar areas of China.

2. Materials and methods

2.1. Study area

The study area is Jiaxing, a prefecture-level city in the Zhejiang Province of East China (Fig. S1). Jiaxing covers a total terrestrial area of 3915 km^2. With a subtropical monsoon climate, the area has a mean annual temperature of 15.9 °C and 1060–1180 mm annual rainfall. The topography of the area is characterized by plains that are approximately 4–5 m above sea level, and the soil types are mainly paddy soils (StagnicAnthrosols) and fluvo-aquic soils (AquicCambosols).

Jiaxing has been one of the fastest developing economic areas in the Yangtze Delta Region since the 1980s. The area has thousand years of paddy rice planting history and currently the main crops grown in this region include rice paddy, rapeseed and vegetables. The main industries in the area include the chemical, paper making, printing and dyeing, leather-making (this region is one of the world's largest exporters of leather goods), cement and electroplating industries.

2.2. Soil sampling and chemical analysis

Based on the predominant crop distribution, soil type, and possible sources of soil pollution, 230 surface soil samples (0–20 cm) were collected across the study area (Fig. S1) using a relatively even sampling distribution. When sampling, the composite samples were collected from the site using a stainless steel auger. Each composite sample from the sites consisted of five subsamples (quincunx sampling pattern). The subsamples collected from each site were fully mixed and then cone and quartered to about 1.5 kg each. The locations of the sampling sites were recorded using GPS and environmental information regarding the land cover around the sites and the possible sources of soil pollution were checked and recorded.

The soil samples were air-dried, ground, and sieved by passing through a 0.15-mm (100-mesh) polyethylene sieve prior to soil heavy metal analysis. The soil total Cu, Zn, Pb, Cr, Ni, and Cd concentrations were determined using inductively-coupled plasma mass spectrometry (ICP-MS, POEMS 3, Thermo Electron, USA), and the total Hg and As concentrations were determined using applying atomic spectro-fluorophotometer (AFS, XGY-1011A, IGGE, China). Soil standard reference materials (GBW07401, GSS-1) and replicate analyses were used for quality control. Overall, the soil contained 21.0 ± 0.67 mg Cu kg^{-1}, 641 ± 24.5 mg Zn kg^{-1}, 101 ± 7.80 mg Pb kg^{-1}, 64.5 ± 3.84 mg Cr kg^{-1}, 20.2 ± 0.65 mg Ni kg^{-1}, 4.27 ± 0.248 mg Cd kg^{-1}, 32.0 ± 2.56 mg Hg kg^{-1}, and 34.1 ± 2.24 mg As kg^{-1} relative to the certified reference concentrations of 21 ± 2 mg Cu kg^{-1}, 680 ± 39 mg Zn kg^{-1}, 98 ± 8 mg Pb kg^{-1}, 62 ± 6 mg Cr kg^{-1}, 20.4 ± 2.7 mg Ni kg^{-1}, 4.3 ± 0.6 mg Cd kg^{-1}, 32 ± 6 mg Hg kg^{-1}, and 34 ± 5 mg As kg^{-1}. The relative standard deviation (RSD) of the duplicate analyses were 0.7–3.8 percent for Cu, 3.8–8.9 percent for Zn, 0.9–6.4 percent for Pb, 0.5–8.2 percent for Cr, 1.2–7.1 percent for Ni, 0.4–12.3 percent for Cd, 4.8–16.4 percent for Hg, and 1.9–8.5 percent for As. The analysis results of the reference materials fluctuated within the allowable ranges of the certified values, and the RSDs of the duplicate analysis were less than the allowed upper-limits of the TSSEM (The Technical Specification for Soil Environmental Monitoring, HJ/T 166-2004) (China Ministry of Environmental Protection, 2004).

2.3. Potential risks of soil heavy metal pollution

In this study, the potential heavy metal pollution risk is defined as the measured metal concentrations that exceed the regulatory limits for background concentrations according to the Chinese Environmental Quality Standard for Soils (CEQS) (GB 15618-1995). The corresponding background values for Cu, Zn, Pb, Cr, Ni, Cd, Hg, and As are 35, 100, 35, 90, 40, 0.2, 0.15, and 15 mg kg^{-1}, respectively (China Ministry of Environmental Protection, 1995).

Areas with potential risk of heavy metal pollution were identified from the probability maps of the soil heavy metal concentrations that exceeded the regulatory limits for the background values in the CEQS and the different critical probabilities (0.95, 0.9 and 0.8 in this study). To obtain the probability maps, sequential Gaussian simulation (SGS) focusing on the global statistics reproduction (such as sample histogram) and spatial structures (the semivariogram model) (Deutsch and Journel, 1998) was used to generate 1000 equiprobable realizations (maps) for each of the considered heavy metals. The SGS used in this study is a conditional simulation because the generated realizations of the heavy metals honour the measured values at their sampling locations. The probability that the soil heavy metal concentration $z(x')$ at location x' exceed a given regulatory limit of the heavy metal background value z_t, denoted as $Prob[z(x') > z_t]$, were calculated based on the following equation:

$$Prob[z(x') > z_t] = n(x')/1000$$

where $n(x')$ is the number of realizations that the simulated heavy metal values generated by the SGS exceed the regulatory limit of heavy metal background value in each of the 1000 realizations (Zhao et al., 2008). Once a critical probability P_c is given, the areas with potential risk of heavy metal pollution can be obtained using $Prob[z(x') > z_t] \geq P_c$.

2.4. Factorial kriging analysis (FKA)

To interpret and identify potential sources of soil heavy pollution at different spatial scales that can be perceived by the sampling design, multivariate FKA (Goovaerts, 1997) was used to decompose the spatial variability structures of the eight heavy metals into spatial components with different scales. For the FKA, a nested variogram model encompassing three basic variogram functions with different ranges (one nugget effect and two spherical models with ranges of 4 km and 33 km) was used to fit the linear model of co-regionalization (LMC) to obtain the co-regionalization matrix (positive semi-definite matrix). Principle component analysis (PCA) was then applied to the resulting LMC matrices at different scales/ranges to explore the relationships between the soil heavy metals concentrations at each scale. The regionalized factors (spatial principle component) yielded from the PCA of the co-regionalization matrix at each spatial scale were mapped using co-kriging. A number of detailed descriptions regarding FKA can be found in the literatures, for example Goovaerts (1997), Webster and Oliver (2001), Zhao et al. (2010), Nanos and Rodríguez Martín (2012).

3. Results and discussion

3.1. Soil heavy metal concentrations

The descriptive statistics for the heavy metal concentrations in agricultural soils in Jiaxing (Table 1) indicate that the eight heavy