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Heavy metal contamination and health risk assessment for children near a large Cu-smelter in central China

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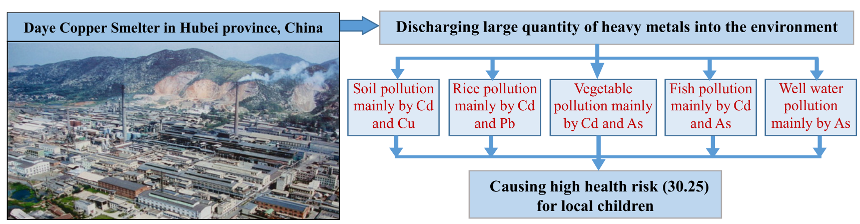
HIGHLIGHTS

- A comprehensive heavy metal pollution and health risk assessment of soil, crop, well water and fish was conducted.
- Elevated concentrations of heavy metals were found in the soil, crop, well water and fish.
- Health risk of heavy metal pollution was high for local children.
- Consumption of crops was the major contribution to risk.
- Most of the risks were due to Cd, As and Pb pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Nonferrous metallurgy is causing significant concerns due to its emissions of heavy metals into environment, degrading environmental quality, and consequently posing high risks to human health. In this study, the concentration levels of Cadmium (Cd), Copper (Cu), Lead (Pb), and Arsenic (As) were investigated in soil, crop, well water, and fish samples collected around the Daye Copper Smelter in Hubei province, China, and the potential health risks were assessed for local children. The results showed that soils near the smelter were heavily polluted by Cd, Cu, Pb, and As, with the mean concentrations of 4.87, 195.26, 92.65, and 35.84 mg/kg, respectively, which were significantly higher than the values of soil Cd (0.18 mg/kg), Cu (32.84 mg/kg), Pb (28.46 mg/kg), and As (13.65 mg/kg) in the reference area ($p < 0.001$). The concentrations of Cd and As in vegetable samples collected from smelter-affected area exceeded the maximum permissible level (MPL) for food in China by 82% and 39%, respectively. The concentrations of Cd and Pb in rice grain harvested from smelter-affected area were 9.35 and 1.35 times higher than the corresponding MPL, respectively. The concentrations of Cd, As, and Cu in fish muscle from smelter-affected area exceeded the national MPL by 72%, 41%, and 24% of analyzed samples, respectively. The concentrations of Cd ($p < 0.05$) and As ($p < 0.01$) in well water were significantly higher in the smelter-affected area than those in the reference area, respectively. The health risks to local children in the smelter-affected area were 30.25 times higher than the acceptable level of 1, and most of the risks were resulted from Cd (46%), As (27%) and Pb (20%). The intake of crops was a major source (78%) to health risks for local children.

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1. Introduction

Heavy metal (HM) pollution caused severe environmental and health-related problems around the world (Spurgeon et al., 2011). They are particularly hazardous due to their persistence and toxicity, and adverse effects to the environment and human health (Cao et al., 2014). In China, about 20 million ha of farmland and 12 million tons of grains were contaminated by HMs every year (G. Li et al., 2011; Z.G. Li et al., 2011). A large portion of this pollution came from metal smelting (Li et al., 2014). HMs emitted from those smelters are transferred to different environmental media, such as air, soil, crop, dust and water, can eventually enter the human bodies through direct ingestion or food chains, and pose potential threats to human health (Carrizales et al., 2006; Spurgeon et al., 2011). Generally, Cd, As and Pb are considered as potential carcinogens and are associated with etiology of many diseases, especially cardiovascular, liver, kidney, bladder, nervous system, blood and bone diseases (Cai et al., 2015). Although Cu is an essential trace element, its excessive concentration can threaten human health (Zhou et al., 2018). Recent studies also showed that Cu toxicity could induce changes in cellular activities, such as regulation of lipid metabolism, neuronal activity, gene expression and resistance of tumor cells to chemotherapeutic drugs (Gaetke et al., 2014). Elevated contents of HM in air, soil, dust, water and plant in smelter-affected areas have been frequently reported in many countries, including France (Douay et al., 2013), England (Spurgeon et al., 2011), Australia (Mackay et al., 2013), and China (Li et al., 2014). Many previous studies reported high contents of HMs in the urine and blood samples of local residents, particularly children living near metal smelters (Cui et al., 2005; Spurgeon et al., 2011).

Metal smelting was considered as one of the most important anthropogenic sources of HM emission (Zheng et al., 2007). Cu, Pb, As and Cd had similar geochemical characteristics, and co-existing in Cu ore together. During Cu smelting process, HMs in Cu ores would be emitted into the surrounding environment via waste gas, waste water, and waste residue. Therefore, their pollution to the surrounding environment from those metal smelters had been widely studied (Douay et al., 2013; Mackay et al., 2013). Smelting activities of the Daye Copper Smelter (DCS), which have been operating for >60 years, discharged a large amount of smelt waste into the surrounding environment without any proper treatment. Previous studies found that soil (Du et al., 2015), river water (Wang and Wang, 2007), and sediment (Zhang et al., 2014) near the smelter were heavily contaminated by HMs. On the other hand, few studies systematically delineated the pollution scope of different environmental media, the extent of human exposure via multi-pathways, and the potential health consequences in the studied area and other areas near large copper smelters around the world (Zhou et al., 2018). Children are especially sensitive to HMs poisoning because of the child-specific physiological and behavior patterns (Cao et al., 2015). Health-related incidents for children such as Cd, As and Pb poisoning have attracted widespread attention (Cao et al., 2014), particularly around smelter-affected areas (Carrizales et al., 2006; Spurgeon et al., 2011). Therefore, assessing health risks for exposure to various HMs through different environmental media and the main pathways in smelter-affected area would be very important for protecting children's health. The aims of the study were: (1) quantify the content levels of HMs in multiple environmental media (i.e., soil, crop, well water, and freshwater fish) near DCS, and (2) assess the daily intakes and health risks of HMs to local children.

2. Materials and methods

2.1. Studied area

Daye city (114°31′–115°20′, 29°40′–30°15′N) is situated at the southeast in Hubei province, central China. The climate represents a temperate monsoonal continent with average annual rainfall of 1385.9 mm and average temperature of 16.9 °C. The primary wind direction is from southeast to northwest. As one of the largest Cu-smelter in China, the DCS located at the north of Daye city (Fig. 1). It was built in 1953 and produces about 250,000 t Cu every year (Wang and Wang, 2007). During Cu smelting process, Cd, Pb, As and Cu are emitted into the surrounding environment in great quantities via atmospheric deposition, sludge applications, and wastewater irrigation. The discharge loadings of Cd and Pb are approximately 0.5 t and 2 t by wastewater annually, respectively (Zhang et al., 2014). According to our field survey, these areas near the north of the DCS are mountains, and villages mainly concentrated in the southwest of the DCS. In addition, some villages had been discarded because of serious pollution from the DCS. Therefore, remaining ten villages (V1, V2, V3, V4, V5, V6, V7, V8, V9, and V10) near the DCS were as the exposed area, and one village (Liurenba) which was not polluted by the DCS as the reference area (Fig. 1). According to our survey, V8, V9, and V10 were mainly affected by atmospheric deposition from the smelter since they were under the direction of the dominant wind, and other villages were mainly contaminated by wastewater irrigation and atmospheric deposition from the smelter.

2.2. Sample collection and analysis

2.2.1. Questionnaire survey

A questionnaire survey was conducted in the study area to obtain key risk factors, such as the dietary behavior and the weight of the local children. The information extracted from the questionnaire included the intake rate of each crop, fish and drinking water per day per child. In total, 65 children who were native-born and aged from 3 to 7 years old participated in the questionnaire survey. The average daily intake rate of each crop and fish over a whole year was calculated (Chen et al., 2018).

2.2.2. Field sampling

Soil samples (1 kg) were obtained from the upper horizon (0–20 cm in depth) at 136 sites, including 102 from the exposed area and 34 from the reference area. At each site, soils were randomly sampled at 3–5 locations and bulked together to form a composite sample (Cai et al., 2015). In the study area, the drinking water was well water. A total of 24 well water samples (20 from the exposed area, and 4 from the reference area) were collected with 1 L acid-washed polyethylene bottles from local families. During sampling, two drops of ultrapure nitric acid were added into water samples, then refrigerated and stored at −20 °C (Cao et al., 2014).

Standing food crop samples including maize, rice, carrot, ipomoea, radish, lettuce, red cabbage, cabbage, pakchoi and celery were also obtained. 18 maize grain, 22 rice grain, 13 carrot, 15 ipomaea, 13 radish, 13 lettuce, 13 red cabbage, 14 cabbage, 15 pakchoi, and 12 celery samples were collected (1 kg) directly from the land with paired soil samples. At each site, 3–5 sub-samples were collected and mixed to form one representative sample (Ji et al., 2013). Additionally, 44 freshwater fish samples including 10 Wuchang carp, 14 grass carp, 11 crucian carp, and 9 bighead carp were obtained from ponds and rivers, because they were consumed relatively in high amounts in the area. All fish samples were washed thoroughly with fresh water for the sake of removing mud and other fouling substances, and were stored in clean polyethylene bags with ice immediately and frozen at −20 °C (Zhong et al., 2018). The types and numbers of samples in every village were shown in Table S1.

2.2.3. Sample treatment and analysis

The water samples were filtered with 0.45 μm filter paper and stored at 0–4 °C before element analysis (Cai et al., 2015). After being air-dried at room temperature for two weeks (ISO-11464, 2006), ground, and sieved with a 1 mm stainless-steel mesh, soil samples (0.1 g each) were prepared with acid digestion (Cao et al., 2015). After washed