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An ecological risk assessment of heavy metal pollution of the agricultural ecosystem near a lead-acid battery factory

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ABSTRACT

Lead-acid battery factories can lead to heavy metal pollution of nearby agricultural ecosystems. To assess the ecological risk and to understand the transport processes of heavy metals in an agricultural ecosystem, the concentrations of heavy metals in agricultural soils (As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn) and in wheat plants at different stages of growth (Cd, Pb, and Zn) were investigated near the Fengfan lead-acid battery factory in Baoding, China. Certain indices, including the contamination factor (C_f), pollution load index (PLI), hazard quotient (HQ) and hazard index (HI), were used to assess the ecological risk of the agricultural soil and human health risk. The results show that the mean concentrations of the heavy metals studied in the surface soils were all lower than the guideline values of China. However, the C_f values of Pb ranged from 2.8 to 5.3, indicating that the most examined soils were strongly impacted by Pb. The PLI range was 0.6–4.2, indicating moderate contamination levels for those most examined soil samples. The As, Cr, Cu, Mn and Ni in the studied area were geogenic elements and Cd, Pb and Zn were mainly derived from the lead-acid battery factory based on the results of a principal component analysis (PCA) and heavy metal spatial distribution. The elements Cd, Pb and Zn entered the soil though atmospheric deposition and accumulated mainly as a bioavailable fraction at the surface. With respect to wheat berries, only the mean Pb content exceeds the tolerance for Pb at 0.84 mg/kg, indicating a potential risk. In relation to health risk, the HQs of individual heavy metals for different exposure populations were all lower than 1, showing a much lower potential health risk. Nevertheless, the potential health risk due to the cumulative risk of all heavy metals through the consumption of wheat berries exceeded unity for rural populations.

1. Introduction

Heavy metals are easily discharged into an agricultural ecosystem due to common human activities, and this result in an adverse impact on the ecosystem. An agricultural ecosystem has a close relationship with human health, thus, heavy metal pollution of agricultural ecosystem has been of concern throughout the world (Bermudez et al., 2011, 2012; Pandey and Pandey, 2008). Heavy metals, as traditional pollutants, are highly toxic, non-degradable and bioaccumulative. Although some heavy metals such as Zn and Cu are essential elements for plants and humans as catalytic components of proteins and enzymes, the great majority of them do not have any beneficial physiological function, and their excess accumulation in the human body can lead to many diseases (Godt et al., 2006). For example, accumulation of Cd in the human body can lead to kidney, bone and pulmonary damage (Godt et al., 2006); Pb can damage the central nervous system, kidneys and blood system (Tong et al., 2000), etc. The diet is a main route of exposure to heavy metals for most people except for occupational exposures at related industries (Sharma et al., 2008). There are many famous cases of heavy metals poisoning through the food chain such as "Itai-Itai" disease in Japan in the 1930s and "minamata disease" in Japan in the 1950s. It has been well known that agricultural soils contaminated by heavy metals and atmospheric metal deposition can result in high levels of heavy metals in crops (Bermudez et al., 2012; Harrison and Chirgawi, 1989; Pandey and Pandey, 2008; Sharma et al., 2008). Accordingly, the ecological

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assessment for heavy metal pollution of agricultural ecosystems is important.

The heavy metal pollution of an agricultural ecosystem is often caused by waste water irrigation, solid waste disposal, vehicular exhaust, fertilisation, industrial activities, etc. (Cheng, 2003; Khan et al., 2008; Liu et al., 2011, 2012). Among these pollution sources, industrial activities are the dominant sources of heavy metals near factories. Kabala and Singh (2001) reported that, in the vicinity of a copper smelter in Poland, the concentrations of Cu, Pb and Zn in the surface soils were significantly higher than their concentrations in the subsurface soils. It was reported that industrial waste can lead to heavy metal pollution of the surrounding soils (Gowd et al., 2010). In China, with the rapid industrial development of recent decades, the heavy metal pollution of soil has become more and more severe. Production of lead-acid batteries is one of the main sources of heavy metals. In China, production of lead-acid battery output is very high, which was 90.77 million kilovolt-ampere-hour (kVAh) accounting for about one-third of the total world output in 2008 (Chen et al., 2012). The Fengfan lead-acid battery factory is famous in China. It was been founded more than a decade ago in Baoding City. The long-term production of lead-acid batteries may cause heavy metal pollution of the agricultural ecosystem near the factory.

Wheat is one of the main crops grown for human consumption in the north of China, which provides some carbohydrates, proteins and certain inorganic micronutrients for the human body. Therefore, high concentrations of heavy metals in the wheat berry may lead to severe potential risk for human health. To guarantee food safety, the Food and Agriculture Organization (FAO), World Health Organization (WHO), the Health Ministry of China and other organisations strictly regulate the allowable concentrations or maximum permitted concentrations of toxic heavy metals in food-stuffs (MHPRC, 1992, 2005; Codex Alimentarius Commission, 1995). The hazard quotient (HQ) and hazard index (HI) have also been proposed by the United States Environmental Protection Agency (USEPA) to assess the potential human health risk induced by heavy metals (USEPA, 1989). This method compares the estimated dose of a contaminant with the reference dose and has been widely used to assess potential human health risk (Bermudez et al., 2011; Huang et al., 2008).

In this paper, the objectives were (i) to obtain As, Cd, Cr, Cu, Mn, Ni, Pb and Zn distributions, bioavailability and mobility in agricultural soils near a lead-acid battery factory; (ii) to investigate Cd, Pb and Zn concentrations in wheat and the heavy metal relationship between the soil and plants; and (iii) to assess the ecological risk to the agricultural ecosystem and the human health risk induced by Cd, Pb and Zn.

2. Materials and methods

2.1. Studied area and sampling

Baoding city, located in the North China plain, has a temperate monsoon climate with an average annual temperature and rainfall of 12 °C and 550 mm, respectively. Agricultural soil samples were collected near Fengfan's non-ferrous metal branch (the lead-acid battery factory) in Baoding city, which was founded in 1995. This general manufacturing plant mainly produces lead alloys, lead-acid batteries and accessories. The annual production capacity of this battery factory has reached 3.5 million KVAh.

The soil samples were collected from the farmland situated to the east of the factory, because it was surrounded by residential areas and roads to the west, north and south. To the north of the study area, there is a pit, into which some household garbage and agricultural waste are deposited. The specific locations of the sampling sites were shown in Fig. 1. A total of 34 surface soil samples, including one background soil sample and 33 soil samples for analysis to the east of the lead-acid battery factory, were collected from the topsoil (0–10 cm) at each sampling site. The location of the background soil site is to the east of the factory approximately 500 meters (N 38°47′32.10″, E 115°30′8.18″). Soil core samples of 50 cm length were collected at sites S4, S5, S6, S11, S12 and S13 using a soil column sampler (Beijing New Landmark Soil Equipment Co. Ltd.) and sliced into specimens with a height of 5 cm. All soil samples were air-dried, grounded into a fine power and sieved through a 0.149 mm polyethylene sieve for further analysis. Wheat samples were also collected at the same sites as the soil samples. In all, 33 wheat plants at the tillering stage, 22 wheat plants at the jointing stage and 22 wheat berry samples were collected. The wheat samples were first washed with tap water to eliminate ash on the leaves and soil on the roots, and then washed with distilled water. The wheat plants were divided into above-ground parts, below-ground parts and grains, and then dried at 60 °C in an oven to constant weight. The dried wheat samples were ground into a powder for analysis.

2.2. Chemical analysis

The main physicochemical properties of the surface soil samples were characterised by the following methods: soil pH was measured using a pH meter (Mettler Toledo FE20, Switzerland) (soil:water = 1:2.5); organic matter (OM) was measured by the $K_2Cr_2O_7$ oxidation method (Nanjing Institute of Soil Science, 1978); cation exchange capacity (CEC) was investigated by the $BaCl_2$ compulsive exchange method (Gillman and Sumpter, 1986) and particle-size distribution was obtained using a laser particle size analyser (Microtrac S3500, America). The soil samples were digested with HNO_3–$HClO_4$–HF (3:1:1, v/v), and the concentrations of heavy metals were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES) (Jarrell-ASH ICAP-9000, USA). The wheat samples were digested with H_2O_2–HNO_3 (1:1, v/v) and the contents of Cd, Pb and Zn were determined similarly with ICP-AES. The analytical quality control was based on the geochemical standard soil (GSS-1 and GSS-2), the certificate of the certified reference material "bush twigs and leaves" (GSV-1) and wheat flour (GBW08503b) provided by the National Standard detection Research Center of China. In the process of soil and plant sample digestion, each batch of samples included some standards and one blank in order to assure the quality. The analytical results and the certified values of the standards shown in Supplementary materials (Suppl. Table 1) did not differ significantly, which suggested that the data obtained is credible.

The Cd, Pb and Zn speciation of the six soil cores was determined by following the modified Community Bureau of Reference (BCR) sequential extraction procedure. The modified BCR method can be briefly described as follows: For the exchangeable and carbonates fraction (F1): 20 mL of 0.11 mol/L acetic acid solution was added to 0.5 g soil samples and shaken for 16 h at 22 ± 5 °C. The extract was separated from the solid residue by centrifugation at 5000 × g for 20 min. For the reducible fraction (F2): 20 mL of 0.1 mol/L hydroxylamine hydrochloride solution adjusted to pH 2.0 with HNO_3 was added to the residue from step 1 in the centrifuge tube, and the mixture was shaken at 22 ± 5 °C for 16 h. The extract was separated as in step 1. For the oxidisable fraction (F3): 5 mL of 8.8 mol/L H_2O_2 was added to the residue from the second step and digested for 1 h at 22 ± 5 °C and for 1 h at 85 ± 5 °C until the volume was reduced to approximately 1.5 mL. Another 5 mL of H_2O_2 was added, and digested for 1 h at 85 ± 5 °C until the volume was reduced to 1 mL. The residue was extract with 25 mL 1 mol/L ammonium acetate solution adjusted to pH 2.0, and shaken for 16 h at 22 ± 5 °C. The extract was separated as described above. The full details of the procedure have been previously reported (Rauret