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Original article

Temporal and seasonal variations of As, Cd and Pb atmospheric deposition flux in the vicinity of lead smelters in Jiyuan, China

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ABSTRACT

Atmospheric deposition from non-ferrous mining and smelting is one of the dominant sources of heavy metal pollution in soil. Jiyuan City in Henan Province, China produces about 900 000 tonnes of lead annually. Heavy metal soil contamination and elevated blood lead levels (BLLs) of local children in Jiyuan have been reported. This work investigated As, Cd and Pb deposition fluxes over 17 consecutive months at collection sites about 1000 m from a major lead smelter in Jiyuan. Mean As, Cd and Pb deposition fluxes were 17.2, 3.45 and 88.8 mg/m^2/(30 d), respectively, lower values occurred from July to September during the traditional rainy season. Decreasing deposition fluxes of Cd and Pb were observed during the 17 month period, while As increased in the same period. Deposition fluxes of As, Cd and Pb of the sites near the smelter were 22.6, 29.2 and 29.4 times of those of a clean background site (0.762, 0.118 and 3.03 mg/m^2/(30 d), respectively) far away from the smelter. Annually, the deposition enriches agricultural soil (0–20 cm plow zone) at the sampling sites with 0.805, 0.161 and 4.16 mg/kg As, Cd and Pb, respectively.

1. Introduction

Nonferrous metal mining and smelting is one of the most significant sources of heavy metal contamination of soils (Bermudez et al., 2012; Li et al., 2014a; Luo et al., 2009). Historic lead (Pb)/zinc (Zn) mining and smelting in some areas of south China have resulted in contamination of soil, water and river sediments with arsenic (As), cadmium (Cd), Pb and other trace elements in provinces of Hunan, Guangdong, Guizhou and Yunnan (Li et al., 2015a; Williams et al., 2009; Xie et al., 2014; Zhao et al., 2015). However, in recent years, Henan Province in north China surpassed other provinces and became the largest Pb producer in China.

Main lead smelting plants in Henan Province lie in cities of Anyang, Jiyuan and Sanmenxia in north and northwest Henan. In recent years, Henan Province produced about 1.5 million tonnes of lead annually (ZGCYXX, 2014), with 0.9 million tonnes from Jiyuan City. Very high blood lead levels (BLLs) have been found in children living near smelters in Jiyuan, Anyang and Sanmenxia in Henan Province (Table 1). High concentrations of heavy metals were also found in soils near some smelters in Henan (Cheng et al., 2014; Li et al., 2015b). Analysis of 65 soil samples collected from farm lands near the Yubei Gold and Lead Co. ltd in Anyang found the median concentrations of total Pb and Cd were 96.9 and 5.00 mg/kg, respectively (Cheng et al., 2014), while soil samples collected from farm land about 700 m from the Yuguang Gold and Lead Co. ltd had total Pb and Cd concentrations of 261 and 2.65 mg/kg, respectively (Li et al., 2015b). These farm land soils are annually plowed to a depth of 20 cm, which causes a dilution of atmospheric deposition placed on the soil surface.

There is no observable evidence of solid or liquid waste from the smelters directly entering farm lands in the vicinity of the smelters in Henan Province. Thus, atmospheric deposition is the dominant pathway through which the heavy metals from the stacks enter the

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Table 1
High blood lead levels (BLLs) of children living near lead smelters in Henan Province reported in the media.

Location	Year	Smelter	Blood lead level	Symptom	References
Beitian Village, Anyang	2004	Yubei	82 children had BLL > 100 μg/L, reported values include 214, 255, 527, 536, 556 and 648 μg/L	Stomachache, fever	ZGW, 2004
Yuling township, Sanmenxia	2011	Zhicheng	Of 350 children, 26 children had BLL < 100, 284 had BLL ≥ 100 and <199, and 29 children had BLL ≥ 200 and <249, the remaining 16 children had BLL ≥ 250 μg/L.	Vomiting, hyperactivity, easy to cry	ZGJJW, 2012
Shibing, Jiyuan	2009	Yuguang	451 children had BLL > 100 μg/L among 452 children, 73 of them had BLL > 450 μg/L. Maxium = 636 μg/L	Hyperactivity	ZGW, 2009
Kejing, Chengliu and Sili townships, Jiyuan	2009	Yuguang, Jinli and Wanyang	1008 of 3108 children had BLL > 250 μg/L		ZGW, 2009

soils in the vicinity of the smelters. The emission particulate matter from the smelters deposit on the soil and enrich the soil with toxic elements, likewise the particulate matter can impact local residents through inhalation and dust ingestion.

Despite vast literature studies about heavy metal contamination of soils near the Pb/Zn mining and smelting areas of China (Cheng et al., 2014; Li et al., 2014a; Teng et al., 2014; Zhang et al., 2012), very limited information is available about atmospheric deposition from the smelters. Atmospheric deposition is a process connecting the smelter stack with nearby soil, which in turn acts as a sink for heavy metals. The peak emission period of the lead smelters in Jiyuan likely occurred in about 2008–2009. Around this time, many children living near the smelters exhibited symptoms of Pb toxicity and high BLLs (Table 1). After the discovery of Pb toxicity, many smelting plants or production lines employing a sintering technique were forced to shut down or modify the smelting process to capture emissions. As a result, the atmospheric emission of heavy metals from the smelters in the Jiyuan area immediately decreased, but was not fully eliminated.

The objectives of this work were to investigate the current temporal and seasonal deposition fluxes of As, Cd and Pb near a major lead smelter in Jiyuan, Henan Province, over a 17-month period to determine the enrichment of As, Cd and Pb in local soil from the deposition.

2. Materials and methods

2.1. Study area description

The air particulate samples for this study were collected from Jiyuan in northwest Henan Province in northern China (Fig. 1). Urban Jiyuan lies to the south of the Taihang Mountain, with an elevation of about 140–150 m above sea level (Tuo et al., 2012), the urban area of Jiyuan is enclosed by mountainous areas to the north, west and south about 5–6 km away from the edge of the urban area. Average annual precipitation and average annual temperature of Jiyuan are 650 mm and 14.6 °C, respectively. Prevailing wind direction from February to September in Jiyuan is east, while from October to January, it is west (Tuo et al., 2012). Summer in Jiyuan is often hot and humid, while it is dry and cold in winter. The Yellow River lies about 22 km to the south of the geographical center of urban Jiyuan (Fig. 1). Ring Road (Fig. 1) forms the edge of urban Jiyuan. To the west of Fengtian Road and Ring Road, the land is mainly used for farming, with some clusters of farm dwellings and industrial plants sparsely distributed in the rural lands. Soils around Jiyuan City belong to Ustic Cambosols according to the Chinese Soil Taxonomy (Chinese Soil Taxonomy Research Group, 2001). According to the results of a soil survey conducted in early 1980s, the background values of As, Cd and Pb in the study area of this work were 9.40, 0.065 and 20.1 mg/kg, respectively (Soil Survey Office of Henan Province, 2004).

Jiyuan City covers an area of 1931 km^2, with a total population of 0.67 million. About half of the population lives in the 42 km^2 urban core area. Jiyuan is well-known for its industry, especially the production of lead, steel and zinc. Globally, most lead smelting plants lie close to lead ore mining; however, there is no lead mining Jiyuan. Lead smelting in Jiyuan began in 1950s, while rapid increase occurred in 1990s. In recent years, Jiyuan produced about 900 000 tonnes of Pb annually. The main Pb smelting plants in Jiyuan are Yuguang, Jinli and Wanyang, located to the west or northwest of urban Jiyuan (Fig. 1). Annual industrial dust and SO_2 emission were 13 780 and 40 594 tonnes in 2013, respectively (BEPJC, 2014); industrial dust emission was approximately 25 360 tonnes in 2000 (Lu et al., 2001). Between 2006 and 2012, mean annual ambient concentrations of PM_{10} in urban Jiyuan ranged between 0.091 and 0.110 mg/m^3, and SO_2 ranged between 0.062 and 0.067 mg/m^3 (Ren, 2013). Discharge of wastes with high concentrations of heavy metals from the lead smelting plants into local rivers has resulted in serious pollution of the water and sediment in Jiyuan. Maximum concentrations of 7600 and 2410 mg/kg of Pb and Cd have been found in the 0–40 cm sediment in the Shihe River near a smelter in Jiyuan (Jiao et al., 2014).

In this work, in order to assess the atmospheric deposition near the lead smelters, six sampling sites were chosen near the Yuguang smelter, they were SB, QD, JH, ZX, JF and BF (Fig. 1). The distances between the main stack of Yuguang and the sampling sites of SB, QD, JH, ZX, JF and BF were 1.21, 0.924, 1.07, 0.769, 0.994 and 0.986 km, respectively. Three additional sites, namely ZC, CQ and PT were chosen as background sites. The sites of SB, QD, JH, ZX, JF and BF lie in a mixed area of road/street, woods and residential buildings. ZC site lies in a village to the south of urban Jiyuan, CQ in downtown Jiyuan and PT in a village to the southwest of urban Jiyuan (Fig. 1), distances between these three sites and the main stack of Yuguang were 13.6, 5.04 and 23.5 km, respectively. There were no tall buildings or trees that obviously affected the deposition existing near the sampling sites.

2.2. Sample collection

Bulk deposition samples were collected monthly from November 2012 to March 2014. The samples were collected according to National Standard GB15265-94 (Ministry of Environmental Protection, 1994), except that glycol was not added in order to avoid its interference in sample digestion. Glass cylinders (diameter 15 cm, height 30 cm) were used to collect bulk deposition samples. The cylinders were mounted on 1.5 m tall