

Toxic Metal Enrichment Characteristics and Sources of Arid Urban Surface Soil in Yinchuan City, China (Postprint)

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Abstract

To investigate the environmental quality of the urban surface soil in Yinchuan City, the capital of Ningxia Hui Autonomous Region (Ningxia), China, we sampled surface soil and measured the concentrations of 8 toxic metals (Pb, Cr, Cu, Zn, Co, Bi, Ni and V) using X-ray fluorescence spectrometry. The enrichment characteristics and sources of these toxic metals in the soil were analyzed by the enrichment factor (EF) and multivariate statistical analysis. The results showed that the mean concentrations of these toxic metals in the soil samples were 25.0, 109.1, 16.8, 26.0, 37.2, 2.7, 25.3 and 59.9 mg/kg for Pb, Cr, Cu, Zn, Co, Bi, Ni and V, respectively, which were 1.2, 1.8, 0.8, 0.4, 3.2, 8.7, 0.7 and 0.8 times the corresponding background values of Ningxia soil, respectively. The variations of Pb, Zn, Co, Bi and Ni concentrations in the surface soil of Yinchuan were larger than those of the other metals. Our results also showed that the toxic metals investigated in the soil had different enrichment levels. Both Co and Bi were significantly enriched, whereas Cr was only moderately enriched in the soil. The other toxic metals were deficient or minimally enriched in the soil. Source analysis results based on the concentration, enrichment characteristics and multivariate statistical analysis indicated that Cr, V and Ni originated from a combination of fossil fuel combustion, traffic pollution and natural occurrence. Pb, Cu and Zn were predominantly derived from natural and traffic sources, while Co and Bi primarily originated from construction sources.

Full Text

Toxic Metal Enrichment Characteristics and Sources of Arid Urban Surface Soil in Yinchuan City, China

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Abstract

To investigate the environmental quality of urban surface soil in Yinchuan City, the capital of Ningxia Hui Autonomous Region, China, we collected surface soil samples and measured concentrations of eight toxic metals (Pb, Cr, Cu, Zn, Co, Bi, Ni, and V) using X-ray fluorescence spectrometry. Enrichment characteristics and sources of these toxic metals were analyzed using the enrichment factor (EF) and multivariate statistical analysis. The results showed that mean concentrations of these toxic metals in the soil samples were 25.0, 109.1, 16.8, 26.0, 37.2, 2.7, 25.3, and 59.9 mg/kg for Pb, Cr, Cu, Zn, Co, Bi, Ni, and V, respectively. These values correspond to 1.2, 1.8, 0.8, 0.4, 3.2, 8.7, 0.7, and 0.8 times the background values of Ningxia soil. Variations in Pb, Zn, Co, Bi, and Ni concentrations in Yinchuan's surface soil were larger than those of the other metals. Our results also revealed different enrichment levels among the investigated toxic metals. Both Co and Bi were significantly enriched, whereas Cr showed only moderate enrichment in the soil. The other toxic metals exhibited deficiency to minimal enrichment. Source analysis based on concentration data, enrichment characteristics, and multivariate statistical analysis indicated that Cr, V, and Ni originated from a combination of fossil fuel combustion, traffic pollution, and natural sources. Pb, Cu, and Zn were predominantly derived from natural and traffic sources, while Co and Bi primarily originated from construction sources.

Keywords: toxic metals; urban surface soil; enrichment factor; arid area; Northwest China

1 Introduction

Many cities have faced serious soil pollution issues due to rapid urbanization and industrialization, as well as extensive growth in motor vehicle usage. Continued increases in anthropogenic activities—including industrial production, traffic emissions, and domestic heating—have released large quantities of pollutants into urban soils, leading to elevated soil contamination (Andersson et al., 2010; Ngole-Jeme, 2016). As one of the most important pollutant groups in urban soil, toxic metals may originate from various sources such as fossil fuel combustion, industrial discharges, construction dust, vehicular exhaust emissions, and airborne particulates (Batjargal et al., 2010; Ngole-Jeme, 2016). Because toxic metals can accumulate in surface soil due to their non-degradability and

persistence (Batjargal et al., 2010; Yang et al., 2011), soils have become important sinks for toxic metals and other pollutants in urban areas (Mielke et al., 1999). Extensive inputs of toxic metals can disrupt natural geochemical cycling in urban ecosystems and result in severe environmental contamination (Mielke et al., 1999; Batjargal et al., 2010; Papa et al., 2010; Yang et al., 2011).

As trace metals have accumulated in surface soils, investigations into their sources and effects have become increasingly important. Although numerous studies of toxic metal pollution in urban surface soil have been conducted in developed countries over the last decade (Wilcke et al., 1998; Manta et al., 2002; Banat et al., 2005; Zhang, 2006; Morton-Bermea et al., 2009; Batjargal et al., 2010; Maas et al., 2010; Acosta et al., 2011; Tume et al., 2011) and in some megacities of developing countries (Zhang et al., 2005; Shi et al., 2008; Xia et al., 2011), limited data are available regarding soil toxicity in the arid and semi-arid areas of Northwest China (Wang et al., 2016). These regions have experienced rapid urbanization and industrialization in recent years (Wang et al., 2016; Zhao et al., 2016), resulting in severe environmental problems (Lu et al., 2014).

Yinchuan is an important commercial city in Northwest China located on the New Eurasian Continental Bridge and the ancient Silk Road. Like other capital cities in China, Yinchuan has undergone rapid urban construction and economic development in recent decades, particularly since the implementation of China's Great Western Development policy in the 1990s. This rapid urbanization and industrialization have increased the urban population and intensified anthropogenic impacts on the urban environment. However, few studies have investigated toxic metal pollution in Yinchuan's urban soil, with the exception of one study on farmland soil in Xingqing County (Wang et al., 2014). There is an urgent need to investigate the environmental quality of urban soil in this region. In this study, we examined the concentrations and accumulation levels of toxic metals in the city's topsoil and identified their possible sources. The results will improve our understanding of soil contamination problems and assist in developing future environmental protection policies for similar arid areas.

2.1 Study Area

Yinchuan City, the capital of Ningxia Hui Autonomous Region, is situated in the center of the Ningxia Plain in the upper reaches of the Yellow River at an altitude of 1010–1150 m. The city has a typical temperate arid continental monsoon climate, with mean annual precipitation of 150–200 mm, annual mean temperature of 8°C–9°C, and annual sunshine hours of 2800–3000 h (NMBS, 2013). The prevailing wind direction is northwest in autumn and winter, and southeast in spring and summer (NMBS, 2013). The main soil types are Sierozem and Aeolian. The urban area of Yinchuan—comprising Xixia, Jinfeng, and Xingqing districts—covers approximately 756.6 km². The urban popula-

tion in 2013 was 2.12×10^6 , with 5.1×10^5 motor vehicles registered in the city that year (NMBS, 2013). Yinchuan serves as an important center for education, culture, economy, and manufacturing in Northwest China. The main industrial facilities are located in the western area (Xixia District), while the eastern area (Xingqing District) is dominated by the coal industry, coal-fired power generation, construction industry, oil refining, and chemical industry.

2.2 Sampling and Experimental Analysis

Ninety-six surface soil samples were collected across Yinchuan using a grid method [Figure 1: see original paper]. The research area was initially divided into 77 grids of $3 \text{ km} \times 3 \text{ km}$, with sampling sites located at grid points. Composite surface soil samples (0–15 cm depth) were collected from a $3 \text{ m} \times 3 \text{ m}$ sampling area. The exact longitude and latitude of each sampling site were recorded using a GPS (Magellan Triton 300-North America, San Dimas, CA, USA). All soil samples were stored in polyethylene bags, labeled, and transported to the laboratory for analysis. Soil samples were air-dried at room temperature and passed through a 1.0-mm nylon mesh to remove plant roots and small stones (Chen et al., 2012; Zhao et al., 2016). A 100-g subsample of sieved soil was then taken from each sample and ground to less than 0.075 mm.

Wavelength dispersive X-ray fluorescence spectrometry (XRF, PW2403, PANalytical, Almelo, Netherlands) was used to determine concentrations of Pb, Cr, Cu, Zn, Co, Bi, Ni, and V in the soil samples. Following methods used by Chen et al. (2012) and Lu et al. (2014), 2.0 g of boric acid and 4.0 g of milled soil sample were placed in a mold and pressed into a 32-mm diameter pellet under a pressure of 30 t/cm^2 . Duplicate samples and standard samples (GSS1 and GSD-12) were measured simultaneously for quality control (Chen et al., 2012). The measured values of standard samples were 95%–102% of certified values, and the relative standard deviations of toxic metal concentrations in 10 duplicate samples were less than 5%.

2.3 Enrichment Factor (EF)

To estimate enrichment levels of the selected toxic metals in the samples, we used the following equation for calculating the EF of each metal (Chen et al., 2014):

$$(1)$$

where C is the concentration of toxic metal i (mg/kg) and C_{ref} is the concentration of the reference element for normalization (mg/kg); sample represents the investigated soil and background represents Ningxia soil.

In EF calculations, K, Al, Fe, Mn, Ti, and Sr are often used as reference elements due to their lack of variability in environmental samples

(Han et al., 2006; Meza-Figueroa et al., 2007). Enrichment levels of toxic metals in the samples were classified according to calculated EF values (Lu et al., 2009; Chen et al., 2014): deficiency to minimal enrichment ($EF < 2$), *moderate enrichment* ($2 < EF < 5$), *significant enrichment* ($5 < EF < 20$), *very high enrichment* ($20 < EF < 40$), and extremely high enrichment ($EF > 40$). The EF value of a toxic metal can also reflect its source (Meza-Figueroa et al., 2007; Chen et al., 2014).

2.4 Multivariate Statistical Analysis

Correlation analysis, factor analysis (FA), and cluster analysis (CA) were performed using SPSS 19.0 software to determine relationships among toxic metals in the soil samples and their possible sources. Correlation coefficients revealed the correlativity between each toxic metal (Tume et al., 2011). FA can reduce complex variables and extract several factors to dissect relationships among investigated variables (Han et al., 2006; Zhang, 2006; Meza-Figueroa et al., 2007; Chen et al., 2014). CA can classify toxic metals into two or more mutually exclusive groups based on internal relationships between them (Facchinelli et al., 2001; Lu et al., 2010; Chen et al., 2014).

3.1 Toxic Metal Concentrations in Urban Surface Soil

Toxic metal concentrations across the study area and background values for Ningxia soil are shown in Table 1. Chromium, cobalt, and bismuth concentrations in all samples, and lead concentrations in 75% of samples, exceeded their background values in Ningxia soil. Copper, zinc, nickel, and vanadium concentrations in all samples were smaller than or close to their background values.

Kurtosis values for Pb, Cr, and Co were greater than 0, indicating steeper distributions than normal (Chen et al., 2012). Skewness values for Pb and Co were greater than 1, indicating positive skew toward lower concentrations (Lu et al., 2010; Xia et al., 2011). Coefficients of variation for Pb, Zn, Co, Bi, and Ni were relatively high (>20%), with maximum concentrations more than three times their minimum concentrations, indicating large spatial variations in these metals across Yinchuan's surface soil.

Comparison of toxic metal concentrations in Yinchuan surface soil with reported levels for other cities (Table 2) revealed that Cr and Co concentrations were higher in Yinchuan. Copper concentration in Yinchuan soil was lower than values reported for other cities shown in Table 2, except for Shenzhen and Murcia. Nickel concentration in Yinchuan soil was higher than that reported for other cities, except for Beijing, Shanghai, Changsha, and Chengdu. Lead concentration was lower than that reported for other cities, except for Murcia,

Damascus Ghouta, and central Catalonia. Vanadium concentration was higher than recorded in other cities, except for Chengdu and Xi'an. Zinc concentration was lower in Yinchuan than reported in other cities. These differences in toxic metal concentrations among urban soils from different cities may relate to variations in soil types, natural environmental conditions, intensity of anthropogenic activity, and urban environmental planning and management.

3.2 Enrichment Characteristics of Toxic Metals in Soil

Enrichment factor values for all toxic metals measured in soil samples relative to local soil background values (CNEMC, 1990), with K as the reference element, are shown in Figure 2 [Figure 2: see original paper]. EF values for Pb, Cr, Cu, Zn, Co, Bi, Ni, and V ranged from 0.7-3.1, 1.6-3.1, 0.6-1.3, 0.2-1.0, 1.6-13.2, 3.2-18.8, 0.4-1.3, and 0.7-1.4, with mean values of 1.5, 2.3, 0.9, 0.5, 4.1, 10.9, 0.9, and 1.0, respectively. EF values for Cu, Zn, Ni, and V in all soil samples, and for Pb in 96% of samples, did not exceed 2.0, indicating deficiency to minimal enrichment. The mean EF for Co (4.1) and 75% of Co EF values ranged between 2.0 and 5.0, indicating moderate enrichment, while 22% of samples showed significant enrichment and 3% showed deficiency to minimal enrichment.

The mean EF for Cr (2.3) and 91% of Cr EF values ranged between 2.0 and 5.0, indicating moderate enrichment. For Bi, 96% of EF values fell within the 5.0-20.0 range, with a mean greater than 10.0, indicating significant enrichment. Based on these EF results, we concluded that Cu, Zn, Ni, and V in Yinchuan surface soils were primarily affected by natural sources, Pb was mainly influenced by natural sources with partial anthropogenic impact, while Co, Cr, and Bi were predominantly affected by anthropogenic activities.

3.3 Results of Multivariate Statistical Analysis

Correlation analysis results for toxic metals in Yinchuan surface soil (Table 3) showed that Pb, Cr, Cu, Zn, Ni, and V concentrations were significantly and positively correlated with each other ($P < 0.01$), indicating similar influencing factors (Lu et al., 2010; Saeedi et al., 2012). Cobalt concentration was negatively correlated with these metals, implying different sources. Bismuth concentration was positively correlated with Co ($P < 0.05$) and negatively correlated with other metals, indicating that Bi and Co shared similar sources that differed from those of other metals.

Factor analysis results showed that three factors accounted for 79.9% of the total variance (Table 4). Factor 1 was primarily loaded by Cr, Co, Ni, and V and moderately by Pb, accounting for 39.4% of total variance. The Pb loading (0.581) was smaller than other metals, suggesting quasi-independent behavior

within this group. The Co loading (-0.869) in Factor 1 indicated negative correlation with Factor 1. Factor 2, dominated by Cu, Pb, and Zn, accounted for 27.5% of total variance. Factor 3 was loaded by Bi and accounted for 13.9% of total variance. Both Bi and Co were negatively correlated with Factors 1 and 2 and positively correlated with Factor 3, although Co loading (0.093) in Factor 3 was small. Relationships among toxic metals based on the first three factors are shown in Figure 3 [Figure 3: see original paper].

A cluster distance of 5-10 was used in hierarchical CA of toxic metal concentrations in surface soil (Fig. 4 [Figure 4: see original paper]), revealing three clusters: Cr-Ni-V, Pb-Cu-Zn, and Co-Bi. These results agreed with FA results. Clusters 1 and 2 merged at a relatively higher level, suggesting these metals derived from the same source.

3.4 Sources of Toxic Metals

Correlation analysis showed that Cr, Ni, and V concentrations were significantly and positively correlated. FA and CA results clearly separated these metals from others, indicating similar sources for Cr, Ni, and V. Chromium exhibited EF values of 1.0-10.0, with concentrations 1.1-2.4 times the Ningxia background value, implying combined natural and anthropogenic influences (Han et al., 2006). Elevated Cr concentrations have been reported in areas surrounding coal-fired power plants (Chen et al., 2014), and Cr is widely used in aluminum alloys, titanium alloys, and automobile parts (Madany et al., 1994). Our results align with these findings: surface soil samples with high Cr concentrations (more than 2.0 times the background value) were primarily distributed in areas surrounding the coal-fired power plant and automotive plant in Xixia District of western Yinchuan, and also located near high-traffic-density roads. Based on concentration, EF values, and spatial distribution patterns, we concluded that Cr in surface soil originated from traffic emissions, fossil fuel combustion, and natural sources. Nickel and V concentrations in soil samples were close to or smaller than Ningxia background values, with EF values near 1 in most samples. However, samples collected near the coal-fired power plant contained higher Ni and V concentrations than elsewhere in the city, indicating that Ni and V principally originated from natural sources with partial contributions from fossil fuel combustion.

Correlation analysis for Pb, Cu, and Zn indicated strong positive correlations. These metals belonged to the same FA component and were classified together in CA. Copper and Zn concentrations in soil samples were close to or lower than their corresponding Ningxia background values, with EF values ≤ 1 , indicating predominant natural sources. Lead concentrations in 75% of soil samples exceeded background values by more than 1.1 times, and EF values in 60% of samples were >1.5 , demonstrating anthropogenic influence. Soil samples collected adjacent to main roads with high traffic density contained higher Pb

concentrations than those near small roads. Previous studies have demonstrated that vehicle emissions constitute the main Pb source in urban soil (Hewitt and Rashed, 1990; Christoforidis and Stamatis, 2009; Yang et al., 2011; Chen et al., 2012), which is consistent with our Yinchuan samples, particularly given the rapid increase in private vehicles in recent years. These results confirm that Pb, Cu, and Zn mainly originated from both natural and traffic sources. Furthermore, correlation analysis (Table 3) and CA (Fig. 4) demonstrated that Pb, Cr, Cu, Zn, Ni, and V shared similar sources: combined natural inputs and traffic emissions.

Correlation analysis, FA, and CA indicated that Co and Bi derived from similar sources. Their concentrations in soil samples were 1.5–9.4 and 2.6–15.2 times the Ningxia background values, respectively, showing moderate and significant enrichment in surface soil. Six percent of Co EF values and 64% of Bi EF values were ≤ 10.0 , indicating influence from local anthropogenic sources. Previous investigations have shown that Co pollution in urban environments primarily derives from construction sources (Lu et al., 2010; Chen et al., 2014), with Co and Bi being widely used in paints, pigments, and coating materials (Lu et al., 2010). Surface soil samples collected near construction and building demolition sites in Yinchuan contained higher Co and Bi concentrations (more than 5 times background values). We therefore conclude that Co and Bi in surface soil samples mainly originated from construction sources.

4 Conclusions

The mean concentrations of Pb, Cr, Cu, Zn, Co, Bi, Ni, and V in Yinchuan surface soil were 25.0, 109.1, 16.8, 26.0, 37.2, 2.7, 25.3, and 59.9 mg/kg, respectively. Chromium and Co showed moderate enrichment, while Pb, Cu, Zn, Ni, and V exhibited deficiency to minimal enrichment. Bismuth was significantly enriched. Comprehensive analyses of toxic metal concentrations, enrichment levels, correlation analysis, FA, and CA indicated that Cr, Ni, and V derived from mixed sources of traffic pollution, fossil fuel combustion, and natural processes; Pb, Cu, and Zn principally derived from natural and traffic sources; and Co and Bi mainly derived from construction sources.

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