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ORIGINAL ARTICLE

Environment impact of heavy metals on urban soil in the vicinity of industrial area of Baoji city, P.R. China

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Abstract Heavy metals in soils are of great environmental concern, in order to evaluate heavy metal contents and their relationships in the surface soil of industrial area of Baoji city, and also to investigate their influence on the soils. Soil samples were collected from 50 sites, and the concentration of Pb, Zn, Cu, Cr, Ni heavy metals and the contents of characteristics in soil from industrial area of Baoji city were determined with X-ray fluorescence method. The concentrations of Pb, Zn, Cu, Cr and Ni in the investigated soils reached the amount of 2,682.00–76,979.42, 169.30–8,288.58, 62.24–242.36, 91.96–110.54 and 36.14–179.28 mg kg^{-1}, respectively. The major element Pb contents of the topsoils were determined. to highlight the influence of 'anthropic' features on the heavy metal concentrations and their distributions. To compare, all values of elements were much higher than those of unpolluted soils in the middle of Shaanxi province that average 16.0–26.5, 67.1–120.0, 17.8–57.0, 46.9–65.6 and 24.7–34.6 mg kg^{-1} for Pb, Zn, Cu, Cr and Ni, respectively. An ensemble of basic and relativity analysis was performed to reduce the precipitate of Pb in soil was extremely high and greatly relativity with other elements. Meanwhile, Pb, Zn, Cu, Cr, Ni heavy metals were typical elements of anthropic activities sources, so it was easy to infer to the tracers of anthropic pollutions from the factorial analysis, which was coming from the storage battery manufactory pollutions. The pollutant distributions were constructed for the urban area which identified storage battery manufactory soot precipitate as the main source of diffuse pollution and also showed the contribution of the topsoils of industrial area of Baoji city as the source point of pollution. Consequently, the impact of heavy metals on soil was proposed and discussed. These results highlight the need for instituting a systematic and continuous monitoring of heavy metals and other forms of pollutants in Baoji city to ensure that pollution does not become a serious problem in the future.

Keywords Environment impact · X-ray fluorescence · Urban soil · Pb pollution

Introduction

Soil is composed of mineral constituents, organic matter (humus), living organisms, air and water, and it regulates the natural cycles of these components. Heavy metals (Pb, Zn, Cu, Cr, Ni and other trace metals) occur naturally in soils, which are formed by geological processes, such as alteration and erosion of the geological underground materials. Besides the parent material, the sources of contamination in soils were multifarious, and include agricultural and industrial emissions pollution (Tuchschmid et al. 1995).

Recently, the high levels of urban soil pollutions have become a major issue. Because urban soils were known to have peculiar characteristics such as unpredictable layering, poor structure and high concentrations of trace elements (Kabata-Pendias and Pendias 1992; Tiller 1992). They were the 'recipients' of large amounts of heavy metals from a variety of sources. Heavy metals in urban soils have been shown to be

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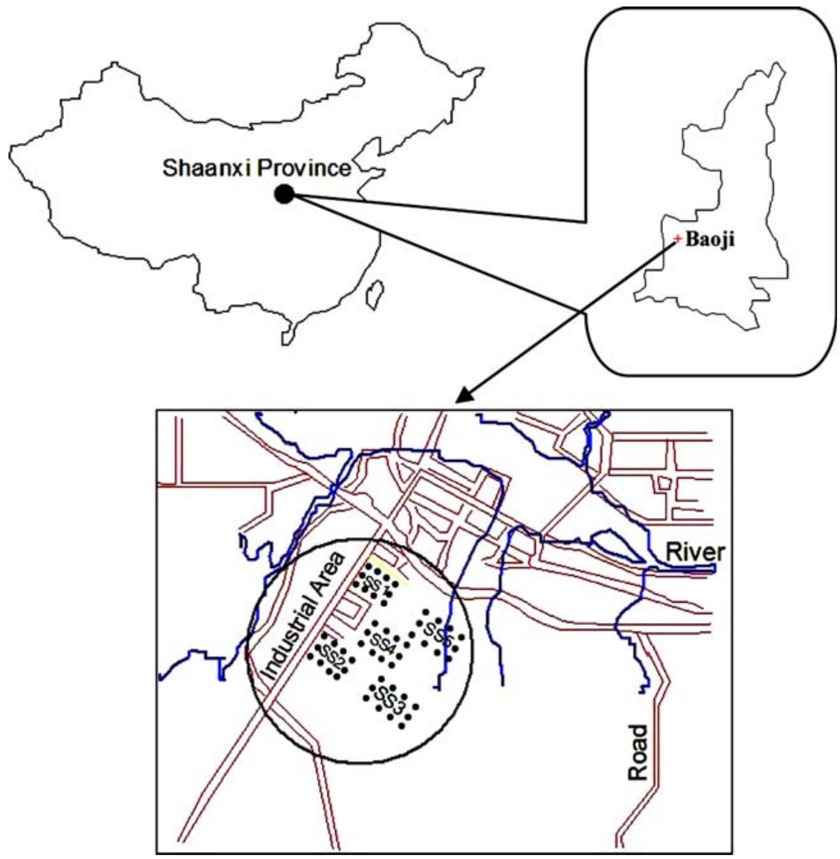

Fig. 1 Location map of the urban soil sampling points in industrial areas of Baoji city, P.R. China

very useful tracers of environmental pollution. Furthermore, industrialization and urbanization were the two main causes for the increasing contamination of heavy metals in urban soil; however, numerous studies have been undertaken into Pb and trace element contamination in soils, plants, waters and sediments in city, derived from industrial activities (Sanchez et al. 1998; David 1998; Jdid et al. 1999; Churl et al. 2001), automobile gasoline combustion, etc. (Julie and Alex 2001). In order to highlight the extent and severity of urban soil contaminations influenced by industrial activities, in this study, we started with a general characterization of bulk geochemistry of topsoils from industrial area of Baoji, and investigated the heavy metals Pb, Zn, Cu, Cr, Ni distributions in the urban soils and consequently, an environment impact assessment of Pb, Zn, Cu, Cr, Ni heavy metals on urban soil in the vicinity of industrial area of Baoji city was obtained and disused.

Materials and methods

Soil samples location

Soil samples were all collected from Baoji city, which is located in E107°08′ N34°23′. It is the second biggest city in Shaanxi province, P.R. China, with about 18,200 km^2 area and a population 3,720,000. Meanwhile, it is the most important industrial city in Shaanxi province. The location map of the urban soil sampling points is listed in Fig. 1.

Soil sampling strategy

Soils were sampled in an undisturbed industrial area of Baoji city within 200 m × 200 m plot, and divided into quadrants; the typical industrial manufactory was located at the center area of square plot. Within each quadrant and center area of square plot, ten individual cores collected over a 20 m × 20 m grid on the upper 10 cm layer of the topsoil were sampled, all sub-samples were taken and then mixed to obtain a bulk sample. Such a sampling strategy was adopted in order to reduce the possibility of random influence of urban un-clearly visible waste. After collection, a representative sample was chosen by twice quartation methods in the bulk sample, and then the chosen representative samples were labeled by SS1, SS2, SS3, SS4, SS5. All the samples were collected with a stainless steel spatula and kept in PVC packages, at room temperature, for not more than 12 h before starting analytical procedures.

Table 1 Measuring condition of elements

Channel	Type	Line	X-tal.	Collimator (μm)	Detector	X-ray tube filter	Voltage (kV)	Current (mA)	Angle 2θ (°)
Cr	Gonio	Kα	LiF 200	300	Duplex	None	60	40	69.3506
Cu	Gonio	Kα	LiF 200	300	Duplex	None	60	40	45.0102
Ni	Gonio	Kα	LiF 200	300	Duplex	None	60	40	62.9896
Pb	Gonio	Lβ1	LiF 200	300	Scint.	None	60	50	28.2162
Zn	Gonio	Kα	LiF 200	300	Scint.	None	60	40	41.767

Preparation of the samples and analytic methods

Each sample were combined and allowed to air-dry in containers. Each horizon was sieved to 2 mm to remove course woody debris. Visible charcoal particles were manually isolated from the >2-mm size fractions using stainless steel forceps and then homogenized in skiving with carnelian mortar. Finally, 4.0 g of each soil samples was weighed and 2.0 g of boric acid was added in the mold, and pressed into a 32-mm diameter pellet under 30 t pressure. The briquettes were stored in a desiccator. Consequently, the concentrations of Pb, Zn, Cu, Cr, Ni in soil samples were directly measured by X-ray fluorescence (XRF, PANalytical PW2403 apparatus), the relative proportions of soils were determined according to methods (Dosanjos et al. 2000; Hartyáni et al. 2000; Imre et al. 2004; Li et al. 2005; Li and Huang 2006). Table 1 has list the determination parameters and measure conditions.

Meanwhile, a series of soil and rock standards were used to calibrate the application. These were the GSS-, GRS- and GSD-series geochemical reference materials (Institute of Geophysical and Geochemical Prospecting, P.R. China), together with NIST-2709, NIST-2710, NIST-2711 (National Institute of Standards and Technology, USA) and soil standards SO-1, SO-2, SO-3 and SO-4 (Canadian Certified Reference Materials Project) were also used. The total organic carbon (TOC) was determined using High-TOC II Elementar (Germany) (Pang et al. 2003), and soil pH was determined by mixing fresh soil with deionized water (1:2, w/v) (Hendershot et al. 1993).

The analytical precision, measured as relative standard deviation, was routinely between 3 and 5%, and never higher than 8%. Accuracy of analyses was checked using standard and duplicate samples. The quality control gave good precision (SD < 5%) for all samples.

Table 2 Selected soil chemical characteristics

Sample label (sample amount)	pH (H_2O)	$CaCO_3$ (%)	Total organic carbon (%)
SS1 (10)	7.51 ± 0.07	7.07 ± 0.03	3.38 ± 0.27
SS2 (10)	7.42 ± 0.02	7.64 ± 0.02	5.26 ± 0.35
SS3 (10)	7.58 ± 0.06	11.34 ± 0.07	5.43 ± 0.53
SS4 (10)	7.49 ± 0.02	6.79 ± 0.01	4.36 ± 0.47
SS5 (10)	7.29 ± 0.05	6.77 ± 0.03	2.37 ± 0.21

Data in the table stand for mean ± S, $S = \sqrt{\frac{\sum_{i=1}^{n}(X_i-\bar{X})^2}{n-1}}$

Statistical analysis

Statistical data processing in this work was carried out by means of the SPSS.12 software packages (SPSS Inc., Chicago, IL, USA).

Results and discussion

Soil characteristics

The pH of the soils varied around 7.40 and was nearly alkalescent throughout the others (Table 2). The concentration of $CaCO_3$% varied from 6.77 to 11.34 mg kg^{-1}, and from 2.37 to 5.43 mg kg^{-1} for TOC%, respectively.

Total heavy metal concentrations in soil

The heavy metal distribution in soils was shown in Table 3 and Fig. 2, a full dataset could be obtained from authors upon request. Heavy metal Pb concentrations in different zones at industrial areas (SS1, SS2, SS3, SS4, SS5) were quite high; on the other hand, Cu, Zn, Ni, Pb concentrations in SS3 and SS4 were higher than others, but except for Cr in SS4, the main reason was that, all the SS4 samples were sampled from the center of the exposed areas of industrial area; there was a typical plant, storage battery manufactory, Pb was main primary raw material to product battery and the geochemical behaviors of Pb and Zn were known to be similar in most natural processes (Reimann 1998). Moreover, SS3 was located at the direct of diffuse zone of waste gas. According to comparable data

Table 3 Total metals in soil samples at different city and soil criteria (mg kg^{-1})

City (industrial areas) and soil criteria	Soil sample (sample amount)	Ni	Pb	Cu	Zn	Cr	Reference
Baoji, China	SS1 (10)	39.26 ± 1.43	2,682.00 ± 3.78	62.24 ± 1.23	169.30 ± 2.76	100.22 ± 2.50	In this study
	SS2 (10)	42.14 ± 1.68	6,573.80 ± 4.65	73.04 ± 1.59	305.40 ± 1.35	110.54 ± 1.69	
	SS3 (10)	63.68 ± 1.01	31,938.12 ± 7.18	117.30 ± 2.27	744.40 ± 2.50	108.12 ± 1.76	
	SS4 (10)	179.28 ± 2.27	76,979.42 ± 7.80	242.36 ± 1.23	8,288.58 ± 3.89	91.96 ± 1.98	
	SS5 (10)	36.14 ± 1.98	8,729.46 ± 5.20	65.78 ± 1.40	312.92 ± 1.78	101.16 ± 2.57	
Nanjing, China	(48)	48.08	46.52			368.69	Zhang et al. (1999)
Nanjing, China	(9)	31.4	74.7	127	400	73	Zhang et al. (2005)
Patancheru, India	(55)	20–91		500	30.1–106	240	Govil et al. (2001)
Thane–Belapur, India	(28)	183.6		104.6	191.3	521.3	Krishna and Govil (2005)
Singapore	(8)		91.1	69.1	360	63.2	Zhou et al. (1997)
Cukarica, Smederevo, Nis, Bor, Prahovo, Pozega, Padinska Skela, Serbia	(59)	66.6	37.7	40.0	103	33.7	Latinka et al. (2004)
The criterion of heavy metal pollution in soils, in China		50	300	100	250	200	GB15618-1995 (1995)
The value of element environment background of China		23.4	23.6	20.0	67.7	53.9	Wei (1990)
The distribution of heavy metal in the middle of Shaanxi province		24.7–34.6	16.0–26.5	17.8–57.0	67.1–120.0	46.9–65.6	Pan et al. (2004)

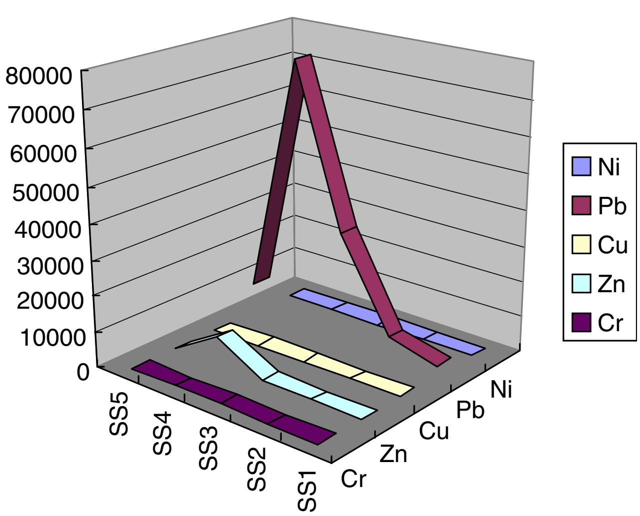

Fig. 2 Heavy metal distribution of urban soil in industrial areas of Baoji city

from literatures and soil criteria, the contents of Cu, Zn, Ni, Pb, Cr were higher than the value of element environment background of China and the distribution of heavy metal in the middle of Shaanxi province. Therefore, these results indicate that the sites have been severely contaminated by the heavy metals, and the effects of Pb distribution were highly outstanding. With the Nemero Index Method (Environment Protect Industry Criteria of P.R. China, HJ/T166-2004), the pollution index was evaluated: Pb > Zn > Ni > Cu > Cr (Table 4). For comparison to the average concentrations in urban soils in the other survey cities (Table 3), the values of Pb in the present study were highest among those reported from some large industrialized cities, but in other heavy metals, their concentrations were changed in different comparable cities, much changes in Thane–Belapur, India for Ni, Patancheru and Thane–Belapur for Cu, Nanjing and

Table 4 Pollution index of heavy metals in residential soil

Soil	PI_{Ni}	PI_{Pb}	PI_{Cu}	PI_{Zn}	PI_{Cr}	PN
SS1	0.7852	8.9400	0.6224	0.6772	0.5011	6.53
SS2	0.8428	21.9127	0.7304	1.2216	0.5527	15.90
SS3	1.2736	106.4604	1.1730	2.9776	0.5406	76.94
SS4	3.5856	256.5981	2.4236	33.1543	0.4598	186.22
SS5	0.7228	29.0982	0.6578	1.2517	0.5058	21.07

Data in the table were evaluated by Nemero Index Method $PI_j = \frac{C_i}{S_{ij}}$ $PN_j = \sqrt{\frac{\left(\max\frac{C_i}{S_{ij}}\right)^2 + \left(\frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{S_{ij}}\right)^2}{2}}$

Singapore for Zn, Patancheru, Thane–Belapur and Nanjing for Cr.

Clustering analysis

R type cluster analysis was used to elucidate the complex relationships between the different heavy metals studied. Numerous factors control their relative abundance. The process of soil formation, as well as anthropogenic factors, such as pollution. The correlation coefficient '*r*' was used as the measurement parameter of relationships, and the single linkage clustering method was used to divide the elements into clusters (Davis 1986). All samples except those collected from the rural environment were used for the calculation of the correlation coefficient of the elements using the following equation:

$$r_{jk} = \frac{\sum_{i=1}^{n}\left(X_{ij} - \bar{X}_j\right)\left(X_{ik} - \bar{X}_k\right)}{\sqrt{\sum_{i=1}^{n}\left(X_{ij} - \bar{X}_j\right)^2\sum_{i=1}^{n}\left(X_{ik} - \bar{X}_k\right)^2}}$$

where *j*, *k* were the number of elements; *i* was the number of soil samples; $0 \le |r| \le 1$.

The results of the calculations are listed in Table 5 and plotted in Fig. 3.

Inter-element relationships provide interesting information on heavy metal sources and pathways

Table 5 Correlation coefficients among heavy metals and soil properties in soil

	pH	Ni	Pb	Cu	Zn	Cr	TOC
pH	1	0.294	0.351	0.343	0.193	0.046	0.667
Ni	0.294	1	0.977	0.993	0.992	–0.726	0.215
Pb	0.351	0.977	1	0.995	0.950	–0.643	0.284
Cu	0.343	0.993	0.995	1	0.972	–0.665	0.283
Zn	0.193	0.992	0.950	0.972	1	–0.777	0.122
Cr	0.046	–0.726	–0.643	–0.665	–0.777	1	0.479
TOC	0.667	0.215	0.284	0.283	0.122	0.479	1

**Correlation is significant at the 0.01 level (two-tailed)

*Correlation is significant at the 0.05 level (two-tailed)

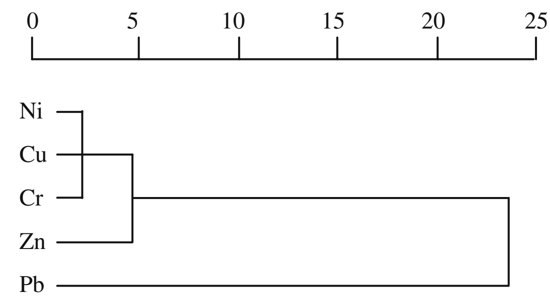

Fig. 3 Hierarchical clustering results of the heavy metal concentrations in urban soil samples of the Baoji industrial areas

(Table 3). Pb was closely correlated with Cu ($|r| = 0.995$) and well with Zn ($|r| = 0.950$) and Ni ($|r| = 0.977$) (Table 5), the excellent correlations were exhibited among Ni, Pb, Cu and Zn by correlation coefficients, which could indicate common contamination sources for these metals. Using *r* to classify the elements, Ni, Pb, Cu and Zn were grouped together, indicating that the natural as well as anthropogenic sources of these heavy metals were closely related in soils. However, Cr showed negative correlation with Pb, Ni, Cu and Zn. Heavy metal concentrations had slight or moderate correlate with pH, and TOC contents. Owing to the narrow range of pH (7.29–7.58) measured in the sample, this parameter has limited importance on the heavy metal distribution, substantially limiting their mobility because of the neutral–subalkaline environment. In order to discriminate distinct groups of heavy metals as tracers of natural or anthropic source, an explorative hierarchical cluster analysis was performed on the available dataset. The obtained results (Fig. 3) enabled the identification of elements.

Because Pb is the main primary raw material to produce battery, but the geochemical behaviors of Pb and Zn were known to be similar in most natural processes, and was commensal mineral (Reimann et al. 1998). Meanwhile, the heavy metal Ni, Pb, Cu, Zn, Cr were typical anthropic elements (Ratha and Sahu 1993). However, the samples of SS4 was from the typical storage battery manufactory areas, it is evidenced that in whole manufactory process, Pb was firstly melted down at the temperature of 773.15–873.15 K, and then foundinged flat of plumbum as electrodes. So those heavy metals including Pb easily formed smoke and precipitated or washed by rainwater into soil (Dianne and Jillian 2002; Faruque et al. 2005). But most Pb existed in soil as modality of $Pb(OH)_2$, $PbCO_3$ and organic affiliated, they moved slowly in the vertical direct of soil profile; consequently, most of them were accumulated in 0–10 cm topsoil layer (Sutherland 2000). On the other hand, the direct of wind would strongly influence the heavy metal distributions. So all those results were consistent with elemental relationships indicating that, the metal's origin from storage battery manufactory was dominated by an anthropic input.

Conclusions

The following were the most significant conclusions derived from this study on urban topsoils. The concentrations of heavy metals in soils were heavily influenced by the typical manufactory. A high level of heavy metal emitted from storage battery manufactory polluted the urban soils of industrial area of Baoji city. The absolute values of Pb concentration in the urban soils of industrial area of Baoji city were much higher than values recorded in some large industrial/business cities (e.g., Nanjing, China, Patancheru and Thane–Belapur, India, Cukarica, Smederevo, Nis, Bor, Prahovo, Pozega, Padinska Skela, Serbia, Singapore). This was a cause for great concern, and not only suggested that the contamination by Pb needed to be monitored closely, but also that, steps should be taken to eliminate the precipitable Pb particles from battery manufactory soot as possible. Meanwhile, X-ray fluorescence was a quick and dependable monitor soil multi-element pollution method.

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