



Fraction distribution and bioavailability of soil heavy metals in the Yangtze River Delta—A case study of Kunshan City in Jiangsu Province, China

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ARTICLE INFO

Article history:

Received 20 April 2011

Received in revised form 4 August 2011

Accepted 2 October 2011

Available online 6 October 2011

Keywords:

Heavy metal

Bioavailability

Fraction

Secondary-phase fraction

Industry zone

ABSTRACT

Mobility and bioavailability of soil heavy metals strongly depend on their fractions. Secondary-phase fraction (SPF) of heavy metal, including acid-soluble, reducible and oxidizable fractions, is considered as direct and potential hazardous fraction to organisms. The ratio of SPF to the total concentration of heavy metal represents its bioavailability. In this study, 126 topsoil samples were collected in Kunshan, Jiangsu, China. Fraction concentrations of heavy metals, and their bioavailability and spatial distributions were determined, and relationships between their fractions and types of industry zones were analyzed. Results showed that Cd and Pb had the greatest SPFs among all metals (78.61% and 62.60%, respectively). Great SPFs of Cd and Pb were observed in the dyeing and paper-making industry zone, while great SPFs of Cr, Cu, Zn, Ni were in the smelting and plating industry zone. For most metals, fraction distributions were controlled by soil organic matter and clay contents. Spatial principal component analysis showed SPFs of heavy metals can be explained by two principle components (PCs). PC1 represented SPFs of Cd, Cr, Cu, Pb and Zn, while PC2 represented SPFs of Ni and Co. The spatial distributions of SPFs were influenced by geochemical character, industrial sewage irrigation and soil physico-chemical properties.

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1. Introduction

Soil heavy metals are toxic to plants, animals and humans through water and food chain transport. With the rapid urbanization, industrialization and agricultural intensification in China, heavy metal contamination in soil has become an increasing concern among scientists, decision-makers, and the public. The Yangtze River Delta, located in the east of China, is one of the most developed areas in China. In recent years, soil heavy metal contamination caused by intensive anthropogenic activities in this area has become an urgent problem [1–3].

The total concentration of soil heavy metal is a useful indicator of contamination assessment [4–6]. However, it does not provide enough information about bioavailability and toxicity of heavy metals [7–10]. The mobility of heavy metals, as well as their bioavailability and related eco-toxicity to plants, greatly depend

on their forms [11,12]. Heavy metals exist in various fractions, i.e. water-soluble, exchangeable, carbonate-associated, Fe–Mn oxides-associated, organic-associated and residual fractions. Among these fractions, water-soluble and exchangeable fractions are considered to be bioavailable; carbonate-, Fe–Mn oxides-associated, organic-matter-bound fractions can also be bioavailable if the pH and redox potential of the soil change [13]; while mostly the residual fraction is unavailable to either plants or microorganisms [14,15]. Therefore, the fractions of heavy metals must be considered when investigating soil heavy metal pollution [16,17].

Sequential extraction procedures (SEPs) are widely applied for assessing heavy metal speciation in soils [18]. These procedures use a series of selective reagents to dissolve different fractions of soil heavy metals, thus giving a more realistic estimation of their actual environmental impacts [19]. The SEPs proposed by the European Community Bureau of Reference (BCR) are widely used to analyze different fractions of heavy metals [16,17,20,21].

Generally, spatial variations of soil heavy metals are determined by the spatial distribution of soil parent material and their geochemical characters. To reveal metal spatial distribution, both spatial structures of each heavy metal and statistical correlations among different heavy metals have to be investigated. Traditional geostatistics can analyze spatial structures of heavy metals. However, it does not consider relationships among different heavy

Abbreviations: SPF, secondary-phase fraction; SEP, sequential extraction procedure; CIZ, chemical industry zone; DPIZ, dyeing and paper-making industry zone; SPIZ, smelting and plating industry zone; LBZ, livestock breeding zone; VPZ, vegetable production zone.

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metals. Principal component analysis (PCA) can analyze the relationships among different heavy metals. However, it ignores spatial structures of these heavy metals. Spatial principal component analysis bridges the gap between the traditional PCA and a univariate geostatistics, which could reveal both the spatial structures and the relationships among multiple variables at a given spatial scale. Therefore, it is usefulness for identifying anthropogenic sources of soil heavy metals [22,23].

Fractions and bioavailability of soil heavy metals have rarely been investigated in the areas with rapid urbanization, industrialization and agricultural intensification in China. In addition, few studies have discussed the relationships between soil heavy metal bioavailability and industry types. Spatial distributions of soil heavy metals and their anthropogenic sources have rarely been studied in the literature. Therefore, the objectives of this research were to (i) analyze fraction concentrations of soil heavy metals in the Kunshan, which is one of the most developed areas located in the Yangtze River Delta; (ii) investigate the relationships between different fractions of soil heavy metals and industry types; and (iii) explore spatial distribution of secondary-phase fraction (SPFs) of different heavy metals and their controlling factors in this study area.

2. Experimental

2.1. Study area

This study was conducted in Kunshan, Jiangsu, China ($120^{\circ}48'21''$ – $121^{\circ}09'04''$ E, $31^{\circ}06'34''$ – $31^{\circ}32'36''$ N). Kunshan has great intensity of foreign-capital enterprises and township enterprises, and high urbanization level (65%). According to the Statistical Yearbook of Kunshan [24], the total volume of waste water discharged in Kunshan was 5.1×10^7 t yr⁻¹, the total volume of industrial waste gas emission was 1.16×10^{10} m³ yr⁻¹, the volume of dust discharged was 1.56×10^3 t yr⁻¹, the industrial solid waste production was 3.34×10^5 t yr⁻¹, the chemical fertilizer consumption was 2.5×10^4 t yr⁻¹, and the pesticide consumption was 1.45×10^3 t yr⁻¹. Therefore, Kunshan is one of the most representative areas for investigating soil heavy metals contamination under rapid urbanization, industrialization and agricultural intensification.

During the past three decades, the rapid industrialization has been increasing at an unprecedented rate, and chemical engineering, paper making, dyeing, smelting and plating industries have been well developed in Kunshan. According to Kunshan environmental quality gazette [25], 38 major point pollution sources including the industries mentioned above were shown in Fig. 1. Waste water discharged from these point sources accounted for 91.01% of the total volume of waste water, while waste gas emission and solid dust discharge from these point sources accounted for 85.67% of the total the waste gas emission, and 99.69% of the total industry solid dust discharge, respectively.

2.2. Soil sampling

A hundred and twenty six sites were selected for topsoil (0–20 cm) sampling with the aid of GPS in this study area. Twenty six of these 126 sites were distributed in the chemical industry zone (CIZ), while 18 sites were distributed in the dyeing and paper-making industry zone (DPIZ), 15 sites were distributed in the smelting and plating industry zone (SPIZ), 38 sites were distributed in the livestock breeding zone (LBZ), and 29 sites were distributed in the vegetable production zone (VPZ). Sampling sites in the industry zones were 50 m away from the major polluting factories, while the samples in VPZ were at the center of the field.

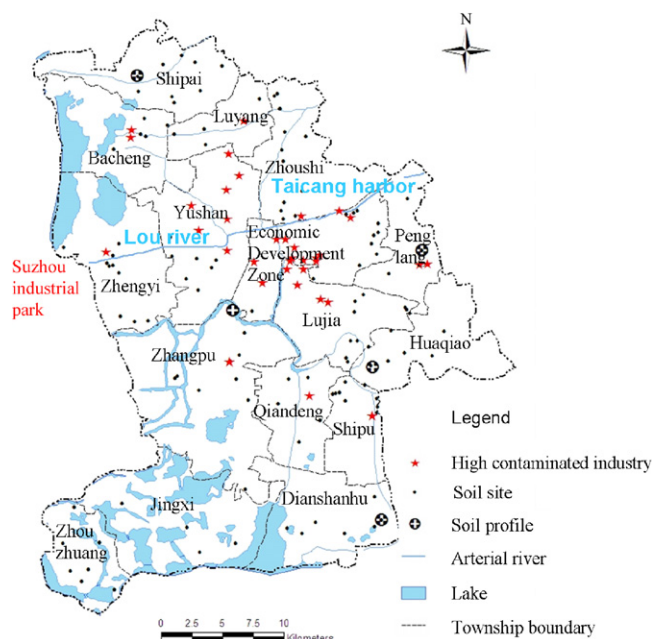


Fig. 1. Spatial distribution of sampling sites, highly contaminated industries, arterial rivers and lakes in Kunshan.

For each site, each sample was obtained by mixing five subsamples collected with a 5 cm diameter open-face bamboo auger.

2.3. Chemical analysis

2.3.1. Physicochemical properties of soil samples

Soil samples were air-dried and sieved through a 2 mm polyethylene sieve. pH was measured with pH meter in a 1:2.5 soil:water suspension [26]. Particle size distribution was analyzed using Laser Grain-size Analyzer (Malvern Instruments Inc., Worcestershire, UK). Soil total organic matter (SOM) was measured by a K₂CrO₇–H₂SO₄ oxidation procedure and cation exchange capacity (CEC) was analyzed by EDTA– ammonium salt quick titration [26].

2.3.2. Total concentration of heavy metals

Soil samples were further hand ground with a wooden roller until fine particles (<0.149 mm) were obtained. Samples were digested with a mixture of acid (HNO₃–HClO₄–HF) following the method of Bao [27].

2.3.3. Fraction concentrations of heavy metals

The BCR SEP is designed to separate heavy metal into four operationally defined fractions: acid-soluble/exchangeable, reducible, oxidizable and residual fractions [20]. Summary procedures of this method are as follows:

Two grams of soil sample were placed in a 100 mL polycarbonate centrifuge tube and subjected to the following extraction regimen.

- 1 *Acid-soluble fraction (F1)*. Extract soil sample with 40 mL of 0.11 mol L⁻¹ CH₃COOH, and shake for 16 h at 20 ± 2 °C
- 2 *Reducible fraction (F2)*. Extract residues from step 1 with 40 mL of 0.1 mol L⁻¹ NH₂OH·HCl (adjusted to pH 2 with HNO₃), and shake for 16 h at 20 ± 2 °C
- 3 *Oxidizable fraction (F3)*. Digest residues from step 2 with 10 mL H₂O₂ (30%) at the room temperature for 1 h with an occasional manual shaking. Heat the mixture at 85 °C for 1 h or longer (water bath) until its volume reduce to a few mini liters. Add another 10 mL H₂O₂ to the mixture and repeat the heating procedures as described above. After cooling, add 50 mL CH₃COONH₄

(1.0 mol L⁻¹, adjusted to pH 2 with HNO₃) and shake for 16 h at 20 ± 2 °C

- 4 The secondary-phase fraction (SPF) of a specific heavy metal is the sum of F1, F2 and F3 of this heavy metal. The SPF is often considered as the direct and potential hazardous fraction to organisms because F1, F2 and F3 bond much less strongly with soil phases than F4 does [28].
- 5 The residual fraction (F4) is held in the crystal lattice of original mineral, so it is identified as “inactive” fraction. The F4 of a specific heavy metal is the difference between total concentration and SPF concentration of this heavy metal.

After each successive extraction, separation was done by centrifugation at 4000 rpm for 20 min. The supernatant was filtered with a 0.45 μm membrane filter, and analyzed for concentrations of different heavy metals. Residuals from each step were washed with 20 mL of distilled water, followed by vigorous hand shaking, and then followed by 20 min of centrifugation before the next extraction step. Concentrations of Cr, Cu, Ni, Pb and Zn were measured by ICP-AES (IRIS Intrepid, USA), while Cd was analyzed using a graphite furnace atomic absorption spectrophotometer (Varian GTA-95, USA). Three replicates of each soil sample were prepared in the extraction and analysis. The analysis quality was controlled by blank samples and Standard reference material (Soil GSS-5, obtained from the National Research Center for CRMs, Beijing, China). The limits of detection (LOD) were 1.5 × 10⁻⁵, 3 × 10⁻³, 4 × 10⁻³, 3.5 × 10⁻³, 5 × 10⁻³, 4 × 10⁻³ and 2 × 10⁻³ mg L⁻¹ for Cd, Cr, Cu, Ni, Pb, Zn and Co, respectively; and their limits of quantification (LOQ) were 3 × 10⁻⁵, 6 × 10⁻³, 8 × 10⁻³, 7 × 10⁻³, 10 × 10⁻³, 8 × 10⁻³, and 4 × 10⁻³ mg L⁻¹, respectively. The recovery for all heavy metals in the standard was within 100 ± 10%. Little variations (coefficient of variation <5%) were observed among the heavy metal concentrations of the three replicates for all samples.

2.4. Statistical and geo-statistical analysis

2.4.1. Spatial principal component analysis

- Step 1: Extract PC. The PCA was carried out using Spss 13.0 (Spss Inc., USA), and PCs before and after varimax rotation were obtained, respectively.
- Step 2: Build semivariogram and theoretic model. Semivariograms of PCs before and after rotation were established (Eq. (1)). Spherical model was used in these semivariograms due to its greater *F*-test values and determination coefficients than other models (Eq. (2)).

$$\gamma^{\#}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

where $\gamma^{\#}(h)$ is the semivariogram, h is the lag distance, $N(h)$ is the pairs of lag distance h , $Z(x_i)$ is the random functions ($i = 1, 2, 3, \dots, N(h)$).

$$\gamma(h) = \begin{cases} 0 & h = 0 \\ C_0 + C \left(\frac{3h}{2a} + \frac{1}{2} \frac{h^3}{a^3} \right) & 0 < h \leq a \\ C_0 + C & h > a \end{cases} \quad (2)$$

where $\gamma(h)$ is the semivariogram, C_0 is the nugget; $C_0 + C$ is the sill, C is the partial sill, a is the range, h is lag distance.

- Step 3: Select model for the semivariogram of each PC. Each PC obtained from multiple regionalized variables by PCA was orthogonal (uncorrelated) in the zero lag distance ($h = 0$). When the lag distance was greater than 0, characteristics of spatial correlation between PCs could be complex. Therefore, a model with little

spatial correlation between PCs was the best model for representing spatial structure characteristic of regionalized variables [22]. The codispersion coefficient was used to assess spatial correlation between any pair of PCs at each lag h . It is defined as the ratio of the cross-variogram to the square root of the product of the corresponding simple variograms [22].

- Step 4: Kriging interpolation. Based on the selected model of PCs semivariogram, spatial distribution maps of different PCs were created using ordinary kriging method in the Geostatistical Analyst module of ArcGIS 9.2 (ESRI, Redlands, CA, USA).

2.4.2. Other statistical analysis

Other statistical analyses including mean, standard error (SE), maximum, minimum and coefficient of variation (CV), and step-wise linear regressions were carried out in Spss 13.0. The one-way analysis of variance (ANOVA) was performed by LSD method in Spss 13.0.

3. Results and discussion

3.1. Total concentrations of soil heavy metals

The statistical summary of pH, SOM, CEC, and contents of clay, silt and sand are included in Table 1. Since soil samples belong to different soil types, their particle size distributions and soil textures varied considerably. The CEC values of these soil samples ranged from 10.30 cmol kg⁻¹ to 29.69 cmol kg⁻¹, and the pH values varied from 3.91 to 8.73. Among all the parameters in Table 1, the SOM and sand content had the greatest variation (CV > 20%), and silt had the least variation (CV = 5.31%).

The descriptive statistics (mean, SE, Min, Max and CV) of total concentrations of heavy metals in all soil samples are listed in Table 2. The Cd had the greatest CV (138%) and max/min ratio (38) among all heavy metals considered, while CVs and max/min ratios of other heavy metals were <40% and 2.5–7, respectively. Except Co, the total concentrations of other metals were significantly higher than their local background values ($P < 0.05$) [29]. The total concentrations of Ni, Zn and Cd exceeded their background values by 90.5%, 88.7% and 87.3%, respectively. The Grade II national standards of soil heavy metal total concentrations were considered as the upper limit safe values for human health and agricultural production in China [30]. However, mean total concentrations of all heavy metals did not exceed these upper limits [30].

3.2. Descriptive analysis of fractions of soil heavy metals

Fractions estimated by BCR SEPs were represented as percentages of total concentrations in soils (per portion) in this study. The Cd had the greatest F1 per portion (15.4%) among values (<4%) of other heavy metals considered. The great F2 per portions were observed in Cd, Co, and Pb (47.24%, 13.16%, and 9.74%, respectively), while those were low in Ni, Cu and Cr (4.48%, 2.76% and 0.79%, respectively) (Table 3). The F3 per portions in all heavy metals ranged from 8.39–52.21%, with the greatest value in Pb and the lowest value in Ni. The F4 were the major fraction of Cr, Cu, Ni, Zn and Co, accounted for 89.01%, 76.57%, 84.57%, 80.02% and 73.68%, respectively, while F4 per portions in Cd and Pb were less than 40% (Table 3). Therefore, the dominant fractions of Cd and Pb were F2, and F3, respectively, while those of Cr, Cu, Ni, Zn and Co were F4. These results were in agreement with the studies of Weltje and Fan et al. [31,32]. It indicated relatively greater bioavailability and mobility of Cd and Pb in the soil environment, and less direct and potential toxicity of Cr, Cu, Ni, Zn and Co to environment. A great F3 per portions in Pb was observed in this study, may be due to its much higher Pb affinity for soil organics [33], and this explanation

Table 1
Statistics description of soil properties.

	pH	TOM (g kg ⁻¹)	CEC (cmol kg ⁻¹)	Clay (%)	Silt (%)	Sand (%)
Mean	6.42	28.3	17.83	12.32	70.79	16.89
Standard error	0.09	0.06	0.29	0.23	0.87	0.38
Min	3.91	7.4	10.30	7.13	61.65	5.40
Max	8.73	44.3	29.69	18.52	80.72	29.13
Coefficient of variation (%)	15.73	22.61	18.62	17.13	5.31	22.08

Table 2
Statistical description of total concentrations of soil heavy metals.

	Cd	Cr	Cu	Ni	Pb	Zn	Co
Mean (mg kg ⁻¹)	0.22**	69.29*	28.48**	35.96**	28.10**	103.33**	12.34
Standard error	0.03	1.76	0.87	0.58	0.97	3.46	0.15
Min (mg kg ⁻¹)	0.07	39.69	13.71	19.39	12.14	47.87	6.54
Max (mg kg ⁻¹)	2.72	162.96	72.50	74.28	83.85	332.40	16.30
Coefficient of variation (%)	138.24	28.49	34.33	17.99	38.56	37.16	13.83
Rate over local background (%)	87.3	48.4	71.40	90.50	76.20	88.70	46.0
Rate over Grade II of the national standards (%)	7.94	0	3.97	19.05	0	4.76	–
Local background ^a	0.12	65.72	22.78	29.12	20.39	73.02	13.00
Grade II of the national standards ^b	0.30	250	50	40	250	200	–

^a The Background Values of Soil Elements in China (SEPAC and CEMCS, [29,30]).

^b Environmental quality standard for soils (SEPAC, [30]).

*, **: significantly greater than the local background level at $P < 0.05$ and $P < 0.01$, respectively.

can be confirmed by the significant relationship between the F3 of Pb and the SOM ($P < 0.01$).

Generally, the greatest CVs of all heavy metals were observed in F1, while the lowest CVs were found in F4 (Table 3). The CVs of different fractions were almost lined in the order of $F1 > F2 > F3 > F4$. There were high CVs of F1 observed in all metals except Co and Ni,

especially in Cd, Pb and Zn, reaching up to 260%, 125% and 128%, respectively. The CVs of F4 in Cr, Cu, Ni, Zn and Co were lower than 40%, while those in Cd and Pb were about 84% and 68%, respectively (Table 3). Apart from F4, CVs of all fractions were high, indicating that F1, F2, and F3 of heavy metals had great spatial variability in our study area.

Table 3
Statistical description of different fractions of soil heavy metals.

	Cd	Cr	Cu	Ni	Pb	Zn	Co
Acid-soluble (F1)							
Mean (mg kg ⁻¹)	0.05	0.08	0.52	0.91	0.18	2.36	0.42
Standard error	0.01	0.01	0.04	0.05	0.02	0.27	0.02
Min (mg kg ⁻¹)	0.00	0.00	0.06	0.33	0.00	0.00	0.01
Max (mg kg ⁻¹)	1.16	0.37	3.44	5.32	2.00	23.30	0.89
Coefficient of variation (%)	260.00	74.36	86.4	56.02	124.72	127.54	39.28
Per portion (%)	15.40	0.12	1.77	2.56	0.65	2.23	3.37
Reducible (F2)							
Mean (mg kg ⁻¹)	0.10	0.52	0.78	1.59	2.63	7.51	1.62
Standard error	0.01	0.03	0.052	0.07	0.17	0.61	0.07
Min (mg kg ⁻¹)	0.02	0.122	0.03	0.7	0.53	1.62	0.74
Max (mg kg ⁻¹)	1.25	2.352	4.11	7.63	18.11	58.69	7.43
Coefficient of variation (%)	139.81	64.60	73.59	47.39	73.38	90.55	48.15
Per portion (%)	47.24	0.79	2.76	4.48	9.74	7.16	13.16
Oxidizable (F3)							
Mean (mg kg ⁻¹)	0.03	6.89	5.64	2.96	14.08	8.69	1.21
Standard error	0.00	0.42	0.36	0.08	0.50	0.53	0.03
Min (mg kg ⁻¹)	0.01	2.02	1.23	1.17	5.04	0.26	0.60
Max (mg kg ⁻¹)	0.27	41.30	22.27	9.36	38.16	46.25	2.70
Coefficient of variation (%)	106.25	68.21	71.10	31.97	39.56	68.81	25.62
Per portion (%)	15.97	10.09	18.90	8.39	52.21	8.59	9.79
Residual (F4)							
Mean (mg kg ⁻¹)	0.04	61.63	21.56	30.4	11.34	83.92	9.32
Standard error	0.00	1.674	0.59	0.52	0.69	3.20	0.17
Min (mg kg ⁻¹)	0.00	32.20	8.00	14.63	0.10	0.18	3.40
Max (mg kg ⁻¹)	0.14	157.96	49.81	51.96	35.39	311.10	13.35
Coefficient of variation (%)	83.78	30.49	30.57	19.34	68.08	42.78	20.71
Per portion (%)	21.39	89.00	76.57	84.57	37.4	82.02	73.68
Secondary-phase (F1 + F2 + F3)							
Mean (mg kg ⁻¹)	0.18	7.49	6.94	5.45	16.89	18.56	3.24
Standard error	0.03	0.43	0.42	0.18	0.61	1.29	0.09
Min (mg kg ⁻¹)	0.04	2.45	1.61	3.17	6.80	2.60	1.75
Max (mg kg ⁻¹)	2.61	43.08	26.59	22.32	58.27	128.24	10.80
Coefficient of variation (%)	161.45	64.89	67.29	36.51	40.62	77.59	29.90
Per portion (%)	78.61	11.00	23.43	15.43	62.60	17.98	26.32

Table 4

Correlation between the total concentration of soil heavy metals and their fractions.

	Cd	Cr	Cu	Ni	Pb	Zn	Co
Acid-soluble (F1)	0.98**	0.15	0.60**	0.42**	0.41**	0.34**	0.07
Reducible (F2)	0.99**	0.07	0.51**	0.40**	0.47**	0.42**	-0.01
Oxidizable (F3)	0.91**	0.31**	0.80**	0.38**	0.67**	0.35**	0.10
Residual (F4)	0.39**	0.97**	0.91**	0.95**	0.77**	0.93**	0.87**

*, ** Significant at $P \leq 0.05$ and $P \leq 0.01$, respectively.

Higher concentration and percentage of heavy metal SPF can not only reflect a greater tendency of bioavailability, but also a higher level of anthropogenic contamination [12,18,34]. In this study area, the SPF concentration of Cd was even greater than its local total concentration background value (Tables 2 and 3). Its maximum value reached 2.61 mg kg^{-1} , being 22 times greater than its local background value [29] (Tables 2 and 3). However, SPF concentrations of other metals were lower than their local background values. Eight of our soil samples even had Cd SPF concentration greater than the total Cd concentration in the Grade II national standards. However, all soil samples had SPF concentrations of other metals less than the Grade II national standards.

The higher SPFs of Cd and Pb suggested that they were more bioavailable than Cr, Cu, Ni, Zn and Co in our study area (Table 3). Soil heavy metal contamination caused by anthropogenic activities can increase SPFs [35–37]. Therefore, the high SPFs of Cd and Pb indicated that concentrations of these two heavy metals were greatly affected by intensive anthropogenic activities in the study area, such as cultivation, management, cropping system.

Significant correlations ($P < 0.05$) were observed between the total concentrations of most soil heavy metals and their different fractions, except F1, F2 of Cr and all the non-residual fractions of Co (Table 4). For Cd, correlation coefficients of F1, F2 and F3 (>0.91) were higher than that of F4 (0.39). However, for the other heavy metals, correlation coefficients of F1, F2 and F3 were lower than

those of F4 (Table 4). This indicated that “active” and “potential active” fractions of Cd were mostly influenced by the total Cd concentration level in the study area, while the residual fractions of Cr, Cu, Ni, Pb, Zn and Co were mostly affected by their total concentration levels.

3.3. Soil heavy metal fractions in different types of industry zones

In order to avoid the possible influences caused by different soil types, only soil samples belong to Huangni soil type were investigated for the fractions in different industry zones. Totally, 70 soil samples were collected. The greatest F1 concentrations of Cu, Zn and Co were observed in industry zone of VPZ, while the greatest F1 of Cd and Pb were observed in SPIZ and DPIZ, respectively (Table 5). Remarkable variances in F2 concentrations of Cr, Cu, Ni, Pb and Co were observed in different industry zones. The F2 of Cr was greatest in SPIZ, but least in VPZ. The F2 of Ni was greatest in CIZ and least in DPIZ, while the F2 of Pb was greatest in DPIZ. The greatest F2 of Cu and Co was observed in VPZ and LBZ, respectively (Table 5). The SPIZ had the greatest F3 in Cd, Cu, Pb, Zn, and Co, while the VPZ had the lowest F3 in these heavy metals (Table 5). The F4 concentrations in different industry zones also showed great variances. The DPIZ had the lowest F4 in Cd, the LBZ had the lowest F4 in Pb and Co, while the SPIZ has the lowest F4 in Cr, Cu, Zn, Ni (Table 5).

Table 5

Fraction concentrations of soil heavy metals in different types of industry zones in Huangni soil.

Industry	Cd	Cr	Cu	Ni	Pb	Zn	Co
Acid soluble (F1)							
CIZ (12)	0.027 ± 0.006^a	0.086 ± 0.018	0.559 ± 0.130	1.21 ± 0.38	0.102 ± 0.022	1.41 ± 0.24	0.353 ± 0.030
DPIZ (16)	0.023 ± 0.003	0.059 ± 0.009	0.470 ± 0.064	0.82 ± 0.06	0.206 ± 0.038	1.59 ± 0.30	0.427 ± 0.027
VPZ (18)	0.030 ± 0.007	0.061 ± 0.006	0.594 ± 0.134	1.05 ± 0.09	0.119 ± 0.017	3.66 ± 0.75	0.434 ± 0.054
SPIZ (9)	0.033 ± 0.010	0.059 ± 0.015	0.491 ± 0.093	0.95 ± 0.08	0.159 ± 0.062	2.16 ± 0.61	0.417 ± 0.036
LBZ (15)	0.018 ± 0.003	0.067 ± 0.011	0.337 ± 0.053	0.91 ± 0.10	0.141 ± 0.035	2.22 ± 0.53	0.344 ± 0.042
Reducible (F2)							
CIZ (12)	0.077 ± 0.011	0.503 ± 0.104	0.669 ± 0.099	2.14 ± 0.52	2.18 ± 0.28	5.98 ± 1.19	1.82 ± 0.24
DPIZ (16)	0.078 ± 0.008	0.460 ± 0.034	0.896 ± 0.118	1.46 ± 0.11	2.93 ± 0.29	7.29 ± 1.50	1.40 ± 0.07
VPZ (18)	0.074 ± 0.007	0.372 ± 0.027	0.894 ± 0.184	1.64 ± 0.12	1.96 ± 0.19	8.60 ± 1.12	1.56 ± 0.12
SPIZ (9)	0.093 ± 0.018	0.629 ± 0.218	0.714 ± 0.040	1.64 ± 0.15	2.05 ± 0.21	7.88 ± 1.97	1.53 ± 0.08
LBZ (15)	0.069 ± 0.006	0.457 ± 0.037	0.593 ± 0.072	1.74 ± 0.18	2.14 ± 0.18	7.26 ± 1.18	2.01 ± 0.26
Oxidizable (F3)							
CIZ (12)	0.021 ± 0.003	7.72 ± 1.66	5.05 ± 0.54	3.33 ± 0.57	12.56 ± 1.13	7.62 ± 1.49	1.07 ± 0.07
DPIZ (16)	0.027 ± 0.002	6.70 ± 0.72	5.76 ± 1.07	2.78 ± 0.14	15.31 ± 1.35	10.51 ± 1.31	1.18 ± 0.07
VPZ (18)	0.023 ± 0.002	4.83 ± 0.38	4.70 ± 0.73	2.88 ± 0.19	10.87 ± 0.82	7.20 ± 0.57	1.18 ± 0.07
SPIZ (9)	0.033 ± 0.005	6.62 ± 0.73	7.13 ± 1.77	3.23 ± 0.29	15.58 ± 2.45	11.72 ± 2.32	1.26 ± 0.04
LBZ (15)	0.023 ± 0.002	5.77 ± 0.63	4.43 ± 0.93	3.31 ± 0.25	13.10 ± 1.25	8.00 ± 1.26	1.22 ± 0.08
Residual (F4)							
CIZ (12)	0.039 ± 0.009	65.19 ± 3.81	18.35 ± 1.53	32.36 ± 2.46	13.41 ± 2.88	85.01 ± 6.12	9.34 ± 0.62
DPIZ (16)	0.020 ± 0.006	64.16 ± 4.45	19.47 ± 1.46	33.00 ± 1.59	9.17 ± 1.91	78.36 ± 4.07	9.63 ± 0.31
VPZ (18)	0.040 ± 0.008	64.20 ± 5.21	23.00 ± 1.58	28.61 ± 1.49	11.40 ± 1.54	76.70 ± 5.01	9.11 ± 0.56
SPIZ (9)	0.039 ± 0.008	55.72 ± 2.94	20.05 ± 2.30	28.05 ± 1.08	10.21 ± 3.21	74.00 ± 7.05	8.96 ± 0.37
LBZ (15)	0.040 ± 0.009	59.15 ± 3.97	19.24 ± 1.20	28.04 ± 1.80	8.39 ± 1.39	86.13 ± 8.42	8.32 ± 0.70

Data in parenthesis is the number of soil samples, $n = 70$. Chemical industry zone (CIZ), dyeing and paper-making industry zone (DPIZ), smelting and plating industry zone (SPIZ), livestock breeding zone (LBZ), vegetable production zone (VPZ).

^a Means \pm standard error.

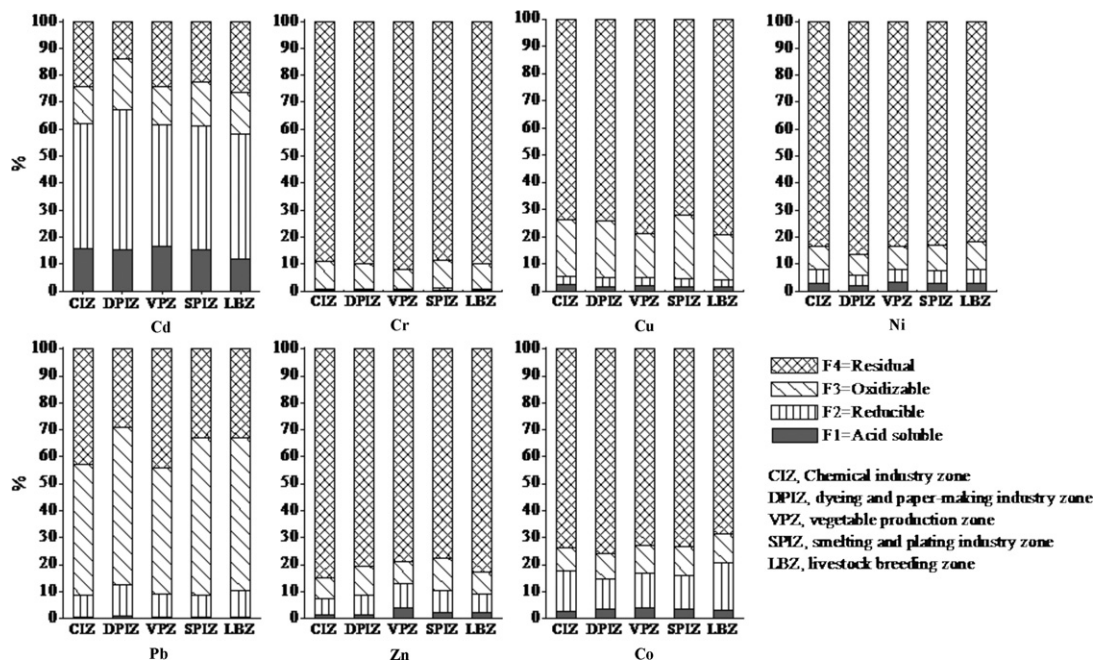


Fig. 2. Fraction distributions of soil heavy metals in different types of industry zones in Huangni soil.

For Huangni soil type, fraction distributions of heavy metals in different industry types are shown in Fig. 2. Direct and potential eco-toxicity fractions (SPFs) of Cd and Pb were greatest in DPIZ, while those of Cr, Cu, Zn, Ni were greatest in SPIZ. Industry type was a controlling factor of direct and potential bioavailability of heavy metals in soil (Fig. 2). Higher SPFs of Cd, Pb in DPIZ can probably be attributed to the dyeing wastes containing high Cd and Pb contents; whereas higher SPFs of Cr, Cu, Zn, Ni in SPIZ might be caused by chromium iron, coated copper and zinc in the waste water and residue of the smelting industry and plating industry [38–40].

3.4. Influences of soil properties on fraction distributions of heavy metals in different types of industry zones

The mobilization-immobilization processes of heavy metal in soil may be affected by a variety of soil properties. Linear stepwise regressions of SPF percentages of heavy metals were performed to assess the influences of soil properties on heavy metal availability in the five industry types (Table 6). The SPF percentage of Cd was significantly influenced by SOM, silt content and CEC ($P < 0.05$) in all five industry types, while that of Cr was not affected by any soil property except clay content in VPZ. SOM, clay and sand contents were the controlling factors for the SPF of Cu in SPIZ, CIZ and LBZ, respectively; while clay content and MnO_x influenced the SPF of Zn in DPIZ, LBZ and CIZ, respectively. Ni was mainly influenced by contents of clay, silt, sand, FeO_x and MnO_x , while Pb was largely affected pH, SOM, CEC, and contents of clay and MnO_x . Soil properties had no effect on the SPF of Co in CIZ, SPIZ and LBZ.

Among these soil properties considered, SOM and clay content were the controlling factors for SPFs of most heavy metals in the five industry types. Most SPFs of heavy metals showed no correlation with pH except SPF of Pb in CIZ (Table 6). The metal–SOM interaction has various and complex consequences both on the solubility, mobility and bioavailability of heavy metals [41] and on SOM turnover process [42]. Generally, solid phase of SOM has great retention of heavy metals, thus decreases mobility and reduces bioavailability of heavy metals [13,43,44]. However, cationic metals that would ordinarily precipitate at high pH values of most soils are sometimes maintained in solution through complexation with

soluble organics [13,45]. From the particle-size fractions (sand, silt, and clay), the finer particles showed higher concentrations of heavy metals due to increased surface areas, higher clay minerals and organic matter content, and the presence of Fe–Mn oxides and sulphides [46,47]. In another aspect, the increase of the metal portion with the sand fractions might be due to the fact that the presence of minerals has a strong retention of heavy metals [46].

3.5. Spatial distribution of SPFs of soil heavy metals

Bioavailability of soil heavy metals mostly depends on their SPFs [12,18,34]. Therefore, PCA method was performed to determine factors governing the spatial distributions of SPFs of different heavy metals. Component matrixes were shown in Tables 7 and 8. Eigenvalues from covariance analysis indicated that the first four PCs accounted for 86.24% of the total variance of data (Table 7). Two main PCs with initial eigenvalues > 1 were retained since eigenvalue < 1 indicated that the factor could explain less variance than an individual attribute itself (Table 7) [48]. An orthogonal rotation of the first two PCs was performed using the Varimax criterion (Table 8).

The semivariograms before and after Varimax rotation were modeled using a nugget effect and two spherical schemes with a range of 12.90 km and 17.16 km by spatial principal component analysis method (Eqs. (3) and (4)).

$$\gamma(h) = 0.310 + 0.787 \times \left(\frac{3}{2} \times \frac{h}{12.90} - \frac{1}{2} \times \frac{h^3}{12.90^3} \right),$$

(Before Rotation) (3)

$$\gamma(h) = 0.509 + 0.632 \times \left(\frac{3}{2} \times \frac{h}{17.16} - \frac{1}{2} \times \frac{h^3}{17.16^3} \right),$$

(After Varimax Rotation) (4)

According to the Eqs. (3) and (4), Varimax rotation increased the spatial correlation between the first two PCs, especially for the first lags, and this result was in agreement with the findings of Wang et al. [49]. Since spatial correlation characteristic was the main

Table 6
Linear regression models between secondary-phase fraction percentage of heavy metals and soil properties in the five types of industry zones.

Industry	Model	R	F	Sig.
Cd				
CIZ	$y = 74.403 + 17.658x_2 - 2.521x_6$	0.741	13.366	0.000
DPIZ	–	–	–	–
VPZ	$y = 58.578 + 18.684x_2 - 1.952x_6$	0.523	4.888	0.016
SPIZ	$y = 124.193 - 3.850x_3$	0.584	6.719	0.022
LBZ	$y = 66.202 + 15.248x_2 - 2.833x_3$	0.619	10.540	0.000
Cr				
CIZ	–	–	–	–
DPIZ	–	–	–	–
VPZ	$y = 0.061 + 0.714x_3$	0.420	5.797	0.023
SPIZ	–	–	–	–
LBZ	–	–	–	–
Cu				
CIZ	$y = 42.615 - 1.494x_3$	0.438	5.463	0.028
DPIZ	–	–	–	–
VPZ	–	–	–	–
SPIZ	$y = -7.630 + 11.508x_2$	0.834	29.660	0.000
LBZ	$y = 8.396 + 0.823x_5$	0.340	4.578	0.039
Ni				
CIZ	$y = -53.634 + 0.981x_4$	0.667	18.395	0.000
DPIZ	$y = -39.882 + 0.529x_4 + 0.935x_5$	0.666	5.981	0.012
VPZ	$y = 28.545 - 5.392x_7 + 0.011x_8$	0.693	11.990	0.000
SPIZ	$y = 8.154 + 0.016x_8$	0.568	6.185	0.027
LBZ	$y = 36.290 - 1.225x_3 - 3.608x_7 + 0.013x_8$	0.843	26.938	0.000
Pb				
CIZ	$y = 126.362 - 9.849x_1$	0.489	7.212	0.013
DPIZ	–	–	–	–
VPZ	$y = 70.705 + 3.928x_3 - 18.548x_7$	0.739	15.653	0.000
SPIZ	$y = -24.875 + 5.412x_6$	0.660	10.039	0.007
LBZ	$y = 94.392 - 9.883x_2$	0.494	11.271	0.002
Zn				
CIZ	$y = 6.166 + 0.016x_8$	0.427	4.897	0.038
DPIZ	$y = 43.299 - 2.002x_3$	0.560	7.306	0.016
VPZ	–	–	–	–
SPIZ	–	–	–	–
LBZ	$y = 35.760 - 1.548x_3$	0.390	6.263	0.017
Co				
CIZ	–	–	–	–
DPIZ	–	–	–	–
VPZ	$y = 30.988 + 1.554x_3 - 9.069x_7 + 0.013x_8$	0.689	7.519	0.001
SPIZ	–	–	–	–
LBZ	$y = 49.815 - 11.18x_2 + 0.939x_5 - 5.810x_7 + 0.028x_8$	0.857	22.066	0.000

pH (x_1), SOM (x_2), clay content (x_3), silt content (x_4), sand content (x_5), CEC (x_6), FeO_x content (x_7) and MnO_x content (x_8). For some industry types and heavy metals, regression models were not listed since they did not pass *F* test at 0.05 level.

Table 7
Total variance explained by principle component analysis of soil secondary-phase heavy metals.

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
PC1	2.86	40.79	40.79	2.86	40.79	40.79	1.86	26.51	26.51
PC2	1.35	19.30	60.08	1.35	19.30	60.08	1.77	25.32	51.83
PC3	0.97	13.80	73.89	0.97	13.80	73.89	1.32	18.87	70.70
PC4	0.87	12.35	86.24	0.87	12.35	86.24	1.09	15.54	86.24

criterion for PC selection, the Eq. (3) (before rotation) was selected as the semivariogram model to generate PCs spatial distribution maps of SPFs of heavy metals in this study (Fig. 3a and b).

The greatest PC1 value (representing the SPFs of Cd, Cr, Cu, Pb and Zn) was observed in the northeast corner of Kunshan (Fig. 3a). This area is the national-level economic and technological development zone in Kunshan, which has a high density of petrochemical, precision machinery, electron, biological pharmaceutical factory, printing and dyeing textile, metallurgic plant and electric plating industries. The environment quality report indicated that more than 85% waste gas, water and industrial residue in Kunshan were discharged from this area [25]. Contaminated water (IV Grade

according to National Water Quality Standard of China) was used to irrigate the crop lands in this area [50,51]. Great PC1 value was also observed in Zhenyi town (Fig. 3a). The Wusong River Industrial Park, which has high density of electron and manufacturing industries, is located in this area. In addition, this area was adjacent to Suzhou Industrial Park, which also has intensive electron, biological pharmaceutical, manufacturing and energy industries. High concentrations of Cd, Cr, Cu, Pb and Zn in the waste water from these industries could increase the SPFs of these heavy metals in soils. The Cd, Cr, Cu, Pb and Zn are sulphophile family elements, with strong thiophile and chalcophile properties and have similar geochemical behaviors. Isomorph of these heavy metals might lead to their

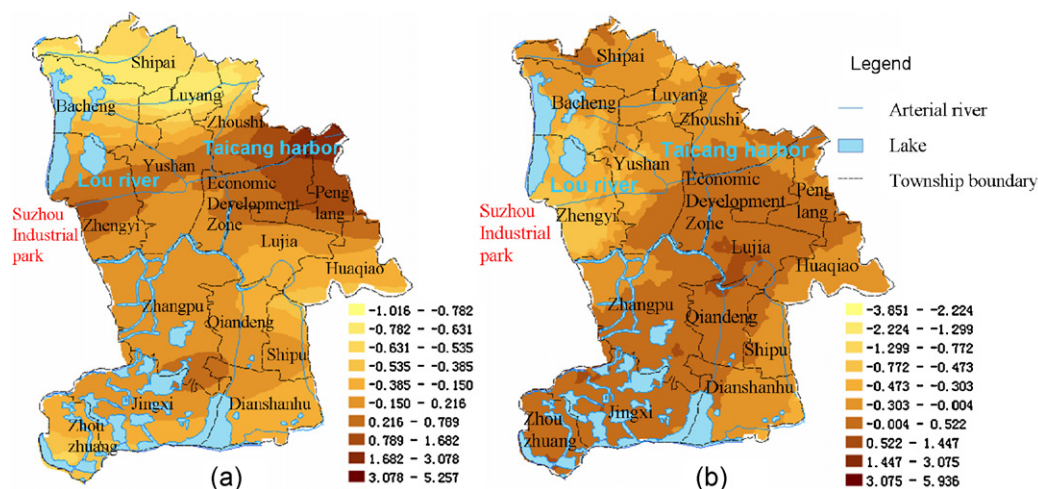


Fig. 3. Kriged maps of (a) first principal component (PC1) and (b) second principal component (PC2) of soil secondary-phase heavy metals in the spatial principle component analysis.

Table 8

Component matrix of factor loadings before and after varimax rotation of the first two principle components of soil secondary-phase heavy metals.

Heavy metal	Factor loadings		Rotated factor loadings	
	PC1	PC2	PC1	PC2
Cd	0.72	-0.29	0.87	0.17
Cr	0.64	0.22	0.46	0.13
Cu	0.84	0.05	0.30	0.87
Ni	0.20	0.83	-0.17	0.12
Pb	0.79	-0.28	0.86	0.31
Zn	0.75	0.17	0.18	0.93
Co	-0.07	0.65	-0.02	-0.01

similar spatial distributions in a certain scale [52]. Besides, the spatial distribution of the PC1 was positively correlated with soil pH, SOM, sand and FeO_x contents with $P < 0.05$. Therefore, the spatial distribution of PC1 in this study area was affected by industrial sewage irrigation, geochemical character and soil physico-chemical properties.

The greatest PC2 value (representing the SPFs of Ni and Co) was observed in the Lujia town (Fig. 3b). In addition, great PC2 value was also observed in the economic and technological development area, including Penglantown, Yushan town, Qiandeng town, Zhangpu town, Jinxi town and Zhouzhuang town (Fig. 3b). Ni and Co are iron family elements, with strong thiophile and siderophile properties and similar geochemical actions in nature. Similar spatial distributions of Ni and Co were observed at a certain scale in the literature [52]. Great PC2 value was also observed in Lujia town with several big circuit board factories, where soil and water were seriously contaminated. High concentration of Ni and Co in the waste water from circuit board factories could increase the SPFs of Ni and Co in surrounding soils. Spatial distribution of PC2 was also significantly ($P < 0.05$) correlated with soil pH, SOM, silt and MnO_x contents with $P < 0.05$. Therefore, spatial distribution of the PC2 was controlled by geochemical character, industrial sewage irrigation and soil physico-chemical properties.

4. Conclusions

Fraction concentrations of soil heavy metals in Kunshan were investigated using BCR sequential extraction procedure. The Cd and Pb were mainly presented in the reducible fraction and oxidizable fraction, respectively, while Cr, Cu, Ni, Zn and Co were mostly presented in their residual fractions. Therefore, the bioavailability of

Cd and Pb was higher than that of Cr, Cu, Ni, Zn and Co in Kunshan. The high secondary-phase fractions (acid-soluble, reducible and oxidizable forms) of Cd and Pb indicated that Cd and Pb concentrations were greatly affected by anthropogenic activities in the study area. The bioavailability of Cd and Pb was great in the dyeing and paper-making industry zone, while that of Cr, Cu, Zn, Ni was great in the smelting and plating industry zone. Soil organic matter and clay contents were the controlling factors for the fraction distributions of most heavy metals in the five types of industry zones. Two PCs were used to represent the spatial distributions of the secondary-phase fractions of soil heavy metals in Kunshan. The PC1 represented Cd, Cr, Cu, Pb and Zn, while the PC2 represented Ni and Co. Great PC1 value was observed in the northeast corner of Kunshan and in Zhenyi town. Great PC2 value was observed in the Lujia town. Spatial distributions of heavy metals in Kunshan were related to the industrial sewage irrigation, geochemical character and soil physico-chemical properties.

Acknowledgments

This work was financially supported by National Basic Research Program (973) of China (Project No. 2002CB410810), the National Natural Science Foundation of China (Project No. 41101278), the State Key Laboratory of Soil and Sustainable Agriculture of China (Project No: Y052010035) and Guangzhou Science Research Program (Project No: 10A033).

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