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Spatial Pattern and Environmental Quality Assessment of Potentially Toxic Elements in Soils of Central Agricultural Areas, China

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ABSTRACT

Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn concentrations in surface soils of central agricultural areas were investigated to evaluate the environmental quality of these potentially toxic elements using 603 samples. The following average concentrations were obtained: Cu, 21.8 mg/kg; Ni, 28.4 mg/kg; Cr, 74.0mg/kg; Co, 13.2 mg/kg; Mn, 677.1 mg/kg; Pb, 28.2 mg/kg; Hg, 0.047 mg/kg; Cd, 0.194 mg/kg; Zn, 63.7 mg/kg. Correlation analysis was applied to evaluate the results and identifying the possible sources of these potentially toxic elements. Distribution maps of the elements were created using the inverse distance weighted interpolation method. The nine metals exhibited generally distinct geographical patterns. Results showed that 6,730 km² of the study area presented higher pollution indices and was slightly polluted.

INTRODUCTION

The accumulation of toxic elements in soils directly affects humans and the ecosystem (Wcislo et al. 2002, Granero & Domingo 2002), and the accumulation of potentially toxic elements in topsoil specifically has a significant effect on crop yields, food quality, and soil microbial groups by entering the food chains (Udom et al. 2004).

Much research on pollution and accumulation of potentially toxic elements in soils has been reported (Carlosena et al. 1998, Ghrefat & Yusuf 2006). The contents of potentially toxic elements can be primarily ascribed to human activities in urban areas (Liaghati et al. 2003, Liu et al. 2004, Ljung et al. 2006). Many studies of trace metal concentrations worldwide have been conducted in the past years (Sierra et al. 2007, De Temmerman et al. 2003, Hammarstrom et al. 2003).

The pollution-induced health risks of potentially toxic elements (Madrid 2010) in contaminated soils, which are released into the environment by both natural and anthropogenic sources (Li et al. 2007), remain a major problem in China (Khan et al. 2008). Some studies have also assessed soil pollution by potentially toxic elements in China (Wang 2002, Liu et al. 2006). Henan province is an important production area of vegetables, fruits, and grains. These agricultural products not only meet the needs of local people,

but also are sold outside the country. Toxic element concentrations increase in the soil of Henan has been reported, which include Pb and other metals by mining behaviour.

The primary objectives of this research were to: (1) Estimate the concentration levels of nine elements in the surface soil, (2) Determine their spatial distribution pattern and pollution condition, (3) Assess the quality of the soil environment. The data provide useful information for evaluating the risk of anthropogenic influence.

MATERIALS AND METHODS

Study region: Henan province is located in the central part of China (Fig. 1), particularly between the latitude $31^{\circ}23'$ to $36^{\circ}22'$ (N) and longitude $110^{\circ}21'$ to $116^{\circ}38'$ (E). It is also in the middle and lower reaches of the Yellow River; its terrain is higher in the west and lower in the east, most of which is under warm temperate while very few areas belong to the subtropical monsoon climate conditions. It is also a very important province as the national agricultural base.

Henan's soils are made up mainly of calcium carbonate (lime) in hardened layers of alluvium. Because of comparatively low precipitation levels, there is little leaching. The higher land of the west is mainly mountain yellow-brown earth, better drained than the plains. The more fertile areas fringing the plains were the sites of early civilization. AlluChunlin Yang et al.



Fig. 1: Location, soil type and sampling sites of Henan Province in China.

vium is spread throughout the plains; it is yellowish and gray, porous, granular and poor in organic matter.

Soil sampling: Soil samples used in this study were collected from locations shown in Fig. 1. The sampling points in each area are selected on the flat terrain and far from major roads based on the map of bedrock distribution. Soil samples from the 603 soil profiles are collected at depths of 0-20 cm for investigating the distribution of 9 elements in surface soil. The concentrations of every element in soils were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Model PS 1000 AT, USA).

Pollution index method: The Nemerow pollution index was selected as the criterion to assess the quality of soil environments (Liu et al. 2004). The concentrations of Cu, Pb, Zn, Cd, Ni, Cr, Co, Mn, and Hg were determined to assess soil pollution conditions in accordance with the second level of Chinese Soil Quality Criterion GB 15618-1995 (6.5<pH<7.5). The reference values of Cu, Pb, Zn, Cd, Ni, Cr, Co, Mn, and Hg were 50, 250, 200, 0.30, 40, 250, 40, 1500 and 0.50, respectively.

RESULTS AND DISCUSSION

Concentrations of potentially toxic elements: Summary statistics for the determined potentially toxic elements in the studied samples are presented in Table 1. The following mean values of the elements were obtained (data are expressed as mg/kg dry weight): 21.8 for Cu, 28.2 for Pb, 63.7 for Zn, 0.194 for Cd, 28.4 for Ni, 74.0 for Cr,0.047 for Hg, 13.2 for Co, and 677.1 for Mn. The mean value of the Cd, Co, Cr, Hg, Ni and Pb concentrations in Henan province soils were higher compared with the reference values of the background levels of Chinese soils. The distributions of the potentially toxic elements were strongly skewed. After logarithmic transformation, each element exhibited a normal distribution (Fig. 2).

Relationships between the elements: Correlation analysis between the concentrations of the nine elements revealed that, most correlations were positive and statistically significant (p < 0.01). This implies that one or more common factors of high importance determined the concentrations. Pearson's correlation coefficients for the elements obtained after logarithmic transformation are summarized in Table 2. Ni, Cr,

Element	Mean	St D. Mean	Geometric Coefficient	Variation	Skewness	Kurtosis background	Chinese
Cd	0.194	0.316	0.167	1.628	13.72	197.20	0.097
Co	13.17	4.88	12.54	0.370	4.72	45.19	11.6
Cr	73.99	17.08	72.63	0.231	6.75	97.63	57.3
Cu	21.82	9.55	20.79	0.438	12.40	238.47	22
Hg	0.047	0.042	0.039	0.897	5.987	48.59	0.04
Mn	677.06	288.58	644.06	0.426	6.84	76.19	710
Ni	28.36	8.04	27.34	0.283	2.07	16.08	24.9
Pb	28.20	56.76	25.22	2.013	22.64	533.35	26
Zn	63.73	18.13	61.83	0.285	3.95	31.49	68

Table 1: Soil heavy metal concentrations in Henan province (mg/kg).

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	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	ОМ	pН	Clay
Cd	1.00											
Co	0.08	1.00										
Cr	-0.02	0.39	1.00									
Cu	0.10	0.62	0.27	1.00								
Hg	0.15	0.07	0.01	0.09	1.00							
Mn	0.05	0.82	0.33	0.37	0.09	1.00						
Ni	0.06	0.88	0.44	0.66	0.10	0.68	1.00					
Pb	0.19	0.06	0.04	0.09	0.09	0.08	0.09	1.00				
Zn	0.44	0.62	0.19	0.56	0.14	0.40	0.63	0.32	1.00			
OM	0.12	0.16	0.06	0.21	0.22	0.23	0.27	0.03	0.26	1.00		
pH	0.09	0.03	-0.11	-0.05	0.00	-0.07	0.02	0.00	0.12	-0.10	1.00	
Clay	0.08	0.54	0.30	0.35	0.09	0.43	0.66	0.09	0.41	0.21	0.07	1.00

Table 2: Correlation matrix for heavy metal concentration.

Table 3: Potentially toxic elements concentration in different land use types (mg/kg).

	Cd	Со	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Irrigated croplands	0.183	13.4	74.7	22.2	0.047	694.6	28.7	25.8	63.3
Rainfed croplands	0.197	13.0	73.6	21.4	0.046	657.1	27.9	33.0	64.6
Forest	0.177	13.4	72.9	22.5	0.056	700.0	28.7	25.0	66.1
Grassland	0.184	14.3	73.3	23.9	0.036	659.2	31.4	25.2	69.6
Artificial surfaces	0.362	11.7	68.8	19.5	0.040	586.3	26.1	23.2	58.4
Bare areas	0.137	12.5	67.0	21.1	0.039	636.5	25.4	24.1	56.1

and Co were associated with same parent materials and soil types, which suggests a common geogenic origin of these three elements. Stronger correlations between Co and Ni (r=0.88) and between Co and Mn (r=0.82) were observed. Co was positively correlated with Mn, because these two elements were from same parent rocks. Navas & Machín (2002) investigated the correlations of potentially toxic elements in soils and found significant correlations between them as well.

Spatial distribution pattern: The geographical distributions of Cu, Ni, Cr, Co, Mn, Pb, Hg, Cd and Zn are shown in Fig. 3. The variability in their large-scale distribution can be ascribed to the different soil types and land use types in

Table 4: Potentially toxic elements concentrations in different soil types (mg/kg).

	Semi- alfisols	Aridosols	Vertisols	Cambisols	Anthrosols	Alfisols
Cd	0.306	0.164	0.170	0.189	0.144	0.162
Co	13.4	13.8	13.7	12.9	12.7	13.3
Cr	79.5	78.6	78.5	69.7	70.7	78.3
Cu	22.1	22.3	25.2	20.9	20.7	21.5
Hg	0.045	0.047	0.054	0.045	0.044	0.046
Mn	668.3	672.1	743.7	639.5	659.5	747.2
Ni	29.2	28.5	30.2	27.6	26.4	28.9
Pb	26.0	25.6	27.9	24.9	26.2	42.5
Zn	70.6	65.6	62.9	63.2	59.6	61.0

Henan province. The maps of Cu, Ni and Cr showed similar spatial distribution patterns mainly controlled by regional parent materials and pedogenic factors. Higher Cu, Ni and Cr concentrations were found in a mining region in western Henan province. Higher Co and Mn were mainly located in areas with alfisols. In addition, the spatial distribution patterns of Pb and Cd are characterized by a distinct anthropogenic activity. Pb and Cd in surface soils in the industrial city areas were enriched.

Relationships between land use and soil types: Land use with different soil properties affected the concentrations of



Fig. 2: Variations of potentially toxic elements concentrations after logarithmic transformation (Asterisk stands for median value).

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Fig. 3: Spatial distributions of nine potentially toxic elements in the studied soils of Henan.



Fig. 4: Land use of Henan.

potentially toxic elements, with the concentrations under different land uses being different (Fig. 4). The samples with higher concentrations of Cr and Hg were obtained from irrigated croplands, whereas most samples with high levels of Pb concentrations came from rainfed croplands (Table 3). Measurements of the analysed elements for each of the studied soil types are given in Table 4. The concentrations of Cu, Hg and Ni are higher in vertisols, whereas Pb and Mn are higher in alfisols. Those of Cd, Cr and Zn are higher in semi-alfisols, and Co concentration is higher in aridosols.

Pollution assessment: Based on the Nemerow synthetic pollution index (Table 5; Fig. 5), 593 samples were safe or unpolluted, 4 were slightly polluted, 1 was moderately polluted, and 5 were severely polluted. The regions affected by severe pollution were mainly located in urban areas and in mining areas of Henan province.



Fig. 5: The pollution class distribution basing on Nemerow synthetic pollution index.

	Min	Max	Mean	St.D	CV
Cd	0.079	8.698	0.414	0.533	1.290
Co	0.120	1.780	0.329	0.122	0.370
Cr	0.105	1.360	0.347	0.119	0.343
Hg	0.011	0.861	0.076	0.081	1.058
Cu	0.025	4.154	0.260	0.196	0.753
Mn	0.178	3.079	0.451	0.192	0.426
Ni	0.080	1.945	0.523	0.175	0.335
Pb	0.175	17.211	0.350	0.710	2.025
Zn	0.073	0.851	0.236	0.071	0.300

Table 5: The single factor pollution indexes of 9 elements.

CONCLUSIONS

Correlation analysis revealed that the concentrations of Pb, Hg and Cd were more influenced by anthropogenic inputs compared with the other elements. In northern Henan, industry development has led to more severe soil pollution. Approximately 6,730 km² of Henan province was found to be slightly polluted. The results of this study provide useful information for establishing reasonable land use planning and warrant further research into the potential environmental risks induced by potentially toxic elements.

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