Plant Soil (2011) 349:241–251
DOI 10.1007/s11104-011-0866-z

REGULAR ARTICLE

Accumulation of trace elements in agricultural topsoil under different geological background

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Received: 3 March 2011 / Accepted: 10 June 2011 / Published online: 23 June 2011

Abstract For establishing rational farming mechanism, it is essential to know the relative contribution of different geological background and anthropogenic activities to trace elements in agricultural soil. In this paper, 282 surface soil samples were collected based on the different geological background. Five harmful trace elements (As, Cd, Cr, Hg and Pb) were analyzed. The results indicated most of trace elements contents were far beyond the threshold of uncultivated soil background, which indicate anthropogenic input strongly influenced on trace elements in agricultural soil. In addition, correlation analysis showed trace element contents exhibited high relationships with soil pH, C/N and physical clay (<0.01 mm) ($p<0.05$). The principal component analysis showed that the first component included Cd, Cr and Hg, while Pb and As formed the second component. Furthermore, in the agricultural topsoil derived from carbonate rock, the high background values of trace elements and alkaline condition made the enrichments of Cd, Cr and Hg were the most significant. In the agricultural topsoil derived from red residua, the Pb and As contents was the highest values among the soil categories, partly because the type of soil had amount of physical clay (<0.01 mm). In the agricultural topsoil derived from shale, the pH or physical clay had significant relationship with Cd, Pb, Hg and As ($p<0.01$). In the agricultural topsoil derived from sand stone, the acid condition and loose texture might account for the lowest values of Cd, Cr, Pb and As content to some extent.

Keywords Agricultural topsoil · Trace elements · Wudang · Parent material · Anthropogenic

Responsible Editor: Juan Barcelo.

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Introduction

With rapid economic expansion in China, intensive cultivation of agricultural soil makes trace elements contamination an increasingly serious problem (Huamain et al. 1999; Wong et al. 2002). Generally, the trace elements in agricultural soil depend primarily on the geological parent material composition during the initial stage of cultivation (De Temmerman et al. 2003). However, these trace elements will be enriched with intensification of agricultural activities (Mantovi et al. 2003; Montagne et al. 2007; Smith et al. 1996). Excessive accumulation of trace elements in agricultural soils may not only result in environmental contamination, but also elevate trace elements uptake by crops and influence on public health via food production (Jarup 2003; Muchuweti et al. 2006).

Wudang district is affiliated to Guiyang, the capital of Guizhou province with 3 million people, in Southwest, China (Fig. 1). The district is situated between latitudes 26°32′N and 26°55′N, longitudes 106°43′E and 107°03E, at mean elevation of 1300 m above sea level. The area has a warm and humid subtropical climate with an average annual temperature and rainfall of 15.3°C and 1197 mm, respectively. The agricultural soils are mainly derived from carbonate rock, red residua, sand stone and shale. The favorable climate and fertile soil make Wudang district an important base of agricultural product supply to Guiyang.

Due to the important production base of foodstuffs and vegetables to Guiyang, with subsequent expansion of the population and industrial development of Guiyang, the use of agrochemicals in this district was increasing in order to sustain the soil fertility. Inorganic and organic fertilizers and pesticides contain some hazardous trace elements such as As, Cd, Cr, Hg, Pb and so on (Mermut et al. 1996; Nicholson et al. 2003; Nziguheba and Smolders 2007; 2008). Most trace elements are extremely persistent in the environment and they can not be degraded by microbe and are easy to cumulate (Springael et al. 1993).

The contamination of agricultural soils can pose long-term environmental and health implications. There is an increasing need to study heavy metal distribution and accumulation in agricultural soils. Thus, the primary objectives of this study were: (i) to investigate the concentration of some trace elements (Cr, Cd, Pb, As, Hg) in agricultural topsoils; (ii) to analyze their mutual relationships; (iii) to investigate the potential sources of trace elements contaminants in the district.

Materials and methods

Sampling and analysis

Soil samples were collected at 282 random agricultural plots under vegetable crop or corn (see Fig. 1). A

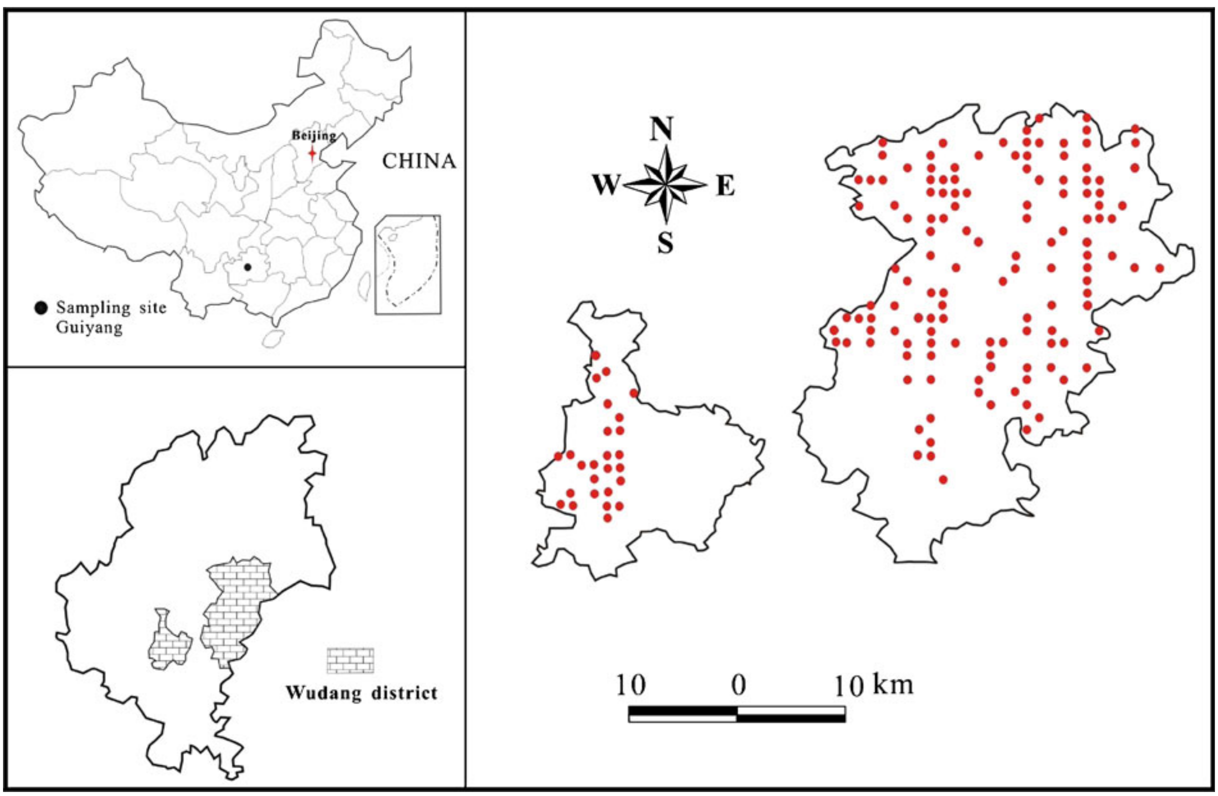

Fig. 1 Location of the study area and distribution of sampling points

composite sample for each plot consisted of 4 to 8 soil cores collected from the surface horizon (0~20 cm). Cores were mixed into one composite sample for each soil and analyzed in twice or triplicate. All soil samples were transported to the laboratory where they were air dried for several days at ambient temperature and sieved to 1 mm for an analysis of soil basic physical-chemical properties. The samples for analysis of trace elements were finely ground and passed through a nylon sieve of 100 mesh and stored in closed bottles.

The basic soil properties relevant to control mobility and bioavailability of the trace elements were analyzed according to the official laboratory methods of the Soil Science Society of China (SSSC). Soil pH value was measured with a pH electrode (Orion) in a ratio of 1: 2.5 (m/v) soil-to-water suspension. Soil particle size composition was calculated by sinking rates. Organic matter (OM) content was determined by dichromate digestion based on Walkley–Black method. Cation exchange capacity was determined by saturation with sodium acetate solution, replacement of the adsorbed sodium with ammonium and determination of displaced sodium by flame atomic absorption spectrometry.

Soil samples used for the analysis of trace elements were digested with nitric acid (HNO_3) and hydrochloric acid (HCl) in a ratio of 3:1 (HNO_3:HCl). Then Cd and Pb concentration in digested solution were measured by graphite furnace atomic absorption spectrophotometer (AAS), As and Hg were analyzed by atom fluorescence spectrometry, Cr was determined by a flame absorption spectrophotometer (AAS) (Varian AA-20).

Results

Soil basic physical-chemical properties

Based on the parent material, the soil samples can be categorized into four types: derived from carbonate rock, red residua, sand stone and shale. The basic physical-chemical properties of the soils in this study are presented in Table 1. The analysis of variance (ANOVA) showed these were significantly different between soil categories, with the exception of C/N (See Table 1). With respect to average value, the pH of soil derived from carbonate rock shows alkali level, the others are below 7.0. The organic matter content in soil (SOM) derived from sand stone is significantly lower than other groups significantly ($p<0.05$). The ratios of C/N are around 11.5 in all soil categories.

Table 1 Descriptive statistics of agricultural topsoil basic physical-chemical properties

Parent material		pH	SOM (g/kg)	C/N	CEC (Cmol/kg)	physical clay (<0.01 mm) (%)
All samples (n=282)	Mean±SD	6.3±1.1	33.0±11.2	11.6±1.7	15.0±4.5	50.8±11.1
	Median	6.3	31.0	11.7	14.3	51.1
	Range	4.2–8.3	10.8–83.1	6.4–16.8	6.4–29.8	24.1–82.0
Carbonate rock (n=60)	Mean±SD	7.7±0.3 a	34.9±14.5 a	11.4±1.4 a	17.2±5.0 c	48.1±11.9c
	Median	7.7	31.5	11.4	16.4	48.2
	Range	6.2–8.3	10.8–83.1	7.8–14.8	6.6–29.8	24.5–71.5
Red residua (n=56)	Mean±SD	6.0±0.8 b	32.9±10.1 a	11.4±1.5 a	14.1±3.5 a	58.5±7.8 a
	Median	6.1	31.2	11.4	13.4	59.8
	Range	4.6–7.8	11.0–70.4	8.8–14.8	7.1–23.8	32.3–73.4
Sand stone (n=17)	Mean±SD	5.8±1.1 b	22.6±7.4 b	11.7±1.6 a	11.7±3.6 b	33.4±9.0 b
	Median	5.4	21.5	12.1	10.8	28.6
	Range	4.4–8.3	11.4–46.0	6.4–14.3	6.4–21.9	24.1–49
Shale (n=149)	Mean±SD	5.9±0.8 b	33.5±10.3 a	11.7±1.6 a	14.8±4.4 ad	50.9±9.4c
	Median	6.0	31.5	11.7	14.1	50.9
	Range	4.2–7.8	13.1–70.4	6.8–16.8	6.9±28.3	32.5–82.0

Mean with different letters indicate there are significantly different at $p\leq0.05$ probability level (LSD) within each column

The CEC in soil derived from carbonate rock has highest value, followed by soil derived from shale, red residua, and sand stone. The mean value of physical clay (<0.01 mm) contents arranged in the following order: red residua>shale>carbonate rock> sand rock, which are 59.8%, 48.2%, 50.9% and 28.6%, respectively.

Comparison of trace elements among soil categories

Descriptive statistics for trace element contents are summarized in Table 2. Compared with the background level of uncultivated soil in Guizhou province (National Environmental Protection Agency of China 1990), the percentages of total soil samples are Cd: 52%, Pb: 61%, Cr: 62%, Hg: 29%, As: 37%, whose trace element contents exceed that of uncultivated soil. As far as the mean value, the Cd, Cr and Hg contents in soil derived from carbonate rock are obviously higher than other categories ($p<0.05$), which are 1.5-, 1.4-, 1.8-fold the lowest value in other soils. The highest values of Pb and As content are in the soil derived from red residua. But by ANOVA test, As content is no statistically significant difference between soil categories ($p>0.05$). The soil derived from sand stone has the lowest values of Cd, Cr, Pb and As content. According to the Environmental Quality Standard for Soils (National Environmental Protection Agency of China 1990), Cd, Pb and Cr contents in most of the soil samples are higher than the threshold values of Guizhou province and nationwide uncultivated background levels, especially Cr content in soil derived from carbonate rock was 1.8 times higher than the uncultivated soil of Guizhou Province.

Correlation matrix

Correlation analysis was carried out to determine the extent of the relationship between trace elements and the basic soil physical-chemical properties (Table 3). For total soil samples, the pH and physical clay (<0.01 mm) shows a significant linear relationship with all trace elements ($p<0.05$). C/N exhibits a significant relationship with all trace elements, with the exception of As ($p<0.05$). The third soil property of correlation with trace element content is SOM, which shows a correlation with Pb and As ($p<0.05$).

Table 2 Descriptive statistics of trace metal contents in agricultural topsoil samples

Parent material		Cd (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Hg (mg/kg)	As (mg/kg)
All samples (*n*=282)	Mean±SD	0.23±0.13	50.60±33.54	148.95±111.33	0.18±0.17	20.34±15.96
	Median	0.21	40.06	107.06	0.11	17.15
	Range	0.04–0.71	5.00–212.11	16.07–640.55	0.00–0.02	1.86–139.5
Carbonate rock (*n*=60)	Mean±SD	0.28±0.15 b①	50.93±27.08 c	178.77±124.86 b	0.24±0.15 b	18.83±16.90 a
	Median	0.22	45.65	170.04	0.20	15.95
	Range	0.08–0.70	21.31–205.36	16.07–622.39	0.01–0.71	3.25–127.83
Red residua (*n*=56)	Mean±SD	0.20±0.14 a	66.09±46.39 a	130.17±79.18 a	0.12±0.07 a	21.62±13.12 a
	Median	0.14	52.24	106.33	0.10	18.17
	Range	0.04–0.71	12.68–212.11	17.06–403.34	0.00–0.34	3.26–63.05
Sand stone (*n*=17)	Mean±SD	0.19±0.11 a	21.64±6.26 b	127.52±100.85 ab	0.13±0.15 ac	15.03±10.79 a
	Median	0.16	18.25	96.01	0.07	13.01
	Range	0.06–0.42	19.91–32.55	17.36–422.79	0.00–0.52	3.01–42.35
Shale (*n*=149)	Mean±SD	0.23±0.11 a	47.96±29.07 c	146.44±115.50 ab	0.18±0.19 c	21.07±16.98 a
	Median	0.22	41.19	102.05	0.11	17.29
	Range	0.05–0.68	5.00–182.91	26.53–640.55	0.00–0.98	1.89–139.5
Threshold of uncultivated soil background in Guizhou province and China②		0.2/0.2	35/35	96/90	0.2/0.2	20/15

① Mean with different letters indicate there are significantly different at $p\leq0.05$ probability level (LSD) within each column. ② National Environmental Protection Agency of China (1990)

Table 3 Correlation (Pearson) coefficient matrix between Trace elements concentrations and basic physical-chemical properties

	pH (H_2O)	SOM	C/N	CEC	<0.01 mm physical clay	Cd	Pb	Cr	Hg
All soil samples									
Cd	0.308**	0.042	0.177**	0.046	0.279**				
Pb	0.199**	0.103*	0.172**	0.008	0.119*	0.135*			
Cr	0.168**	−0.025	0.112*	−0.013	0.114*	0.451**	0.030		
Hg	0.162**	0.048	0.223**	0.059	0.219**	0.325**	0.094	0.294**	
As	0.284**	0.107*	−0.023	0.047	0.151**	0.351**	0.148**	0.100*	−0.048
Carbonate rock									
Cd	0.332**	0.034	0.096	0.238*	0.249*				
Pb	0.115	0.091	0.128	0.134	0.096	0.276*			
Cr	0.392**	−0.103	0.207	0.051	0.274*	0.522**	0.124		
Hg	0.135	−0.137	0.427**	0.001	0.142	0.490**	0.434**	0.458**	
As	0.163	0.058	−0.198	0.055	0.104	0.471**	−0.010	0.240*	−0.188
Red residua									
Cd	0.363**	−0.085	0.188	0.081	0.188				
Pb	0.118	−0.359**	0.397**	−0.150	0.004	0.093			
Cr	0.194	−0.059	−0.039	−0.030	0.119	0.455**	0.081		
Hg	0.183	0.165	0.004	0.115	0.071	0.090	−0.206	−0.211	
As	0.493**	−0.077	0.070	0.006	0.112	0.597**	0.092	0.114	0.392**
Sand stone									
Cd	0.334	0.415*	−0.066	0.263	0.293				
Pb	0.080	0.303	0.084	−0.245	0.509*	0.555*			
Cr	−0.177	0.537*	−0.023	−0.014	0.231	0.291	0.158		
Hg	0.595**	0.140	0.786**	0.083	0.425*	0.057	−0.083	0.160	
As	0.059	0.239	−0.285	0.087	0.029	0.361	0.334	0.265	−0.337
Shale									
Cd	0.238**	0.120	0.050	−0.051	0.250**				
Pb	0.234**	0.019	0.160*	0.042	0.162*	0.125			
Cr	0.037	0.007	0.019	−0.014	−0.042	0.411**	−0.014		
Hg	0.120	0.201**	0.069	0.096	0.177*	0.303**	0.133	0.263**	
As	0.292**	0.100	0.051	0.039	0.200**	0.242**	0.215**	0.039	−0.027

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

On the other hand, the relationships between trace elements are strong ($p<0.05$) excepting for Pb/Cr, Pb/Hg and As/Hg.

For soil samples derived from different parent material, the relationships between trace elements and the basic physical-chemical properties show diverse results. In the soil derived from carbonate rock, strong relationships ($p<0.05$) were found only in pH/Cd, pH/Cr, (C/N)/Hg, CEC/Cd, physical clay/Cd and physical clay/Cr. Between trace elements, Cd has significant association ($p<0.05$) with all other trace elements, and correlations with no significance were only in Cr/Pb, As/Pb and As/Hg. In the soil derived from red residua, strong relationships ($p<0.05$) were found only in pH/Cd, pH/As, SOM/Pb, Cd/Cr, Cd/As and Hg/As. In the soil derived from sand stone, strong relationships ($p<0.05$) were found only in pH/Hg, SOM/Hg, (C/N)/Pb, physical clay/Pb and physical clay/Hg. Between trace elements, there are no significant relationships with exception of Cd/Pb. In

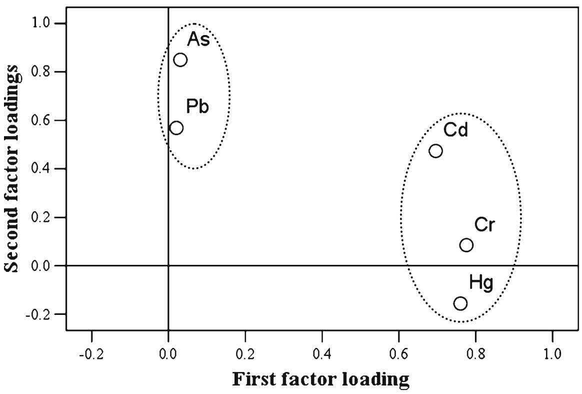

Fig. 2 Principal component analysis loading plots for the two rotated components

the soil derived from shale, the pH and physical clay show a significant relationship with all trace elements ($p<0.05$), except for Cr and Hg. Cd exhibits a significant relationship with all trace elements, with the exception of Pb ($p<0.05$).

Principal component analysis (PCA)

Principal component analysis (PCA) can explain the major part of the variation and can be used to understand their interrelationships by reducing the dimensionality of the dataset (Chen et al. 2005; Lucho-Constantino et al. 2005; Wong et al. 2002). The results of the PCA for trace element content in all soil samples are reported in Table 3. According to these results, the Cd, Pb, Cr, Hg and As concentrations could be reduced to two components, which accounted for 59.31% of the total variance for the data (Table 3). All the elements were well represented by two components. Spatial representation of the two rotated components is shown in Fig. 2.

The first component, explaining 36.91% of the total variance, was strongly and positively related to Cd, Cr and Hg (Table 4). The second component, explaining 22.40% of the total variance, showed high positive component loading on Pb and As. This trend of covariance is strongly suggestive of common sources for the elements.

Discussion

Parent material and anthropogenic controls

Usually, the initial source of trace elements in soil is derived from its parent material, and the input of

Table 4 Total variance explained and component matrixes (two principal components selected) for trace elements contents

Total Variance Explained

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%
1	1.85	36.91	36.91	1.85	36.91	36.91	1.66	33.28	33.28
2	1.12	22.40	59.31	1.12	22.40	59.31	1.30	26.03	59.31
3	0.94	18.76	78.07						
4	0.65	12.97	91.03						
5	0.45	8.97	100.00						

Component matrix

Element	Component matrix		Rotated component matrix	
	1	2	1	2
Cd	0.839	0.062	0.695	0.473
Pb	0.302	0.482	0.020	0.569
Cr	0.714	−0.314	0.776	0.085
Hg	0.580	−0.515	0.760	−0.156
As	0.451	0.721	0.031	0.850

Extraction Method: Principal Component Analysis (PCA)

Table 5 Trace element background value of uncultivated soil derived from different parent materials in China[①]

Parent material		Cd (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Hg (mg/kg)	As (mg/kg)
Carbonate rock (*n*=60)	Mean±SD	0.22±0.28	32.7±17.2	78.1±31.8	0.11±0.12	18.7±11.5
	Median	0.14	28	70.3	0.05	15.6
	Range	0.00–8.22	10.1–163	8.1–455.9	0.01–45.9	3.5–158.6
Red residua (*n*=56)	Mean±SD	0.08±0.06	29.3±13.7	63.8±25.4	0.09±0.09	14.3±8.3
	Median	0.06	25.3	63.8	0.06	13.8
	Range	0.00–0.45	9.6–108	13.5–132	0.01–0.63	2–68.3
Sand stone (*n*=17)	Mean±SD	0.08±0.06	25.5±11.1	68.3±33.8	0.06±0.04	12.5±8.2
	Median	0.07	23.6	60.6	0.04	10.7
	Range	0.00–0.59	3–145	7.3–1209.7	0.00–3.97	1–12.5
Shale (*n*=149)	Mean±SD	0.09±0.07	26.3±8.2	76.6±34.5	0.07±0.07	14.8±9.2
	Median	0.08	25	89.7	0.05	12.2
	Range	0.00–4.5	9–143	12.4–1426	0.00–6	2.3–89.5

① National Environmental Protection Agency of China (1990)

anthropogenic trace elements in fertilizer, manure and other sources may be lower than the content in soil (Facchinelli et al. 2001). So trace element content in agricultural soil would be strongly associated with its parent material even for a long cultivation time (Mico et al. 2006; Montagne et al. 2007; Wang and Wei 1995). Furthermore, trace element concentrations in soil derived from different parent material are not equal. According to the trace elements background value of uncultivated soil published by National Environmental Protection Agency of China (1990), the Cd, Pb and As contents in the soil derived from carbonate rock have higher average value than other soils. In the soil derived from shale, the mean content of Cr is the biggest and the range of Cr content in any type of soils is very wide (Table 5). The soil derived from sand stone has the lowest background values of As, Cd, Hg and Pb content. Obviously, the trace elements in agricultural topsoil were similar to these uncultivated soils in this study, which indicated that the soil parent material influenced the element contents to a great extent.

Many reports had strongly suggested that the agricultural soil received a comparatively high input of anthropogenic trace elements, possibly related to the use of agrochemicals, other amendments and atmospheric deposition (Alloway 1995; Kachenko and Singh 2006; Montagne et al. 2007; Smith et al. 1996). According to the present investigation, the trace element contents of common fertilizers in Guizhou province are not above the national standard for fertilizer products (Table 6) (Chen et al. 2006), but it is possible that intensive use of fertilizers may result in trace elements accumulation in agricultural soil. In addition, our early research about atmospheric deposition showed that the rain water and Total Suspended Particulates (TSP) contained a certain amount of trace elements in Guiyang, even far from urban areas, which mainly consisted of emission of cars and manufacturers (data not showed) (Hu et al. 2005;

Table 6 Trace element contents of common fertilizers in Guizhou province (Chen H et al. 2006)

Type of fertilizer	Cd Mean±SD (mg/kg)	Pb	Cr	Hg	As
N-P-K mixed fertilizer	0.18±0.12	1.79±2.03	84.2±56.12	1.57±1.47	6.68±3.88
common superphosphate	0.11±0.10	8.35±8.19	60.35±14.10	2.31±2.49	not available
Ca-Mg-P mixed fertilizer	0.10±0.08	6.26±3.08	156.93±121.40	0.27±0.40	4.37±5.18
inorganic-organic fertilizer	5.00±2.92	42.20±4.82	47.00±52.31	2.40±0.55	23.20±13.14
organic fertilizer	2.25±0.50	26.50±3.70	48.75±28.34	2.00±1.15	18.00±7.44

Wu et al. 2008). Thus, the input of anthropogenic trace elements is also an important source to agricultural topsoil in Wudang district.

On the other hand, many documents reported there were some high relationships between soil trace elements, which meant that there might be the same sources (Li et al. 2009; Rodríguez Martín et al. 2006). In this study, the relationships between trace elements were inconsistent among the soil categories. Based on our investigation, the fertilization level has variation due to soil properties in the different types of soils. For example, the soil derived from sand stone or shale has loose texture, and is not fertile. Local people always give more fertilizer to this type of soil, especially organic fertilizer, such as grass and plant ash, animal wastes and compost. So the diversity of relationships between trace elements is mainly on account of different sources and fertilization level except the effect of parent material. In addition, the PCA can help in identifying the source of trace elements (Mico et al. 2006). In our study, the result of the PCA (Table 4 and Fig. 2) for total soil samples indicated Cd, Cr and Hg formed the first component, which can be considered to be an anthropogenic component. The reasons for it were that the three trace element contents in most of the soil samples were far beyond the uncultivated soil background and there were significant relationships between them ($p < 0.01$). Beside, fertilizers include amount of trace elements (Table 6), which can remain in soil for a long time. Pb and As were dominated by the second component, and the association of Pb with other elements was weak, which might mean the source of Pb and As was different from other trace elements. Some reports showed that the parent material of soil, Pb-containing agrochemicals and Pb emitted from gasoline combustion are main sources of Pb in agricultural soil (Markus and McBratney 2001). Compared with some developed districts of China, Pb content in most of soil samples, with exception of the soil derived sand stone, is higher in Wudang (Huang et al. 2007; Wong et al. 2002), whereas the amount of automobile and factories in Wudang are less than that in these developed districts. Therefore, high background value in parent material and Pb-containing agrochemical had more responsibilities for the high Pb content in Wudang than other districts. For As, the government of China has forbidden use of inorganic forms of As in agriculture as insecticides, herbicides, fungicides, desiccants, defoliants and as additives to animal feeds from the 70s of the last century (Chen et al. 1997), and the As was not related with C/N, which might indicate fertilizers were not influenced on As content and As was mainly controlled by geological parent materials.

Soil properties control

The soil pH is known to influence the mobilization of cations and solubility of heavy metals (Basta et al. 1993; Kashem and Singh 2001; Yang et al. 2006). Normally, under acidic conditions, most of trace metal elements can be activated and the availability for plants can be enhanced. Contrarily, it is helpful for trace metal elements accumulation in soil under alkaline condition (Nan et al. 2002; Remon et al. 2005). Therefore, enrichment of trace elements in the agricultural soil derived from carbonate rock could be attributed to the alkaline condition. Acidic circumstance in other soil categories could reduce the amount of trace elements by enhancing their solubility and mobility. Moreover, overall the correlations between the trace elements and soil pH are significant for total soil samples ($p<0.01$), but the relationships are inconsistent among these soil categories. Obviously, besides the soil pH, there are other factors which control accumulation of trace elements in this region. Similarly, other researches also found there were no significant correlation between soil pH and trace element (Dragovi et al. 2008; Manta et al. 2002; Tume et al. 2006).

With the use of organic fertilizer, amounts of trace elements were put into agricultural soil and it is easy for trace elements to form chelate complexes with SOM, which is hard to biodegrade (Chen et al. 1997; Huang and Jin 2008; Wu et al. 2003). In addition, the adsorptions of some trace elements were found to be increased with higher soil organic matter content (Alloway 1995; Bradl 2004; Weng et al. 2001). So a lot of papers show organic matter has a positive linear relationship with trace elements (Dragovi et al. 2008; Li et al. 2009; Liu et al. 2006; Mico et al. 2006; Rodríguez Martín et al. 2006). On the contrary, Tume et al. (2006) also found some trace elements had no significant relationship with SOM in Spain uncultivated surface soil. In this study, the relationships between trace element and SOM were very weak.

As main base of agricultural product supply to Guiyang, cropping index of soil in Wudang district is very high. Organic fertilizers are hard to satisfy the demands of agricultural production. So, in order to sustain land productivity, amount of inorganic agrochemicals, such as nitrogen or phosphatic fertilizer, pesticides and sewage sludge were put into the soil. Although the trace element contents in these agrochemicals were not beyond the national standard, these were still may be potential source of trace elements (Kachenko and Singh 2006; Montagne et al. 2007).

For total soil samples the C/N has significant correlation with the trace element contents with exception of As and the mean values of C/N are around 11.5. But the correlations among four types of soils are inconsistent. This result may be influenced by interaction of some soil properties. Normally, people consider that C/N reflects the humification level of SOM and soil microbial activity. A high C/N ratio suggests poor humification of SOM. Farmers always adjust the C/N ratio and satisfy the crop N nutrition by using inorganic chemical fertilizers to improve the release of available nutrition from SOM. However, there were few reports that showed whether C/N affected trace elements forms and contents indirectly by changing humification level of SOM and soil microbial activity in soil.

As it is known, alkaline and alkaline earth cations are absolutely dominant in soil cation exchange capacity (CEC), and the proportions of other cations are very small. In addition, CEC only reflects the form of exchangeable parts, and does not reflect the total amount of trace elements. Our result showed CEC had not significantly influenced any trace elements, consistent with those obtained by Lucho-Constantino et al. (2005) except Pb, and contradicted those obtained by Mico et al. (2006) and Li et al. (2009).

Similar to soil pH, overall correlations between the trace elements and physical clay (<0.01 mm) are significant for total soil samples ($p<0.05$), but the relationships are inconsistent among these soil categories. Chen et al. (1999) reported concentrations of five trace elements were strongly correlated with clay in Florida surface soils. Mermut et al. (1996) also found there was strong correlations between concentration of As, Cd, Cr, Pb and the clay content in Canadian soils. They suggested that clay content was an important factor in controlling the level and distribution of trace elements. In contrast to these significant positive linear correlations, some scientists presented there were inverse or weak correlations between trace elements and clay content (Li et al. 2009; Lucho-Constantino et al. 2005; Navas and Mach 2002). They suggested that clay content was not important in determining the distribution and content of trace elements in soils. In our study, there was no significant relationship ($p>0.05$) between trace elements and physical clay in the agricultural soil derived from red residua, but it had the highest mean values of Pb, As and physical clay content among the four soil categories. So we considered that the highest mean values of Pb and As content, partly because the type of soil had amount of physical clay (<0.01 mm).

Conclusion

By comparison with the threshold of uncultivated soil background in Guizhou province and the trace elements background value of uncultivated soil derived from different parent materials in China, our data revealed there were serious enrichment of Cd, Cr and Pb, and slight accumulation of As and Hg in Wudang district. Agrochemicals were important sources to agricultural topsoil beside the parent materials. The soil pH, C/N and physical clay content (<0.01 mm) significantly influenced the trace element contents ($p<0.05$).

The PCA showed that the first component included Cd, Cr and Hg, determined principally by anthropogenic activities, while Pb and As formed the second component, controlled by both anthropogenic activities and parent material.

In the soil derived from carbonate rock, high background values and alkaline condition resulted in that the Cd, Cr and Hg contents were significantly higher than other soil categories ($p<0.05$). In the soil derived from red residua, a great amount of physical clay content (<0.01 mm) had partial responsibility for the highest values of Pb and As content. In the soil derived from shale, the pH and physical clay had significant relationship with Cd, Pb, Hg and As. In the soil derived from sand stone, beside the relative low background values of trace elements, the acid condition and loose texture were the main reasons for the lowest contents of Cd, Cr, Pb and As.

Acknowledgements This work is financially supported by the Foundation of Chinese Academy of Sciences (Grant no. KZCX2-XB2-08), the front field foundation of Institute of Geochemistry, Chinese Academy of Sciences and the Bureau of Science and Technology of GuiZhou province (Grant no.2008-2243).

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