Trace element contents and correlation in surface soils in China's eastern alluvial plains

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Abstract A study investigating the contents of 13 trace elements and the correlations between these trace elements and soil parameters of the surface soils in the eastern alluvial plains of China is summarized and discussed in this paper. The results show that the contents of some elements studied differ from region to region. Close relations have been noted between all the trace element contents in the soils of the eastern alluvial plains and the relevant surface materials of erosion regions, which demonstrate the effects of parent materials, while climatic conditions and human interventions are also found to be important factors. Close relations were found between the transition elements of the Quaternary period and the chalcophile elements (except Cu). The chemical and geochemical properties of these elements are identified as beeing important inherent characteristics that affect the relations of these elements in the soils.

Key words Soil · Trace element · Alluvial plain · China

Introduction

Trace elements are essential for crop production and may cause serious problems if deficientor excessive. The trace element contents in uncontaminated soils, remote from industrial installations, are of great interest since such data are essential for assessment of the degree of soil contamination with trace elements from industrial and urban wastes and agricultural activities. The contents of trace elements variy from region to region. Mitchell (1974) stated that the trace element content of a soil depends almost entirely on that of the rocks from which the soil parent material was derived in and on the weathering processes to which the soil-forming materials have been subjected. Tang (1987) pointed out that the

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element composition of parent rock is the major factor affecting the trace element contents. No detailed studies have been undertaken to assess the soil composition in the eastern alluvial plains of China. Therefore, the Environmental Monitoring Center of China has undertaken such a study and the results presented in this paper are part of the whole study.

Soils are rarely derived directly from the solid rock material underlying them. More often they are formed from a variety of transported material from different processes, such as colluvial, fluvial, glacial, and aeolian. The eastern plains of China include a number of alluvial plains with a high degree of variability, ranging from northeast China with cold snowy forest and dark brown soils, to South China with a moist subtropical and tropical climate and red soils. Most of the large rivers like the Yangtze, Yellow and Pearl River flow from west to east and help to form these alluvial plains. In addition, a number of other rivers of the eastern exterior drainage pass through the studied area and have influenced soil formation, resulting the in contents of trace elements and other physicochemical parameters. The eastern region is very important for both industrial and agricultural activities and is heavily populated. The understanding of trace element contents and relations in the soil of this area would obviously be of great value to agricultural research, regional environmental quality assessment and environmental planning for the maintenance of healthy soil produce quality food for the large population.

The purpose of this paper is to present current information on the contents of trace elements in surface soil samples from the alluvial plains in eastern China, which is far from industrial installations, and to assess the relationships between the contents of these elements and physico-chemical properties of soils.

Materials and methods

Sampling

Two hundred samples from surface soils have been collected from ten eastern alluvial plains, located far from industrial installations, as shown in Fig. 1. In addition, one region from the western region of China, the Loess Plateau (region 11), has been included in the study; twenty surface soil samples were collected from this region.

The main reason for including this region is to study the relationship of soil properties and composition between regions 11 and 5 (Huanghe) as the Yellow River flows from the Loess Plateau to region 5. Sampling has been carried out uniformly by collecting 20 samples from all 11 regions during the late 1980s.

As mentioned previously regions 5, 8 and 10 have been influenced greatly by the flow of three rivers. To determine the influence of soil formation, particularly the composition of the soil and climate, additional samples from surface soils were collected in 1990 from these three regions (six samples each from regions 5 and 8 and three samples from region 10) to determine the clay mineral content with the help of X-ray diffraction.

Chemical analysis and quality control

Chemical analyses were carried out for 13 elements, copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni),

chromium (Cr), mercury (Hg), arsenic (As), selenium (Se), cobalt (Co), vanadium (V), manganese (Mn), and fluorine (F) considered as of high environmental concern by different laboratories located in various provinces, Peking University, the Environmental Monitoring Center of China and others. Analyses were carried out by all the laboratories uniformly based on the standard methodology (including quality control) developed by the Environmental Monitoring Center of China (1990). Soil samples were air-dried, ground in an agate mortar and passed through a sieve of 2–mm mesh, before measuring of grain size and determining pH value and organic matter content. For the determination of trace elements, soil samples were ground further and passed through a sieve of 100–mm mesh. Flame atomic absorption spectrophotome try was used to determine the contents of Cu, Pb, Zn, Cd, Ni, Cr, As, Se, Co, V and Mn elements, after digestion with nitric acid–perchloric acid–hydrofluoric acid. A sodium nitrate–nitric acid–sulphuric acid digestion system and flameless absorp tion spectrophotometry were used for measurement of Hg. F (fluorine) was determined by ion electrode after digestion with sodium hydroxide. All the laboratories involved in physico-chemical analyses gave their result to the Environmental Monitoring Center of China for validation, storage and for the use of the results. The Center acts as a nodal organization for the whole study and also as a repository of results/data of all measurements in China. The data used in this paper were taken from this repository, apart from the measurement conducted by the authors in 1990 for X-ray diffraction analysis.

The Environmental Monitoring Center of China was responsible for designing the sample collection, standardizing the methodology of analysis to be followed by all the laboratories, fixing the quality of all reagents used and monitoring of the work. The quality of the reagents used for the analysis was of high standard. Deionized water was used throughout the analytical work. Glassware was soaked in 10% nitric acid (v/v) for 24 and rinsed with deionized water before use.

Environmental Standard Soil Samples (ESS-1, ESS-2, ESS-3 and ESS-4) were developed and supplied by the Environmental Monitoring Center of China to each group for determination of trace element contents for quality control and check. All the laboratories underwent a strict examination conducted by the Center before their work began for the purpose of quality control and to ensure the standard methodology. The analytical results obtained by the laboratories were given to the Center for verification and certification of results based on the Environmental Standard Soil Samples. This was followed to avoid any analytical error.

The data relating to detection limits and detection ratio (the ratio of the number of samples in which the element was found in measurable concentrations to the total number of samples analyzed) for the samples collected from all over China are presented in Table 1. The detection ratios for all the analytical results of the 200 samples used for this study have been found to be 100%.

Table 1 Detection limits and detection ratio for all samples collected in China (Environmental Monitoring Center for China 1990)

Element	Detection limits (mg kg $^{-1}$)	Detection ratio			
Cu	1.0	4089: 4092			
Zn	1.0	4092: 4092			
Ni	2.0	4081: 4092			
Hg	0.002	4083: 4090			
Se	0.002	2936: 2936			
V	5.0	4072: 4089			
E	5.0	4090: 4090			
Pb	1.0	4092: 4092			
C _d	0.002	4090: 4092			
Cr	2.5	4089: 4091			
As	0.5	4074: 4092			
Co	2.0	3985: 4091			
Mn	5.0	4090: 4092			

Results and discussion

Contents of trace elements and their regional distribution

The analytical results of all the samples collected from the ten regions are presented in Table 2, showing average

contents and ranges of all the 13 elements (Cu, Pb, Zn, Cd, Ni, Cr, Hg, As, Se, Co, V, Mn, F), the contents of organic matter, pH value and the contents of clay particles $(< 0.01$ mm). As previously stated, that the contents of trace elements in the soils of Chinas eastern alluvial plains are mainly dependent on the erosion of surface materials in the eastern exterior drainage. To demonstrate thi s, a comparison of the trace element contents of the surface soils of the current study area with that of the eastern exterior drainage (means of 3000 samples for all but one trace element less than 2000 for Se) was made and presented in Fig. 2. Figure 2 shows that there is no significant difference between the contents of elements in soils from the alluvial plains of eastern China and those from the eastern exterior drainage, which proves the importance of parent materials in the trace element contents of the alluvial plains (Ortel 1960).

A similar relation can be observed in each of the regions. The surface materials in region 5 are mainly from the Loess Plateau (Environmental Monitoring Center of China 1990). The comparative result of trace element contents of regions 5 and 11 shows that region 11 (the Loess Plateau) has demonstrative influence on the soil contents of region 5, as the results show no significant differences between these two regions (Fig. 3).

Table 2 also shows that no significant regional variations exist for the contents of most of the trace elements among these plains. This might be attributed to the fact

Table 2 Average results and ranges for trace element contents (in mg kg^{-1}) and physico-chemical parameters

Region	Cu	Pb	Zn	Cd		
	$21.5(9.7-29.8)$	$24.2(16.5-27.4)$	$61.9(39.4-109)$	$0.079(0.045 - 0.14)$		
	$18.6(10.6-26.7)$	$24.6(17.0-47.0)$	$54.4(34.1-69.6)$	$0.076(0.041 - 0.12)$		
	$18.3(5.8-37.0)$	$15.9(6.2 - 66.0)$	$49.0(17.0-95.0)$	$0.091(0.026 - 0.14)$		
4	$27.1(14.3-44.6)$	$21.1(15.3-41.8)$	$82.3(52.0-134)$	$0.084(0.002 - 0.14)$		
	$25.6(13.3-39.0)$	$21.5(11.0-27.2)$	$69.5(35.7-105)$	$0.11(0.050-0.23)$		
6	$18.6(6.4-34.8)$	$21.0(10.0-64.0)$	$51.7(17.8-98.4)$	$0.066(0.013-0.36)$		
	$21.8(11.5-35.0)$	$25.2(16.0-40.0)$	$60.2(23.1-91.0)$	$0.044(0.008 - 0.21)$		
8	$25.7(13.5-43.7)$	$26.3(14.4-45.0)$	$73.1(38.9-132)$	$0.11(0.022 - 0.27)$		
9	$20.5(7.0-36.0)$	$39.3(25.2 - 66.6)$	$95.0(47.0-132)$	$0.15(0.027-0.39)$		
10	$18.0(5.4-40.5)$	$41.6(6.5 - 71.4)$	$64.5(16.9-137)$	$0.074(0.020-0.33)$		

Table 2

OM, organic matter (%); P, clay particles <0.01 mm (%)

that, compared with the eastern plains, the relevant erosion areas are much larger and the parent rock composition is extremely complicated. More than one kind of parent rock was found in all the relevant erosion areas (Environmental Monitoring Center of China 1990). However, some elements show strong regional variation in a few plains. The contents of Pb in the soils of regions 9 and 10, for example, are significantly higher than those in other Regions. Unlike other areas of eastern China, large areas of granite are distributed in South China (the erosion areas of regions 9 and 10). The content of Pb is quite high in granite, due to the fact that the potassium ion is easily replaced by the lead ion (they have similar ionic radii: K⁺ 1.59–1.68; Pb²⁺ 1.37–1.57) (Liu 1987).

The understanding of the importance of ionic size stems from Goldschmidt's (1954) early recognition. Initially, the trace element composition of a soil will be that of its geological parent material. However, with time, composition will diverge progressively under the influence of pedogenic processes which in turn are determined by vegetation, topography and, in particular, climatic conditions (Jenkins and others 1979). These plains are located from north to south with significantly different climatic conditions. Figure 4 illustrates the great differences of the contents of clay from soil samples collected in regions 5, 8 and 10. It is clear that the amount of imvite in soils decreases sharply from north to south, while the amount of kaolinite shows the opposite trend. Weathering and eluviation processes can alter the patterns of element contents in the soils of these areas

Fig. 4 Contents of clay in regions 5, 8 and 10

through leaching, reprecipitation, adsorption and other processes. However, it is difficult to quantitatively estimate the effects of climatic factors on the contents of trace elements in Chinese eastern plains. On the one hand, studies have shown that the effects of parent material are usually stronger than the climatic factors (Mitchell 1974), and thus conceal the effects of the latter to some extent; on the other hand, the effects of weathering and eluviation processes on trace element content and distribution are extremely complex. As pointed out by Jenkins and Jones (1979), the mobility of a trace element is determined firstly by the stability of the host minerals in the particular weathering environment. Once mobilized within the soil by dissolution of the host minerals, the fate of a trace element depends upon the behavior of its aqueous ionic species, which in turn can be related to such parameters as ionic potential and effective hydrated ionic diameter. Solubility is then a function of such environmental factors as pH, Eh, Pco₂, etc. The trace element in solution may be either leached from the soil or reprecipitated as an hydroxide, carbonate, sulphate, phosphate, etc., or incorporated into a pedogenic silicate, and may be adsorbed onto charged surfaces of clay particles or organic matter. An artificial activity such as cultivation can also affect the above processes. Generally speaking, with the increasing of precipitation, lowering of pH and reduction of clay particle contents in soils, the leaching process will play a major role and the contents of most trace elements in soils will decrease (the effect of organic matter on trace elements in the soil is complicated in long-term cultivated land; this will be discussed below). In the sampling area of this study, it is estimated that the high contents of most elements in region 4 are partly caused by the very dry environment of the Yellow River basin, where the precipitation is lower than any of the other studied areas, resulting in low loss through leaching. Trace elements have been selectively extracted, concentrated and applied to soils either directly in the form of fertilizers, herbicides and pesticides, or indirectly as pollutants all over the world. The purpose of this study is to provide the background information on soil trace elements. It is estimated that industrial activities could not have significant effects on the contents of trace elements in the studied areas due to the fact that the samples have been collected far from the industrial installations (Envi-

ronmental Monitoring Center of China 1990). The study has shown that atmospheric precipitation could contribute to the increase in trace element contents in the soils in some areas outside China (Bergkvist and others 1989). However, it has been demonstrated that the atmospheric precipitation has no major influence on the trace element contents in China' s soils, especially in those areas far from urban areas and industrial pollution sources, in spite of the recent development of modern industry (Environmental Monitoring Center of China 1990). All ten alluvial plains are important agricultural regions in China. Thousands of years of cultivation activities habe been undertaken in most of these areas. The traditional farming could not change the contents of trace elements significantly. In some areas, however, the utilization of chemical fertilizers and pesticides in recent years could alter the contents of trace elements in soils. For example, soils in regions 7, 8, 9 and 10 (especially region 10) are rich in Hg. For a long time, farmers in these areas utilized mercury-containing pesticides in their paddy fields. This is believed to be the main reason altering the contents of Hg in the soils of these regions (Tao 1995). As one of the most significant sources of soil pollution, wastewater from industrial and domestic sources introduces a huge amount of inorganic and organic contaminants, including heavy metals, into agricultural land through the practice of wastewater irrigation. This is particularly an acute problem in areas adjoining large urban areas, especially in northern China where scarcity of water necessitates wastewater reuse for a variety of different purposes, most importantly crop production (Zhang and others 1988). However, some studies have demonstrated that most heavy metals were absorbed in the sediment in irrigation channels and thus cause little deposition in the cultivated land, and only very few areas near large cities were polluted with heavy metals such as Cu, Pb and Cr (Wang and others 1997). Therefore, wastewater (both domestic and industrial) irrigation in part of the northern China farming lands could not cause much increase in trace elements in the soils of the studied regions. Sewage sludge was also applied in a few farming areas near large cities in northern China, and caused significant increase in the contents of some trace elements (Wang and others 1997). However, no samples for this study were collected from these polluted areas. An attempt has been made to compare the trace element contents of soils of China and the USA as these countries have some similar attributes and territories. There is little

significant difference in the latitude position and the cli-

NA, not available

^a Environmental Monitoring Center of China (1990)

^b Shacklette and Boerngen (1984)

matic conditions. Both countries have diversified parent rocks and soils. Relevant data are presented in Table 3, illustrating the available data on the trace element contents in the soils of China (Environmental Monitoring Center of China 1990) and the conterminous USA (Shacklette and Boerngen1984). The conterminous USA samples were analyzed using a semiquantitative emission spectrographic method. The comparison shows close correspondence for some of the elements but less than a twofold difference for others. Vast territories, complicated parent rock composition and similar climate might be the possible reasons for such a result.

Table 4 Correlation matrix for trace elements and soil properties

Correlations between elements and soil parameters

The associations that exist between elements in the surface soils of the studied areas are inherited from parent rocks and parent materials, and are also affected by the weathering processes and the agricultural activities. The understanding of relations between trace elements and soil parameters in soils could help in understanding the behavior of these elements in soil. These kinds of relations can even be used to predict the contents of some elements in soil (Wang and Chen 1994). Correlation and partial correlation matrices for the contents of elements and properties in the surface soils (200 samples from 10 plains) from the Chinese eastern alluvial plain s are presented in Tables 4 and 5. It can be seen therefore that the siderophile elements, such as V, Cr, Mn, Co and Ni, are closely correlated to each other. It his, however, unreasonable that, being a chalcophile element, Cu shows weak correlations with most of the other chalcophile elements, but shows strong correlations with siderophile elements. The possible explantation may be that the approximate ion radii make Cu and other siderophile elements presen similar geochemical behavior under earth surface circumstances (they all transition elements of the Quaternany period) (Wang and Chen 1994). It has also been observed in many studies that there are correlations between trace elements and clay particles due to the high affinities of trace elements to clay minerals (Ravihovitch and others 1961; Adriano 1986; Wang and Chen 1994). Similarly, high correlations between trace elements and clay particles were found out in our study, which reflect the close relations of trace element contents in soil with parent material.

As regards the organic material behavior, some studies have observed that trace elements show a marked affinity

OM, organic matter $(\%)$; P, clay particles < 0.01 mm $(\%)$ $+$ and $-$ represent positive and negative correlations with significant differences between 0.01 and 0.05; $++$ and $--$ represent positive and negative correlations with significant differences at the < 0.01 level

						Cu Pb Zn Cd Ni Cr Hg As Se Co V Mn F	
OM							
						pH ++ -- ++ ++ -- -- ++ ++ ++ ++	

Table 5 Partial correlation matrix for trace elements and soil properties

OM, organic matter $(\%)$; P, clay particles < 0.01 mm $(\%)$ $+$ and $-$ represent the positive and negative correlations with significant differences between 0.01 and 0.05; ++ and $-$

towards organic materials with the formation of complexes (Berrow 1981; Aoyama 1982). However, such correlations have not been significantly observed in our studied area. This can be attributed to the long-term agricultural activities in these areas. Agricultural cultivation alters the contents of organic matter significantly from season to season and from year to year, and thus lowering the correlation between trace elements and organic matter.

It is interesting to observe the significant correlations between pH values and the trace elements, especially the transition elements of the Quaternary period such as Cu, Ni, Cr, Co, V and Mn. These elements have similar ion radii and geochemical characteristics in surface soil. As pointed out earlier , the climatic conditions are one of the factors affecting the distribution and relations of trace elements in the soils of these areas. The pH values of surface soil under different climatic conditions have been found to be varied significantly (from slightly acidic in regions 1, 9 and 10 to slightly basic in most other regions). It has also been observed that once mobilized within the soil by dissolution of the parent minerals, the solubility is a function of environmental factors such as pH (Jenkins and Jones 1979). Metals are more easily leached with a low pH, and pH thus can serve as an indicator of climatic condition. Compared with organic matter, in alluvial plains where long-term agricultural activities exist, the pH value shows a much stronger correlation with trace elements in soil.

The relations between trace elements and soil parameters can also be demonstrated through factor analysis. The result of R-mode factor analysis (of 200 samples from 10 plains) shows that, after the varimax rotation, the first three principal factors contribute 52.0, 22.2 and 18.4% of the variances, respectively. Figure 5 presents the loadings on principal factors rotated by varimax criterion from Rmode factor analysis. Cu, Co, Ni, V, Cr and Mn are found in the positive direction of factor 1, which reflects the characteristics of the transition elements of the Quaternary period. Organic matter and clay particles are in the positive direction of factor 2, while the pH value is in the negative direction of this factor (if we use the content of H^+ ion replacing pH value, it will show in the positive direction of this factor). It is clear that factor 2 displays the characteristics of soil parameters, which to some extent represent the effects of climatic conditions and artifi-

represent positive and negative correlations with significant differences at the <0.01 level

Fig. 5 Plot of loadings on the principal factors (*F1*

cial activity. Factor 3 expresses the characteristics of chalcophile elements since Pb, Hg, Zn, Cd and Se are in the positive direction of this factor. Considering the different contribution of these factors (52.0% for factor 1, 22.2% for factor 2, and 18.4% for factor 3), it is clear that the chemical and geochemical characteristics as well as the climatic and human activity factors all contribute to the relations between trace elements in the study area, while the former plays a more important role.

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