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Preliminary Study on Environmental Geochemistry in the Paleo-sediment of the Yellow River of Wuzhi, China

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This work studied trace elements in the paleo-sediment of the Yellow River of Wuzhi, Jiaozuo, Henan Province, using the flame atomic absorption spectrometry and atomic fluorescence spectrometry to analyze the concentration of trace elements (Cu、Ni、Mn、Zn、Pb、Cr、Fe、As). The concentrations of the eight trace elements in the paleo-sediment of the Yellow River ranged between 6.42 and 28.35 $mg\cdot kg^{-1}$ (mean 15.09 $mg\cdot kg^{-1}$), 13.69 and 39.24 $mg\cdot kg^{-1}$ (21.31 $mg\cdot kg^{-1}$), 158.8 and 338.65 $mg\cdot kg^{-1}$ (219.56 $mg\cdot kg^{-1}$), 178.25 and 309.75 $mg\cdot kg^{-1}$ (239.49 $mg\cdot kg^{-1}$), 14.16 and 27.19 $mg\cdot kg^{-1}$ (20.22 $mg\cdot kg^{-1}$), 27.25 and 67.71 $mg\cdot kg^{-1}$ (37.84 $mg\cdot kg^{-1}$), 17830 and 34080 $mg\cdot kg^{-1}$ (25942 $mg\cdot kg^{-1}$) and 26.315 and 532.01 $mg\cdot kg^{-1}$ (141.71 $mg\cdot kg^{-1}$), respectively. The results showed that the impact of human activities is one of the main factors, especially the destruction of natural vegetation of the middle reaches of Loess Plateau in the Qin and Han Dynasties and the development of industry and agriculture.

Keywords: Paleo-sediment of Yellow River, Trace elements, Ecological damage; Human activity

1 INTRODUCTION

Yellow River, the second long river of China, is the mother river of the Chinese nation and the cradle of Chinese civilization. Yellow River Basin has had activities of human interest as early as ten thousand years ago. Far away in four thousand years ago there were legends about Dayu controlling flood, dredging nine rivers and subsiding flood. In the history of this river, the middle and lower reaches of the Yellow river wandered through movement to develop into recent pattern. According to the statistics of the Yellow River Commission, the Yellow River in North China Plain had been overflowed 1593 times, largely transferred 26 times, significantly transferred 9 times[1]. Every important watercourse transferring resulted from the effect of human activities on the the middle and upper reaches of the Yellow River (Fig.1). In recent years,

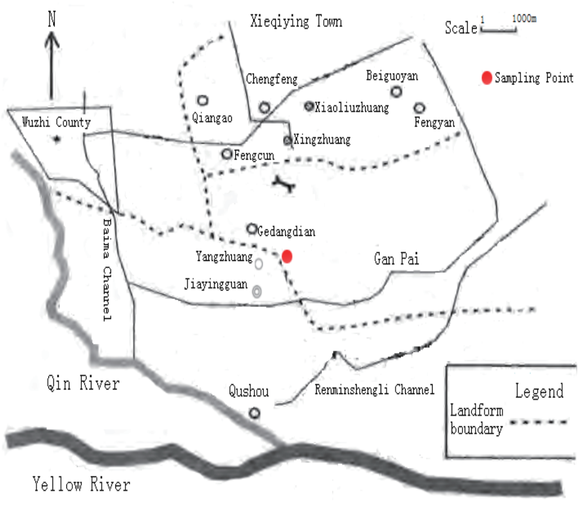

Fig. 1 Changes of the lower Yellow River over the years

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domestic and foreign scholars carry out a more detailed study on REE geochemistry of the sediments of the modern Yellow River. They reported REE abundance and distribution patterns in the Yellow River sediment, and indicated that the REE composition is the same as other rivers in the world(2-3), as well as the significance of REE composition on the tracer of the continental crust or the material flowing into the sea from land(4). However, there is no study about the Environmental Geochemistry of trace elements in the paleo-sediment of the Yellow River. This article expected to provide a basis data for environmental pollution monitoring, evaluation and the establishment of the environmental baseline, as well as accurate and reliable information to scientific research and production for future through the research on the type of trace elements, content and distribution which contains in the paleo-sediment of the Yellow River in Wuzhi of Jiaozuo City, Henan Province. Besides, the paleo-sediment of the Yellow River were mainly from the erosion of the Loess Plateau in the middle reaches(5), and trace elements in sediments have special significance on the restoration of the paleo geographic environment. Thus we can estimate indirectly the status of the civilization for thousands of years of Chinese various dynasties, as well as the destruction of vegetation on the Loess Plateau during different periods, according to the content and the distribution of trace elements in paleo-sediment. And we can provide experiences and lessons to the comprehensive management of the Loess Plateau on the middle reaches of the Yellow River for future.

2 SAMPLING AND ANALYSIS

2.1 Sampling site

The sample profile was located at 113°30'35"E, 35°2'38" N, in the east of Yangzhuang in Jia Yingguan Village of Wuzhi, Jiaozuo City, Henan Provinc (Fig.2). It was divided into 15 layers in accordance with the characteristics of sediments such as color, structure, texture (Fig.3) and the total depth was about 530cm. Some layers were thick and were divided 2-3 samples, we collected 48 samples using grooving method with a stainless steel sampler (10cm×1cm).

2.2 Analytical method

Soil samples were dried at room temperature in the laboratory, and then powered to <0.149 mm particles with a agate mortar by hand. Samples were digested in crucibles using $HCl-HNO_3-HF-HClO_4$(6). Trace elements (Fe, Mn, Cu, Zn, Ni, Pb, Cr and As) were analyzed using flame atomic absorption spectrophotometer(analytical instruments of Germany Jena AG product, Model:contrAA300)or dual-channel atomic fluorescence spectrometry (Beijing Kyrgyzstan Instruments Co., Ltd. product, Model: AFS-830). Detection limit of each element is 3 $mg\cdot kg^{-1}$ (Fe),1 $mg\cdot kg^{-1}$ (Mn), 5 $mg\cdot kg^{-1}$ (Cu), 1 $mg\cdot kg^{-1}$ (Zn), 1 $mg\cdot kg^{-1}$ (Ni), 5 $mg\cdot kg^{-1}$ (Pb), 5 $mg\cdot kg^{-1}$ (Cr), 0.004 $mg\cdot kg^{-1}$ (As), respectively. In the process of elemental analysis, we carried out blank samples analysis, parallel sample analyze and duplicate samples analysis. The results showed that the analytical relative error of each element was less than 10%.

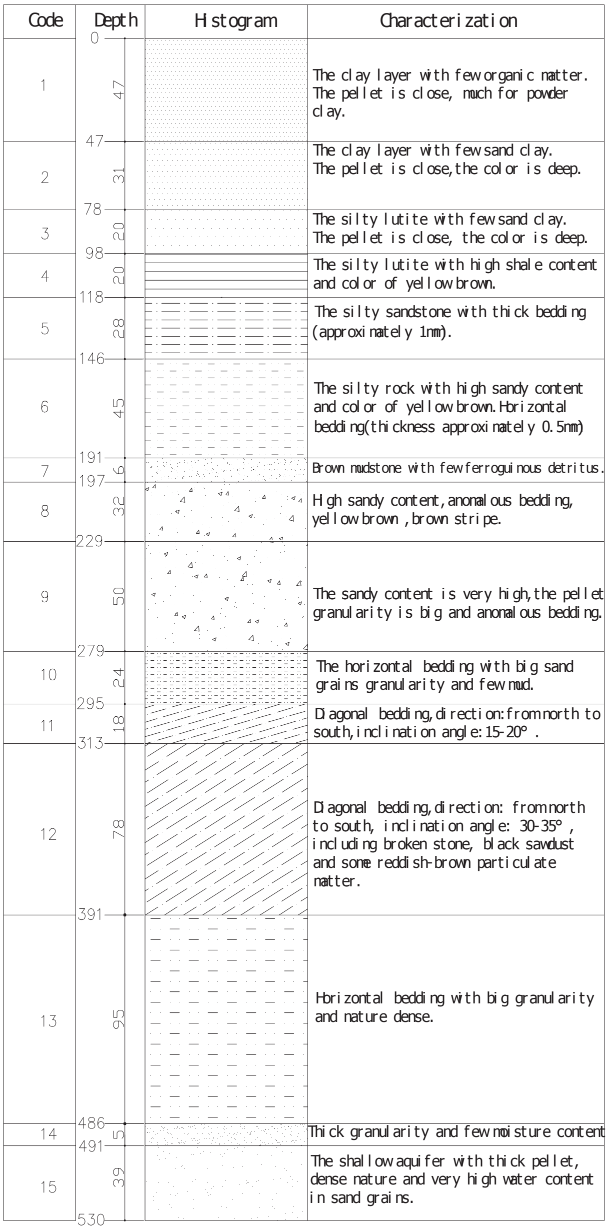

Fig. 2 The location of sampling points

3 RESULTS AND DISCUSSION

3.1 The distribution characteristics of trace elements

The concentrations and trends of trace elements in the paleo-sediment of the Yellow River of Wuzhi were shown in Fig.4.

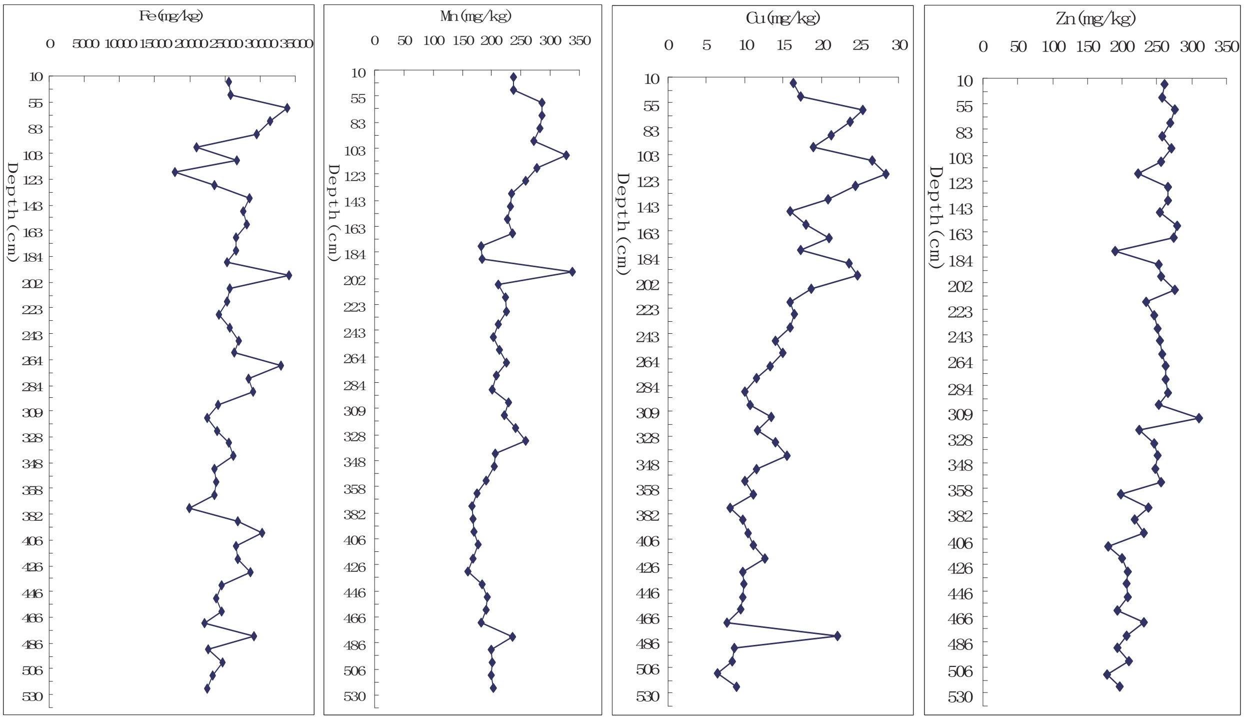

Fig. 3 The histogram of the sampling profile

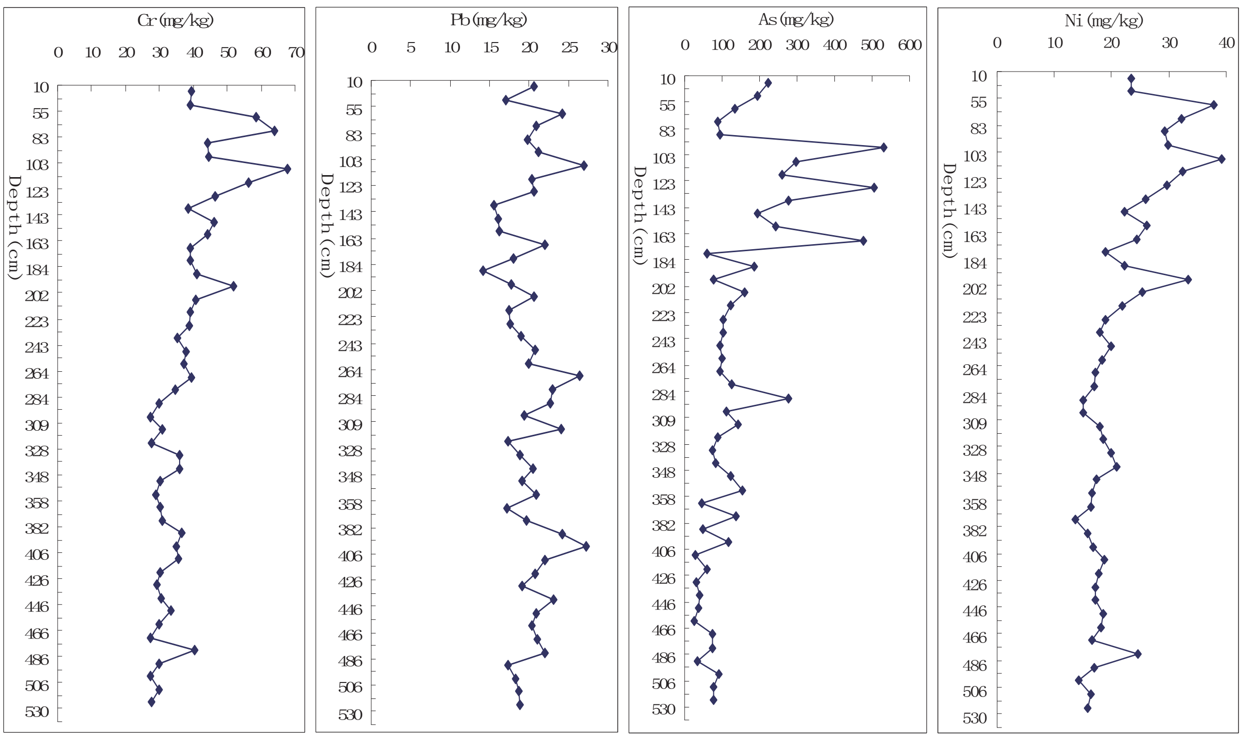

Fig. 4 Concentrations and trends of trace elements

Concentrations of eight trace elements(Cu, Ni, Mn, Zn, Pb, Cr, Fe, As) in the paleo-sediment of the Yellow River of Wuzhi ranged between 6.42 and 28.35 mg·kg^{-1} (mean 15.09 mg·kg^{-1}), 13.69 and 39.24 mg·kg^{-1} (21.31

mg·kg^{-1}), 158.8 and 338.65 mg·kg^{-1} (219.56 mg·kg^{-1}), 178.25 and 309.75 mg·kg^{-1} (239.49 mg·kg^{-1}), 14.16 and 27.19 mg·kg^{-1} (20.22 mg·kg^{-1}), 27.25 and 67.71 mg·kg^{-1} (37.84 mg·kg^{-1}), 17830 and 34080 mg·kg^{-1} (25942 mg·kg^{-1}) and 26.315 and 532.01 mg·kg^{-1} (141.71 mg·kg^{-1}), respectively.

The concentrations of Fe, Cu, Cr, Ni and As in the paleo soil profile generally showed the trend of decline with depth, Mn, Zn, Pb were relatively stable in the vertical profile.

3.2 The relationship between the distribution of elements and the development of Chinese civilization

According to historical data, the Yellow River watercourse is roughly same as present from Lung Mun to Mengjin before the Spring and Autumn Period. And Wuzhi and Huojia are the earliest old course which can be seen from ground today [7]. So we infer that the history of the paleo-sediment of the Yellow River in Wuzhi should be two thousand years at least. With the distribution of trace elements in the paleo-sediment and the sedimentary characteristics of the profiles, the profile could be divided into four represented stages.

The first stage (530cm—394cm): The concentrations of elements in the sediment were low. The mean concentrations of Cu, Ni, Mn, Zn, Pb, Cr, Fe, As were 10.34 mg·kg^{-1}, 17.48 mg·kg^{-1}, 187.66 mg·kg^{-1}, 204.28 mg·kg^{-1}, 21.01 mg·kg^{-1}, 31.65 mg·kg^{-1}, 25422.57 mg·kg^{-1}, 58.70 mg·kg^{-1}, respectively. The sediment concentration of the Yellow River at that time was much lower than today. Meanwhile, the granularity of sediment was silm in flood season, and bigger in non flood season, relatively[8]. Since the sizes of the sediment particulates were bigger in the profile compared with other layers, thus it indirectly proved that the natural vegetation of the Loess Plateau was in good condition at that time. In that period the level of social production was backward, herdsmen lived for fishing and hunting as well as collecting and planting, and human factors had little impact on the Loess Plateau. Therefore we can infer that the trace elements of the profile in this section represented the natural background values which mostly caused by natural factors. According to the study of ZHU Ke-zhen, the Yellow River basin was in "Yang shao Warm Period" during this period[9], annual average temperature was 3—5 degrees higher than today. And then the climate of the Loess Plateau was humid and there were more dense vegetation. It is speculated from Xia Dynasty to Warring States period. In the vicinity of 486 cm, there were large peaks of elements, especially Cu. According to historical data, two countries of Qin and Wei once occupied the Loess Plateau, located counties, built the Great Wall, and farmed in small scale, smelted bronze tools and weapons. As a result, vegetation of the Loess Plateau was suffered little destruction so that sediments in the river had increased. And also, bronze smelting sediments led to the increase of trace elements concentrations, especially Cu. This stage was roughly speculated in the period of Spring and Autumn and Warring States period.

The second stage (394cm—358cm): The concentrations of six elements (Mn, Ni, Zn, Cr, Cu, As) in the paleo-sediment appeared a small-group variation with the depth, while Fe and Pb represented the opposite situation. The mean concentrations of Cu, Ni, Mn, Zn, Pb, Cr, Fe and As were 11.24 mg·kg^{-1}, 16.97 mg·kg^{-1}, 188.63 mg·kg^{-1}, 238.09, 19.50, 31.32, 23398.20 and 108.60 mg·kg^{-1}, respectively. Compared with the first section, the concentrations of most trace elements were bigger, while the concentrations of Fe and Pb decreased 8% and 7%, respectively. In this section, the profile had obvious oblique bedding mixing with a small amount of gravels, black bits of wood and reddish-brown particulates. The typical oblique bedding can be indirectly proved the bad floods at that time. So we infer most Fe was oxidized Fe_2O_3 that were reddish-brown particulates, and the reddish-brown particulates were not analyzed. As the high specific gravity and chemical stability, Pb most probably deposited at the bottom of 394 cm, making the concentrations of Fe and Pb increase with the depth. According to historical data, after the initial period of Western Zhou Dynasty (in 1000 BC) a series of warm and cold changes had been taking place. The temperature ranged between 1 ℃ and 2 ℃, changing very little. It only made the vegetation of the Loess Plateau gradually change from sub-tropical forests and warm temperate grasslands to warm temperate deciduous broad-leaved forests, warm temperate forest steppe, temperate grasslands and temperate desert grasslands. But the climate change effects on vegetation were also nothing more[9]. In Qin Dynasty and Western Han Dynasty, a large number of han nationality moved into the Loess Plateau in order to consolidate the northwest border, making a large-scale agricultural reclamation with iron implements in this region. The reddish-brown particulates may be kept at that time. The villages and farmlands appeared instead of the grassland and forest. The destruction of forest cover resulted in the increase of soil erosion. The Yellow River had overflowed four times, bursted seven times and diverted two times during 200 years [10]. So we infer the floods of Yellow River at that time mainly because of the vegetations destruction of the Loess Plateau due to human activities. This stage was roughly speculated from Qin Dynasty to Western Han Dynasty.

The third stage (358cm—270cm): The concentrations of trace elements in the paleo soil profile were relatively stable on the whole. The mean concentrations of Cu, Ni, Mn, Zn, Pb, Cr, Fe and As were 11.90, 17.22, 226.50, 260.23, 20.89, 31.06, 25554.33 and 136.73 mg·kg^{-1}, respectively. Compared with the section section, the concentrations of trace elements were bigger except Cr. It can be seen from Figure 3 that between 279 cm and 295 cm, there appeared horizontal bedding and the sizes of sediment particulates were bigger than them in the second section. Through analyzing these characteristics, we considered that the floods were very few at that time. According to historical data, from New Wang Mang period to Sui Dynasty (about 600 years), the Loess Plateau partly recovered natural vegetation because nomadic tribes played an important role in this area so that the Yellow River was in the stable phase during that period [10]. In that period, the Yellow River only overflowed seven times and transferred one time, and in the Sui Dynasty, there were no floods. The floods of this period were much fewer than them in the Western Han. The formation of this situation had a great relationship with the recovery of vegetation because of nomadic tribes, so that the soil erosion destruction of the Loess Plateau was greatly reduced. Therefore we speculated that this stage was roughly from New Wang Mang period to Sui Dynasty.

The fourth stage (270cm—0cm): Elements concentrations in this section showed a wide range of variation and changed dramatically in the near-surface. The mean concentrations of Cu, Ni, Mn, Zn, Pb, Cr, Fe and As were 19.65, 25.65, 243.89, 255.82, 19.73, 44.79, 26912.48 and 200.73 $mg \cdot kg^{-1}$, respectively. Compared with the third section, the concentrations of most trace elements were bigger except Zn and Pb. The concentrations of Cu, Ni, Mn, Cr, Fe and As increased 65%, 49%, 8%, 44%, 5% and 47%, respectively, while the concentrations of Zn and Pb decreased 2% and 6%, respectively. It can be seen from Figure 3 that between 191 cm and 197 cm, the profile had a few iron crumbs. Besides, in this section, the sedimentary characteristics were irregular. According to historical records, from Late Ming Dynasty to Early Qing Dynasty, smelt iron was a leader in the world. So we supposed that the age of this stratum was during Late Ming Dynasty and Early Qing Dynasty. Besides, after the rebellion of An and Shi in the Tang Dynasty, a large number of poor farmers fled to north of Shanxi Province and lived on farm work. And then the size of farming is larger than before so that the vegetation of the Loess Plateau suffered extensive damage. Since then, in the period of Yuan, Ming, Qing and the Republic of China, the north of Shanxi Province was not only the agricultural area but also industrial district due to the needs of the war. In the past long years, natural vegetation of the Loess Plateau had been suffering continuous, large-scale and ruinously destruction, ultimately resulting in the modern situation that the percentage of forest cover of the entire plateau is about 3%. The floods had become more and more serious with the ages (from Tang Dynasty to 1940). The reasons for the devastating results were excessive reclamation, development of industry and agriculture and the severe destruction of vegetation. So it was speculated from Tang Dynasty to Present.

4 CONCLUSION

(1) Concentrations of eight trace elements (Cu, Ni, Mn, Zn, Pb, Cr, Fe, As) in the paleo-sediment of the Yellow River of Wuzhi ranged between 6.42 and 28.35 $mg \cdot kg^{-1}$ (mean 15.09 $mg \cdot kg^{-1}$), 13.69 and 39.24 $mg \cdot kg^{-1}$ (21.31 $mg \cdot kg^{-1}$), 158.80 and 338.65 $mg \cdot kg^{-1}$ (219.56 $mg \cdot kg^{-1}$), 178.25 and 309.75 $mg \cdot kg^{-1}$ (239.49 $mg \cdot kg^{-1}$), 14.16 and 27.19 $mg \cdot kg^{-1}$ (20.22 $mg \cdot kg^{-1}$), 27.25 and 67.71 $mg \cdot kg^{-1}$ (37.84 $mg \cdot kg^{-1}$), 17830 and 34080 $mg \cdot kg^{-1}$ (25942 $mg \cdot kg^{-1}$) and 26.315 and 532.01 $mg \cdot kg^{-1}$ (141.71 $mg \cdot kg^{-1}$) , respectively.

(2)The concentrations of Fe, Cu, Cr, Ni and As in the paleo soil profile generally showed the trend of decline with depth, Mn, Zn, Pb were relatively stable in the vertical profile.

(3)The distribution characteristics of trace elements in the paleo-sediment have proved the trend of vegetation changes of the Loess Plateau for thousands of years. Before Qin Dynasty, the impact of human activities on the Loess Plateau was very little so that the floods of the Yellow River were very few. After Qin Dynasty and Western Han, there presented a contrasting situation. This showed that the destruction of vegetation of the Loess Plateau was mainly affected by human activities.

(4)Vegetation changes of the Loess Plateau had a direct relationship with the changes of production mode of agriculture and industry and grassland farming, namely that industrial and agricultural development resulted in the destruction of vegetation on the Loess Plateau and forestry and animal husbandry could promote the recovery of vegetation.

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