Pollution Assessment of Heavy Metal Pb in Surface Soil of Cixi, Zhejiang Province in Recent 1,000 Years

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Abstract: The work aimed at evolving weathering process of heavy metal element Pb in surface soil of Cixi District. Surface soil samples at different soil ages were collected to analyze mass variation of heavy metal element Pb in evolution process by enrichment factor method. We found that the soil masses increased in 285 and 1,000 years of soil formation, with artificial pollution rates of 21% and 15%. This is caused by natural accumulation and human pollution. Other surface soils are formed by natural accumulation.

Key words: Soil Formation Time; Natural Accumulation; Human Pollution; Enrichment Factor Method; Surface Soil

1. INTRODUCTION

In 2005, Zhejiang Province firstly finished 1: 250,000 multipurpose regional geochemical survey. Result shows that surface soils of Cixi District have anomalies of heavy metal elements, where Pb is enriched around the city (Dong, 2007). However, the formation of abnormal Pb content and its evolution in the past 1,000 years remain problems to be solved after evaluation of agricultural geological survey.

At present, scientists (Barrett, 1992; John, 1998) have tried to use soil sequence to indicate the evolution of soil elements, achieving good results. However, the method is difficult to distinguish between natural process and human pollution. Hernandez, Sutherland, Tengyan Guo and Zhang Xiuzhi successfully distinguished the source of abnormal elements in the soil. Teng Yanguo considered that the enrichment factor was an important parameter to evaluate the effect of human activity to enrichment content of potential toxic elements in environmental media (Teng, 2006). The enrichment coefficient reflected pollution degree of the element. The work collected the surface soil samples of different soil forming time in Cixi area to analyze the evolution process of heavy metal element Pb in recent 1000 years. After that, the enrichment factor method was used to distinguish human pollution from natural process.

2. SURVEY OF RESEARCH AREA

Cixi City is located on the south coast of Hangzhou Bay in Eastern Zhejiang, and is 60 km from Ningbo in the east, 148 km from Shanghai in the north and 138 km from Hangzhou in the west. The coordinates are Longitude 121° 02′ —121° 43′ E and Latitude 30° 20′ —30° 34′ N. Cixi consists of hilly area, strand plain (Three North Plain) and intertidal zone outside the seawall, covering a total land area of 1,718 km2. It has a subtropical monsoon climate, with an average annual sunshine of 2,038 hours, annual sunshine percentage of 47%, annual average temperature of 16.0°C and average annual rainfall of about 1,272.8 mm.

3. MATERIALS AND METHODS

The places with little human disturbance were selected as samples to reflect real status of heavy metals in soil. According to block shape, surface soil samples were sampled by S-shape multi-point method. Five to seven points constituted one soil sample. The samples were collected with new sacks, and put in clean place for air-seasoning. After being taken by quartation, some samples were crushed, and screened by 25 meshes for later use. The positions of sampling points were recorded by GPS. Using core cutter method, we measured bulk density of soil profile. Figure 1 shows the distribution of sampling points.
Figure 1. Soil samples located in Cixi city natural beaches

4. EXPERIMENTAL RESULT AND ANALYSIS

4.1. Evolution characteristics of heavy mental elements in soil

Satellite photography of Cixi District observed by Wang Qingyi shows that Cixi has lake and sea plains formed at late ice age in the south, marine sedimentary plain formed at middle ice age in the middle part and coastal sea plain formed recently in the north (Wang, 2004). Feng Lihua et al. accurately determined the formation time of seawalls by discussing seacoast vicissitude and beach reclamation in Cixi District (Feng, 2006). Table 1 shows the formation time of different seawalls.

<table>
<thead>
<tr>
<th>Name of Seawall</th>
<th>Construction Year</th>
<th>Name of Seawall</th>
<th>Construction Year</th>
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<tbody>
<tr>
<td>Xieling Seawall—Great Ancient Seawall</td>
<td>1047-1341</td>
<td>Seventh Seawall (Chengqing Seawall)</td>
<td>1892</td>
</tr>
<tr>
<td>Second Seawall (Jie Seawall)</td>
<td>1489</td>
<td>Eighth Seawall</td>
<td>1952</td>
</tr>
<tr>
<td>Third Seawall (Yuliu Seawall)</td>
<td>1724</td>
<td>Ninth Seawall</td>
<td>1968</td>
</tr>
<tr>
<td>Fourth Seawall (Liji Seawall)</td>
<td>1734</td>
<td>Tenth Seawall</td>
<td>1992</td>
</tr>
<tr>
<td>Fifth Seawall (Yanhai Seawall)</td>
<td>1796</td>
<td>Eleventh Seawall</td>
<td>2002</td>
</tr>
<tr>
<td>Sixth Seawall (Yongqing Seawall)</td>
<td>1815</td>
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Figure 2 shows soil bulk density, special gravity and porosity during soil development. The longer the soil-forming age, the smaller the soil bulk density and specific gravity are; the greater the porosity is. This is related to soil organic matter content and human interference.

Figure 3 shows the evolution process of heavy metal element Pb content. In Figure 3, the contents of Pb rise year by year, reaching maximums of 32.6 and 33.4ug/g in 285 and 1000 years of soil formation. The evolution rule of Pb is similar with that of organic matter. This indicates that the increment of organic matter content accelerates enrichment of Pb in soil formation process.

Figure 2. Bulk density, special gravity and porosity during soil formation process
**4.2. Human pollution discrimination**

Enrichment factor is calculated by the following equation.

\[
EF = \frac{C_i}{C_n} = \frac{M_i}{M_{i,p}}
\]

where \(C_i\) is mass concentration of Element \(i\) (mg/kg); \(C_n\) the mass concentration of inert elements (mg/kg); \(M\) the mass of Element \(i\) in soil; \(P\) and \(W\) are the soils before and after weathering. There is no uniform standard for enrichment factor. E.g., Tania et al. take \(EF>2\) as the standard for element enrichment; Blaser et al. take \(EF>1\) as the standard. We consider that \(EF=1\) is the base value to judge element pollution. \(EF>1\) indicates that the mass of Element \(i\) increases after chemical weathering. This increment is considered as external human pollution. Because of strong adsorption, \(\text{Pb}\) has little leaching loss which can be ignored.

There are 2 methods for the selection of inert elements. The first is to select lots of elements (such as Si, Al and Fe). Because of high content, the reacting dose can be ignored. The second is to select the elements behind periodic table of elements such as Ti, Nb, Zr and Y. These elements are not easy to produce chemical reaction because of stable enthalpy. In the work, Zr is selected as inert element. Figure 4 shows Zr content and bulk density distribution in soil profile of 1000 year and Zr content in surface soil during soil formation process.

![Figure 3](image.png)

**Figure 3.** Variation curve of heavy metal element Pb during soil formation time

![Figure 4](image.png)

**Figure 4 a.** Zr contents and bulk densities in typical soil profile of different depths
Figure 4 b). Zr contents in surface soil during soil formation process

Zr concentration in soil profile is 240-280ug/g with little change. Zr concentration in surface soil is higher than that in deep soil, and inversely proportional to bulk density. In soil evolution process, Zr content decreases with the increase of organic matter content in soil. This indicates that Zr is an ideal inert element in primary mineral.

Taking Zr as inert element and the soil with shortest soil formation age as parent soil, we obtain the evolution process of heavy metal EF value (See Figure 5). The Pb masses increase in 285 and 1,000 years of soil formation (EF value>1), and decrease at other time (EF<1). This shows surface soil has been obviously polluted by man in 285 and 1,000 years of soil formation. Pb content in surface soil of this district is caused by superposition of natural background and human pollution values. Enrichment factor method provides possibility for quantitative discrimination between human pollution and natural background values. The equation is

\[
\frac{G_{\text{Pb}, w} - G_{\text{Pb}, p}}{G_{\text{Pb}, w}} = 1 - \frac{1}{EF}
\]

This method shows that about 21% and 15% of Pb contents in surface soil are derived from human pollution in 285 and 1,000 years of soil formation.

Before 200 year of soil formation, soil has not high curing degree and unstable structure. Few human activities, quick airiness and less dry-wet deposition result in little change of Pb mass in surface soil. With the increase of soil formation time, soil curing degree and human activities, industrial and agricultural degrees are improved. Factories and cars discharge lead dust with high concentration. Unrestricted pesticide fertilizer and sewage irrigation cause the increase of Pb mass in surface soil. Located in the soil body of 1,000 years, Cixi City has the most serious Pb pollution in surface soil. This may be related to point pollution source. The specific reason needs further verification.

Figure 5. EF values of Pb in soil formation process while taking Zr as inert element

The EF ratio develops surface soil is polluted by human actions when 200 years. The Dagu seawall is the severely polluted, where Hg quality is more 4.5 times than the ten seawall. Coal and fuel-fired are approximately the most Hg inputs. The human pollution ratio in surface weathered soil shows 79 percent of surface soil in Dagu seawall, 50 percent in the second seawall, 53 percent in the third seawall and 52 percent in the fourth seawall are polluted by element Hg respectively. EF ratio in different seawall displays the pollution depth, simultaneously; the polluted soil in deeper profile indicates Hg environment risk, which mostly is dissolved into shallow groundwater.
5. CONCLUSION
Taking Zr as inert element, we evaluated the variation of Pb mass in soil formation process by enrichment factor method. Result showed that Pb masses increased in soil formation of 285 and 1,000 years (EF value>1), and decreased at other time (EF<1). Therefore, surface soil has been obviously polluted by man in 285 and 1,000 years of soil formation, with estimated human pollution rates of about 21% and 15%. Pb content in surface soil of this district results from superposition of natural background and human pollution values.

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REFERENCES