Distribution and assessment of heavy metals in the surface sediment of Yellow River, China

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ARTICLE INFO

Received 31 July 2015
Revised 28 October 2015
Accepted 29 October 2015
Available online 29 December 2015

Keywords:
Single factor index
Nemerow pollution index
Potential ecological risk index
Heavy metal pollution
Surface sediment

ABSTRACT

Large amounts of heavy metals discharged by industrial cities that are located along the middle reach of Yellow River, China have detrimental impacts on both the ecological environment and human health. In this study, fourteen surface sediment samples were taken in the middle reach of the Yellow River. Contents of Zn, Pb, Ni, Cu, Cr, Cd, As were measured, and the pollution status was assessed using three widely used pollution assessment methods, including the single factor index method, Nemerow pollution index method and potential ecological risk index. The concentrations of the studied heavy metals followed the order: Zn > Cr > Cu > Ni > Pb > As > Cd. Nearly 50% of sites had Cu and Cr accumulation. The concentration of Cu at the Yiluo River exceeded the secondary standard value of the Environmental quality standard for soils. Comparison of heavy metal concentrations between this study and other selected rivers indicated that Cu and Cr may be the major pollutants in our case. The single factor index indicated that many samples were at high levels of pollution for Cu and Cd; the Nemerow pollution index indicated that the Yihe River, Luohe River, Yiluo River and Huayuankou were polluted. According to the results of potential ecological risk assessment, Cd in the tributaries of Luo River, Yihe River, and Yiluo River showed high risk toward the ecosystem and human health, Cd in Huayuankou and Cu in Yiluo River showed a middle level of risk and other samples were at a low level of risk.

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Introduction

Due to their characteristics of toxicity, easy bio-accumulation and non-degradation, heavy metals are considered to be serious pollutants in the environment (Bozkurt et al., 2000). Once heavy metals accumulate in the bodies of aquatic organisms and then enter the human food chain, they are difficult to degrade or excrete by organisms and humans. In addition, excessive heavy metals may have negative impacts on the growth of organisms and may interfere with the physiological functions of the human body (Deniseger et al., 1990). Therefore, heavy metals could pose potential risks to humans and organisms. Together with the heavy metals from natural sources, a great deal of heavy metals from anthropogenic sources has been carried into the aquatic environment. The main anthropogenic sources include industrial and urban discharge, agricultural activities, and atmospheric deposition. The heavy metals in natural water could undergo some physical and chemical processes affecting their speciation, such as sorption, precipitation and complexation (Islam et al., 2015), and then settle down and be deposited in the sediments.
Sediment is the primary sink for various heavy metals and could also act as a source of heavy metals in aquatic systems (Adams et al., 1992; Rowlatt and Lovell, 1994). It shows relative stability over space and time, which makes more consistent assessment of heavy metal pollution possible (Pekey, 2006; Tuncer et al., 2001). Thus, sediment could be an effective indicator to evaluate the pollution conditions and find the causes of pollutants.

The Yellow River is the second longest river in China with a length of 5464 km. The basin area and the average discharge are 752,443 km² and 2571 m³/s, respectively. Because of the large amount of sand and mud, the Yellow River is the most sediment-laden river in the world (Yue et al., 2014). The middle reaches of the river flow between Hekou Town in Inner Mongolia and Zhengzhou, Henan. There are 30 large tributaries along the middle reaches, which increase the water flow by 43% at this stage. The middle reaches also contribute 92% of the river silts. Large amounts of sediment contain heavy metals, nutrients, minerals and organic matters (Milliman and Meade, 1983; Lin et al., 2016). The length of the stream passing through northern Henan is 711 km, and eight cities are located along this distance. The Yellow River has served as a major source of water for domestic, industrial and agricultural activities in these cities. After decades of rapid population growth and booming industrialization, a large amount of heavy metals has been discharged into the river, which has a detrimental impact on both the ecological environment and human health in the long run.

Therefore, the objective of the current study was to obtain a better understanding of the distribution of the main heavy metals in the sediments of the Yellow River and to assess the risks posed by the heavy metals from the Yellow River basin using the single factor index method, Nemerow pollution index method and potential ecological risk index (Hakanson, 1980).

1. Materials and methods

1.1. Sample collection and analysis

The study was carried out in the middle reaches of the Yellow River, between Xiaolangdi of Luoyang and Kaifeng, Henan Province, with the total length of 200 km. The surface sediment samples were collected with an Ekman grab sampler from fourteen sites in this region (Fig. 1).

At each site, three to five 5 cm deep samples were taken and mixed evenly. Then the samples saved in prepared brown glass bottles were sent back to the laboratory within 24 hr and frozen in order to avoid contamination of the samples. Geographical information of the samples was recorded by the Global Positioning System (GPS) (Table 1).

All the collected samples were freeze-dried, crushed, and then sieved through a 100-mesh sieve. Approximately 0.5 g dried surface sediment samples were digested in 5 mL aqua regia (HNO₃:HCl = 1:3) and heated at 140°C until the samples turned grey. Then 3 mL HClO₄ was added into the cooled samples (Qiao et al., 2011). The residues were diluted with deionized water to 25 mL for determining concentrations of heavy metals. Sample solutions were stored in the refrigerator at 4°C and then were analyzed for the main heavy metals including Cr, Cd, Cu, Pb, Zn, Ni and As with an inductively coupled plasma–optical emission spectrometer (ICP-OES, Teledyne Leeman Labs, Hudson, NH, USA).

The heavy metal concentrations were the average of three repeated measurements for each sample. For quality control, reagent blanks and standard reference materials (GSS-6 soil; China National Center for Standard Material, Beijing, China) were applied.

1.2. Pollution assessment methods

Three methods of pollution assessment of heavy metals were conducted here, including the Single factor index method, Nemerow pollution index method, and Hakanson potential ecological risk index (Hakanson, 1980).

The single factor index method was applied to assess the pollution degree of one pollutant in the sediment samples (Chen, 2010). This method could highlight the most important pollutant which contributes most to the pollution at each site in an easy and clear way. The pollution index for a single pollutant was established according to Eq. (1):

\[ P_i = \frac{C_i}{S_i} \]

where, \( P_i \) is the single pollution index; \( C_i \) (mg/kg) represents the measured average concentration of heavy metals; \( S_i \) (mg/kg) is

Fig. 1 – Map of the sampling sites in the middle reaches of Yellow River.
the background value of soil in Henan Province as the standard value.

The Nemerow pollution index was used to evaluate the comprehensive pollution status of sediments with all the heavy metals (Chen, 2010). Since different heavy metals may have impacts on one site, this method could provide a reasonable interpretation of the heavy metal pollution at each site as a whole. The Nemerow pollution index can be calculated by Eq. (2):

$$P_N = \sqrt{\left( P_i + P_i^{(\text{max})} \right) / 2}$$

where $P_N$ is Nemerow pollution index; $P_i$ is the arithmetic mean of the pollution index of all the pollutants; $P_i^{(\text{max})}$ is the maximum pollution index among the pollutants, based on the single pollution index at each site.

The potential ecological risk index, which was introduced originally by Hakanson (1980), could be used to evaluate the ecological risk by considering the toxicity of the pollutant and a comparison between the concentration of the pollutant and the background value. The method has been widely applied in the assessment of heavy metal pollution in surface sediment. The potential ecological risk index (RI) was defined as following Eq. (3) (Li et al., 2013):

$$\text{RI} = \sum_{i=1}^{m} E_i = \sum_{i=1}^{m} \left( T_i \times \frac{C_i}{C_i^{\text{st}}} \right)$$

where, $C_i^{\text{st}}$ and $C_i$ are the heavy metal concentrations measured in the sediment samples and the background values of metals in the soil, respectively. $T_i$ is the biological toxicity factor for a given substance. $E_i$ values for the metals in this study are as follows: Cd = 30, As = 10, Cu = Ni = Pb = 5, Cr = 2 and Zn = 1 (Hakanson, 1980; Xu et al., 2008). $E_i$ is the monomial potential ecological risk factor.

The classification of pollution degree of $P_i$ and $P_N$ (Chen, 2010), and the relations between $E_i$, RI and their corresponding pollution degree are listed in Table 2.

### 2. Results and discussion

#### 2.1. Heavy metal concentrations in sediments

The concentrations of all the seven heavy metals in each sampling site are shown in Fig. 2.

The concentrations of heavy metals in the different sites showed a wide variation. The concentration ranges of the heavy metals were: Zn, 41.8–114 mg/kg; Pb, 4.27–42.5 mg/kg; Ni, 15.0–39.6 mg/kg; Cu, 6.99–261 mg/kg; Cr, 42.6–132 mg/kg; Cd, ND-0.252 mg/kg; and As, ND-8.67 mg/kg, respectively. The average metal concentrations and the standard deviation values in the samples were: Zn, 68.4 ± 23.5 mg/kg; Pb, 15.2 ± 12.8 mg/kg; Ni, 23.6 ± 7.01 mg/kg; Cu, 40.7 ± 66.1 mg/kg; Cr, 62.4 ± 22.8 mg/kg; Cd, 0.085 ± 0.092 mg/kg; and As, 2.46 ± 2.70 mg/kg, respectively, ranking in decreasing order as follows, Zn > Cr > Cu > Ni > Pb > As > Cd.

Since little criteria on heavy metals in stream sediments exist nowadays, in this study, we compared the heavy metal concentrations in surface sediment samples with the mean values of national stream sediments (given as NV) (Tan et al., 2014; Yan et al., 1995), the highest background values of sediments before global industrialization (given as GV) (Hakanson, 1980), the primary standard values (given as PS) and the secondary standard values (given as SS) of the soil. PS and SS are from the Environmental quality standard for soils. The results of comparison are illustrated in Fig. 2.

All of the heavy metals had accumulated to different extents, with the exception of As. Nearly 50% of sites showed Cu and Cr accumulation. The enrichment factors of Cu and Cr were in the range of 1.12–12.4 and 1.09–2.28, respectively, suggesting that Cu and Cr are the two main metals that could have detrimental impacts on the riverine ecosystem. In addition, the Cu concentrations at sites Y8, Y10, and Cr concentration at site Y12 were higher than the corresponding GV values (50 mg/kg and 90 mg/kg). Heavy metals mainly accumulated in the section from Y4 to Y7, namely the Yihe River, Luohu River and Yiluo River; and from Y10 to Y12, namely the Wuhui float bridge and Huayuankou.
For each heavy metal, the concentration in each sampling site was quite different. Most values did not exceed the primary standard values. However, the Zn concentration at sites Y4 and Y5, Cr concentration at site Y12, Cu concentration at sites Y4 and Y10, Pb concentration at sites Y4 and Y5, and Cd concentration at sites Y4, Y5 and Y7 exceeded the primary standard but were under the secondary standard. Only the concentration of Cu at site Y8 exceeded the secondary standard value.

One of the biggest industrial cities in China is located upstream of the Yiluo River, which is Luoyang City. The industrial and domestic sewage of the city is mainly discharged into the Yihe River and Luohe River. This may be the reason that the concentrations of several heavy metals were higher than the primary standard at Luohe River (Y4) and Yihe River (Y5), and even led to the severe Cu pollution downstream. The results indicated that the heavy metals, which have high concentrations, have accumulated in the sediments through sedimentation and adsorption, becoming major sources of secondary pollution in the rivers.

Table 3 presents the heavy metal concentrations in sediment samples from the Yellow River and other selected rivers from the references. Comparison reveals that the concentrations of Cu were higher than those of other heavy metals in the South Yellow Sea, China (Yuan et al., 2012), Yellow River, China (Yuan et al., 2008), Yangtze Estuary, China (Zhang et al., 2009) and the middle reach of the Yellow River in present study. For specific heavy metals, Cu concentration was higher in this study than those in other studies, and Cr concentration was higher than that in Yellow River (Yuan et al., 2008) but lower than that in the Yangtze Estuary, China (Zhang et al., 2009). The concentrations of other heavy metals were all lower in the present study. The comparison indicated that Cu and Cr may be the major pollutants in our case, thus more attention should be paid to these heavy metals since they may have main impacts on the river sediments and in turn on organisms and humans.

2.2. Assessment of heavy metal pollution

The Single factor pollution index and Nemerow pollution index calculated by Eqs. (1) and (2) for the studied metals in fourteen sites are illustrated in Fig. 3.

The $P_i$ values of all heavy metals at sites Y1–Y3 and Y13 were less than 1, indicating that no pollution occurred in
Xiaolangdi, Luoyang Yellow River and Kaifeng Yellow River. One possible reason for this is that due to the topographic features in this region, the level of industrial development is lower.

At site Y4, Pb and Cu pollution was moderate and Cd reached the high pollution level, while other metals had low or no pollution. At site Y5, Pb and Cd pollution belonged to moderate grade \((2 < P_i \leq 3)\). At site Y6, only Cu and Cr showed moderate pollution. The \(P_i\) value of Cd was 3.47 at site Y7, meaning Cd pollution was serious in this place, while the pollution from Zn, Pb, Ni, Cu and Cr was low. The pollution grades of Cr and Cu were low level and high level at site Y8, respectively, and the \(P_i\) values of Cu even reached 13.6, significantly higher than 3. Y9 was slightly polluted by Cu. However, Y10 was severely polluted by Cu (high level) and Zn, Cr, Cd (low level). At site Y11, Cd pollution showed moderate degree and others had low pollution. Cr pollution at Site Y12 was moderate and Zn, Pb ranked at low level. Y14 was only slightly contaminated by Cu.

The mean pollution degree of heavy metals decreased in the order Cu > Cd > Zn > Cr > Ni > Pb > As. Cu and Cd were the most important pollutants since their \(P_i\) values were relatively higher than others at many sampling sites, reaching moderate or high pollution levels. The Single factor pollution index also has its limits, because it is more suitable for an area which is affected only by a single pollutant. The reality is that areas are always influenced by many different pollutants. Therefore, the Nemerow pollution index could be used to analyze the comprehensive pollution status in the sediments.

From the perspective of Nemerow pollution index, the pollution degree of Y8 was high level, of which the \(P_N\) value was up to 9.77. The \(P_N\) of Y10 and Y7 were between 2.5 and 7, belonging to moderate level. Six sites ranked at low pollution level, including Y4, Y5, Y9, Y11, Y12 and Y14. No pollution was posed to the remaining sites.

The main contaminated areas were located at Yihe River (Y5), Luohe River (Y4), Yiluo River (Y6, Y7 and Y8) and Huayuankou (Y11, Y12). As mentioned above, Luoyang city, a large industrial city, is located at the upstream of the Yiluo River. This demonstrated that the anthropogenic inputs were probably the essential contributor for the pollution in these places. The sources of the heavy metals were mainly from human activities, including urbanization, industrialization, deposition of industrial wastes and the like. In addition, non-point source pollution from pesticide application in the coastal areas might also cause pollution in the river.

### 2.3. Potential ecological risk assessment of heavy metals

The potential ecological risk assessment properly combines ecological effects and toxicology. It has been widely used to assess the risks posed by heavy metals toward the ecosystem and human beings. In this study, this method was performed to analyze the heavy metal pollution status in the surface sediments of Yellow River. The calculated results of potential ecological risk from the single elements \((E_i)\) and the overall potential ecological index \((R_I)\) using Eq. (3) are presented in Table 4.

**Table 3** – Comparison of heavy metal concentrations in surface sediments between this study and other selected rivers from the references.

<table>
<thead>
<tr>
<th>Location</th>
<th>Zn (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>As (mg/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow River</td>
<td>Range</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Reference</td>
</tr>
<tr>
<td></td>
<td>41.8–114</td>
<td>(68.4)</td>
<td>(83.2)</td>
<td>(15.0–39.6)</td>
<td>(40.7)</td>
<td>(62.4)</td>
<td>(0.085)</td>
<td>This study</td>
</tr>
<tr>
<td>South Yellow Sea</td>
<td>Range</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Reference</td>
</tr>
<tr>
<td></td>
<td>24.4–244</td>
<td>(93.7)</td>
<td>(17.8)</td>
<td>(16.9)</td>
<td>(0.30)</td>
<td>(3.47)</td>
<td>(1.54)</td>
<td>Yuan et al. (2012)</td>
</tr>
<tr>
<td>Yellow River</td>
<td>Mean</td>
<td>(75.66)</td>
<td>(21.42)</td>
<td>(21.81)</td>
<td>(51.34)</td>
<td>(0.31)</td>
<td>(12.94)</td>
<td>Reference</td>
</tr>
<tr>
<td>Yangtze Estuary</td>
<td>Range</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Reference</td>
</tr>
<tr>
<td></td>
<td>47.6–154</td>
<td>(94.3)</td>
<td>(27.3)</td>
<td>(31.8)</td>
<td>(30.7)</td>
<td>(78.9)</td>
<td>(0.261)</td>
<td>Reference</td>
</tr>
</tbody>
</table>

**Table 4.** Comparison of heavy metal concentrations in surface sediments between this study and other selected rivers from the references.

**Fig. 3** – The Single pollution index \((P_i)\) and Nemerow pollution index \((P_N)\) of the samples.
As shown in Table 4, the range of the mean $E_i$ for each metal was from 1.17 to 35.2, which indicated that they were all at a low degree of ecological risk. The mean $E_i$ for seven heavy metals decreased in the order Cd > Cu > Ni > Pb > As > Cr > Zn. Cd posed a relatively higher risk at sites Y4, Y5 and Y7 (89.6–104.1), reaching the third level of pollution degree ($80 \leq E_i \leq 160$), and at site Y11 (74.5), it reached the moderate level ($40 \leq E_i < 80$). The ecological risk factor $E_i$ of Cu at site Y8 was 68.1, belonging to the moderate level.

For the comprehensive potential ecological risk index (RI), the average value of all the sampling sites was 59.7, which denoted that the overall risk was at the low degree. The RI values of each site decreased in the order Y7 > Y4 > Y5 > Y11 > Y8 > Y10 > Y2 > Y14 > Y1 > Y13 > Y6 > Y9 > Y12 > Y3. Cd was the chief contributor to the RI in all the sampling sites except for Y8 and Y12, in which Cu and Pb were the major contributors, respectively. Among all the sites, the RI value of Yiluo River #2 (Y7) was 134, which almost reached the threshold value (150). Therefore, more attention should be paid to the Yiluo River, Yihe River and Luohe River because of their high risk of heavy metal pollution in the sediments.

3. Conclusions

In this study, the concentrations of seven heavy metals (Cr, Cd, Cu, Pb, Zn, Ni and As) in the surface sediment samples were measured. Meanwhile, the degree of pollution and the potential risk of heavy metals in the sediment were assessed. The mean concentrations of metals were ranked in the following sequence: Zn > Cr > Cu > Ni > Pb > As > Cd. All metals were below the secondary standard at each site except for Cu, which exceeded the secondary standard at site Yiluo River. The enrichment factors of Cu and Cr, which were relatively higher than other heavy metals, indicated that these metals could create adverse effects for this river. Comparison of heavy metal concentrations between this study and other selected rivers indicated that Cu and Cr may be the major pollutants in our case. The Cu concentration at Yiluo River and Cr concentration at Huayuankou were over the GV values. More attention should be paid to the main polluted regions, including the Yihe River, Luohe River, Yiluo River and Huayuankou.

The single factor index of heavy metals showed that the pollution degree was decreased in the following order: Cu > Cd > Zn > Cr > Ni > Pb > As. Cu and Cd had more severe pollution than others. The results of the Nemerow pollution index indicated the Yiluo River had a high pollution degree. The potential ecological risk assessment indicated that Cd at Yihe River, Luohe River and Yiluo River showed high ecological risk, and Cd at Huayuankou and Cu at Yiluo River showed moderate risk. The comprehensive potential ecological risk of heavy metals was found to be at low degree.

Acknowledgments

This study was supported by the National Basic Research Program (No. 2015CB453103), the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB14020102) and the National Natural Science Foundation of China (Nos. 21477150 and 21321004).

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