The distribution, accumulation and potential source of seldom monitored trace elements in sediments of Beijiang River, South China

Bo Gao, Jin Lu, Huai-Dong Zhou, Shu-Hua Yin and Hong Hao

ABSTRACT

A geochemical study of Beijiang River sediments was carried out to analyze the concentrations, distribution, accumulation and potential sources of the seldom monitored trace elements (SMTEs: Sc, V, Co, Ga, Y, Sn and Sb). The mean concentrations of Sc, V, Co, Ga, Y, Sn and Sb were 8.2, 60.3, 9.6, 17.2, 28.6, 85.6 and 39.0 mg/kg, respectively. The concentrations of the SMTEs, together with their spatial distribution showed that the SMTEs were mainly due to anthropogenic inputs from the metal smelting industries and local mining activities in the upper region of the river. The assessment by geoaccumulation index indicates that Sc, V, Co, Ga and Y are at the unpolluted level, Sn is at the ‘strongly contaminated’ level, and Sb is at the ‘extremely contaminated’ level. The pollution level of the SMTEs is: Sb > Sn > Y > Ga > Co > V > Sc. The results of correlation analysis and principal component analysis indicated the Sn and Sb were positively correlated with each other, indicating a common source in sediments. In conclusion, our results indicate that the sediments in Beijiang River have been severely contaminated by Sn and Sb.

Key words | accumulation, Beijiang River, geoaccumulation index, sediments, seldom monitored trace elements

INTRODUCTION

Environmental pollution by commonly monitored trace elements (i.e. As, Cd, Co, Cr, Cu, Ni, Pb and Zn) in river sediments has been a focus for decades (Yang et al. 2009; Yi et al. 2011). Increasing industrial use of seldom monitored trace elements (SMTEs: Sc, Co, Ga, V, Y, Sn and Sb) would in theory lead to increased environmental concentrations (Grahn et al. 2006; Duan et al. 2010). Coal and fossil fuel combustion and metal manufacturing plants are the major source in the environment. However, rather less attention has been focused on these SMTEs. Especially, the aquatic geochemistry of these elements is poorly known. Because of their very low abundance, these trace elements are particularly sensitive to surrounding environmental conditions, which influence their physical-chemical species and behavior in the ecosystems. In addition, SMTEs are deemed potential pollutants because of toxicity, persistence and non-degradability in the environment (Filella et al. 2002; Crans et al. 2004).

The Pearl River (PR) is one of the major rivers in China, with a length of 2,214 km and a drainage area of 453,690 km². It flows to the South China Sea and consists of three main rivers: Xijiang River, Dongjiang River and Beijiang River. The lower reaches of the three rivers form the Pearl River Delta (PRD), which is one of most developed areas in China. However, rapid economic development in this region has led to the excessive discharge of pollutants to these rivers. In recent years, most studies paid much attention on the metal pollution in the PRD. The researchers measured the concentration and distribution of the commonly monitored trace elements in sediments (Li et al. 2000; Zhang & Wang 2001; Ip et al. 2005), agricultural soils (Wong et al. 2002) and aquatic organisms (Ip et al. 2005) in the region of PRD. However, little concern has arisen over SMTEs in sediment in this region, especially for the Beijiang River. In fact, as an important tributary of the PR, a large number of mining activities and metal smelting processing in the upstream of the Beijiang River have already led to serious metal pollution in this river, including commonly monitored trace elements and thallium (Gao et al. 2008; Xu et al. 2009).
Sediments are important deposits of metal accumulation and one of the most important tools to assess the contamination level of aquatic ecosystems (Förstner et al. 1989). Because of their bioavailability and toxicity, SMTEs should be of global interest, but there is little information on geochemical characteristics and behaviors of SMTEs in sediments. The knowledge of the concentrations, distributions and enrichment of SMTEs in sediments plays a key role in detecting sources of SMTEs and assessing the ecological risks of SMTEs in aquatic systems. The objectives of this study were: (1) to determine the SMTEs concentration and distribution in the sediments of Beijiang River; (2) to evaluate the enrichments of SMTEs in the sediments of Beijiang River; and (3) to discuss the origins of SMTEs in sediments of Beijiang River.

METHODS

Sample sites

In total, 19 sediments (0–10 cm) were collected along Beijiang River in March 2006. The sediment samples were dried at a temperature below −40 °C, crushed, and sieved to less than 200 μm before the chemical measurements were taken as described below. A map of the sampling locations is shown in Figure 1. Among them, there are 13 sample stations (from

Figure 1 | Sampling sites of Beijing River.
1 to 13) distributed along the mainstream from Shaoguan city to Qingyuan city. To investigate the SMTEs pollution of tributaries in Beijiang River, six stations were located in the river mouth of Wu River (B1), Zhen River (B2), Maba River (B3), Ba River (B4), Bin River (B5) and Longtang River (B6).

**Analytical methods**

All chemical treatments were in the ultra-clean laboratory, and all reagents were high purity grade. Total metal concentrations in the sediments were measured using established methods (Liu et al. 1999). Briefly, a mass of 40 mg of dry sample was weighed and dissolved into 10 mL Teflon bombs. About 2 mL concentrated HNO₃ + 0.2 mL concentrated H₂O₂ were added to samples and was left on a hot plate for one day. This step was to remove organic materials from sediment samples. The samples were then dried at 120°C. The residue was dissolved in 1 mL HNO₃ + 1 mL HF of sample. After 30 min ultrasonic procedure, the samples were taken into sealed bombs and were placed in an oven at 190°C for 48 h. This procedure resulted in clear solutions for sediment sample. After evaporation at 120°C, samples were dissolved in 1% HNO₃. Inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer Elan DRC-e) was used to determine the total concentrations of Sc, V, Co, Ga, Y, Sn and Sb.

**Data quality**

The quality controls for the strong acid digestion method included reagent blanks, duplicate samples, and standard reference materials. The QA/QC results show no sign of contamination in all the analysis. The accuracy of the analytical procedures employed for the analysis of the trace elements in sediments was checked using the certified reference material of stream sediment (GSD-12, GBW07312), obtaining good agreement with the certified values.

**Geoaccumulation index**

The geoaccumulation index ($I_{\text{geo}}$) introduced by Müller (1979) was also used to assess metal pollution in sediments of Beijiang River. Geoaccumulation index is expressed as follows:

$$I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5B_n} \right)$$

where $C_n$ is the measured concentration of trace metal ($n$) in the sediment, $B_n$ is the geochemical background value of element $n$, and 1.5 is the background matrix correction factor due to lithogenic effects. In present study, $B_n$ was selected from the literature (Taylor & McLennan 1995). Geoaccumulation index includes seven grades from Class 0 ($I_{\text{geo}} \leq 0$) to Class 6 ($I_{\text{geo}} > 5$). The $I_{\text{geo}}$ is associated with a qualitative scale of pollution intensity; samples may be classified as unpolluted ($I_{\text{geo}} \leq 0$), unpolluted to moderately polluted ($0 \leq I_{\text{geo}} \leq 1$), moderately polluted ($1 \leq I_{\text{geo}} \leq 2$), strongly to extremely polluted ($3 \leq I_{\text{geo}} \leq 4$), and extremely polluted ($I_{\text{geo}} \geq 5$). Class 6 reflects at least 100-fold enrichment above the background values.

**RESULTS AND DISCUSSION**

**SMTE concentrations in sediments**

SMTEs concentration and statistics results of the all investigated sediment samples are summarized in Table 1. SMTEs

<table>
<thead>
<tr>
<th>Results</th>
<th>Sc</th>
<th>V</th>
<th>Co</th>
<th>Ga</th>
<th>Y</th>
<th>Sn</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>2.64</td>
<td>16.80</td>
<td>2.18</td>
<td>6.11</td>
<td>7.53</td>
<td>7.38</td>
<td>0.94</td>
</tr>
<tr>
<td>Max.</td>
<td>15.16</td>
<td>113.50</td>
<td>19.02</td>
<td>29.35</td>
<td>52.69</td>
<td>496.90</td>
<td>418.40</td>
</tr>
<tr>
<td>Mean</td>
<td>8.22</td>
<td>60.27</td>
<td>9.64</td>
<td>17.25</td>
<td>28.56</td>
<td>85.61</td>
<td>38.98</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>3.4</td>
<td>29.4</td>
<td>4.8</td>
<td>6.3</td>
<td>11.7</td>
<td>121.8</td>
<td>91.9</td>
</tr>
<tr>
<td>Relative standard deviation (%)</td>
<td>41.8</td>
<td>48.7</td>
<td>50.0</td>
<td>36.6</td>
<td>40.9</td>
<td>142.3</td>
<td>235.7</td>
</tr>
<tr>
<td>Beijiang River (1998)</td>
<td>8.49</td>
<td>103</td>
<td>15</td>
<td>12.4</td>
<td>30.9</td>
<td>1.4</td>
<td>6.3</td>
</tr>
<tr>
<td>Stream sediment in China</td>
<td>–</td>
<td>87</td>
<td>13</td>
<td>–</td>
<td>26</td>
<td>4.1</td>
<td>1.42</td>
</tr>
</tbody>
</table>


$^b$Chi & Yan (2007).
concentrations in Beijiang sediments from 1998 (Zhang & Wang, 2001) and in stream sediment (Chi & Yan 2007) in China are also presented. As can be seen, the mean concentrations of Sc, V, Co, Ga, Y, Sn and Sb were 8.22, 60.27, 9.64, 17.25, 28.56, 85.61 and 38.98 mg/kg, respectively. Among SMTEs, the average contents of Sn and Sb in sediments of Beijiang River were obviously higher than those in stream sediments of China (Chi & Yan 2007). Compared with the results monitored in 1998 (Zhang & Wang 2001), the significant increase of SMTE concentrations of sediments was observed, especially for the obviously high concentrations of Sb and Sn, indicating the occurrence of an anthropogenic source of SMTEs. The large number of mining activities and metal smelting processes in upper region of Beijiang River may be responsible for this metal pollution. In fact, the mines of Lechang and Fankou and the Shaoguan Smelter are geographically located in the upper reaches of Beijiang River. Although the predominant products of mining and smelting were Pb and Zn, other elements such as SMTEs may have been produced in large quantities as co-products. These pollution sources may discharge large quantities of SMTEs into the Beijiang River. In addition, high relative standard deviation values (RSD > 100%) of Sn and Sb concentrations in sediments also suggested that anthropogenic input are possibly the main source of SMTEs (Table 1). A previous study also showed that mining activity and metal smelting were the important factors for commonly monitored heavy metal pollution (Cu, Pb, Zn, Cd, Ni, Cr, As and Hg) in Beijiang River (Xu et al. 2009).

Spatial distribution of SMTEs in sediments

The spatial distribution of STMEs in sediments of Beijiang River is shown in Figure 2. In general, the STME concentrations have a tendency of decreasing from upstream to downstream for the mainstream of Beijiang River, except for sampling site 13. The higher STME concentrations were found in sampling site 13 (Shijiao town), especially for Sn, Sb, and Ga. A large number of E-waste processing activities and electroplating plants in this sampling site can explain this surprising enrichment of SMTEs.

For tributaries, Maba River has the highest concentrations of SMTEs among six tributaries to the Beijiang River. This is mainly because it receives a large amount of wastewater discharged from metal smelters in its upper area. Tributaries in downstream (Binjiang River and Longtanghe River) have lower SMTE concentrations than those in the upstream of Beijiang River. In order to better investigate the SMTEs of tributaries, more samples will be collected because only one sample was collected in each tributary in this study.

Pollution assessment

Based on the $I_{geo}$ data and Müller’s geoaccumulation index, the results of the calculated $I_{geo}$ values with respect to average SMTEs are presented in Table 2. In general, the results of the average $I_{geo}$ values of are $-2.57$ for Sc, $-2.66$ for V, $-2.33$ for Co, $-0.75$ for Ga, $-0.19$ for Y, $3.64$ for Sn and $5.55$ for Sb. The order of average $I_{geo}$ values was: Sb > Sn > Y > Ga > Co > V > Sc. The average $I_{geo}$ of Sb had highest value and was ranked to ‘extremely contaminated’ indicating that Beijiang River has significant accumulation of Sb metal apparently from anthropogenic input. Sn was classified as Class 4 which indicated sediment quality as ‘strongly contaminated’. Furthermore, Sn was ranked as ‘strongly to extremely strongly contaminated’ in several sampling sites, including 1, 5, 13 and B3. For the mainstream, 1, 5 and 13 was extremely strongly contaminated for Sn and Sb. Maba River (B3) is the worst polluted by Sn and Sb among the tributaries. In contrast, the values of $I_{geo}$ of Y in sampling sites 1, 3, 5, 8, 13, B2 and B4 were more than zero, which was ranked to ‘uncontaminated to moderately contaminated’ level. The $I_{geo}$ values of Ga in sampling site 13 showed relative low values ($0 \leq I_{geo} \leq 1$), suggesting that this station is moderately contaminated by this element.

Origins of SMTEs in sediments

In a further attempt to assess the sources responsible for the observed pollution levels, correlation analysis and principal component analysis (PCA) were applied to the data set of SMTE concentrations of surface sediments in Beijiang River. Correlation analysis results indicated that Sc, V, Co, Ga and Y have significant correlations with each other, suggesting that they had the same source (Table 3). However, non-significant correlations of Sb with other five elements (Sc, V, Co, Ga and Y) may be possibly due to different sources and external inputs in sediments. In addition, the correlation result also showed that Sn and Sb were positively correlated each other, demonstrating a common source in sediments.
The method of PCA is a multivariate statistical technique that can be employed to reduce the dimensionality of a data set while attempting to preserve the relationships present in the original data and was used to assess trace metal behavior in the aquatic system. The rotated component matrices of the PCA of SMTEs are presented in Table 4. The results of the PCA indicated that Sc, V, Co, Ga, Y, Sn and Sb concentrations could be reduced to two components (PC1 and PC2), which explained 87.5% of the total variance for the data.

The first component (PC1) with high loading for Sc, V, Co, Ga and Y, explained about 62.2% of the total variance. This factor has been identified as ‘natural factor’. The second component (PC2), which explains 25.3% of the total variance, appears to represent an ‘anthropogenic factor’, as it is strongly correlated with the elements Sn and Sb, and to a lesser extent with Sc, V, Co, Ga and Y. Although the predominant products of smelting and mining were Pb and Zn, Sb and Sn may have been produced in large quantities as co-products. In this region, E-waste processing, mining activities and metal refining activities in the upper region of Beijiang River could be responsible for these excess SMTEs.

**Figure 2** | Spatial distribution of SMTEs in sediments of Beijiang River.
CONCLUSION

Our investigation of SMTEs such as Sc, V, Co, Ga, Y, Sn and Sb in sediment samples in Beijiang River and its tributaries, shows that the mean concentrations of Sn and Sb in sediments of Beijiang River were higher than those in stream sediments of China and previous results for the Beijiang River in 1998, indicating the occurrence of an anthropogenic source of SMTEs. The assessment by geoaccumulation index suggests that Sc, V, Co, Ga and Y are at the unpolluted level, Sn at the ‘strongly to extremely strongly contaminated’ level, and Sb at the ‘strongly to extremely strongly contaminated’ level. The pollution level of the SMTEs is: Sb > Sn > Y > Ga > Co > V > Sc. The results of correlation analysis and PCA indicated the Sn and Sb were positively correlated with each other, suggesting a
common source in sediments. Our results indicate that the sediments in Beijiang River have been severely contaminated by Sn and Sb. These results will provide fundamental pollution information of SMTEs in Beijiang River. Further research is required to investigate the behaviors and fates of SMTEs in river sediments and evaluate the bioavailability, toxicity and ecological risks in an aquatic environment.

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REFERENCES


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