Heavy Metal Characterization and Leachability of

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HEAVY METAL CHARACTERIZATION AND LEACHABILITY OF ORGANIC MATTER-RICH RIVER SEDIMENTS IN HANOI, VIETNAM

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ABSTRACT

Industrial wastewater, including both domestic and production waster, with high organic matter content, discharged into the To Lich and Kim Nguu Rivers has degraded the quality of sediments in the river system. The present study shows that sediments are heavily polluted with heavy metals (220 to 475 mg/kg for Cu, 260 to 665 mg/kg for Pb, 250 to 535 mg/kg for Zn, 2.5 to 40 mg/kg for Cd, 505 to 655 mg/kg for Cr, and 48 to 165 mg/kg for Ni). Total heavy metal concentration in the sediment was correlated with organic matter content for Cu, Pb and Ni while no correlation was found for Cd, Zn and Cr. The heavy metals were bound with sediment particles through phases such as exchangeable, carbonate, oxide, organic matter and residual. The percentage of each phase was different among metal types; the organic matter and the oxide were predominant for the group of Cu, Pb and Ni and the group of Zn and Cd, respectively, and each phase was almost equal for Cr. The EDTA caused high heavy metal leachability compared to water, acetic acid and nitric acid. Average potential leachability decreased in the order: Cd > Ni > Cr > Cu = Zn > Pb.

Keywords: Heavy metal, sediment, organic matter, selective sequential extraction, leachability

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1. INTRODUCTION

Heavy metal contaminated sediment is still an unresolved environmental problem. In recent years, there has been an increasing awareness of the importance role of suspended sediment in the transport of number of point- and diffuse-source pollutants, including metals and organic matter. Most of the contaminants are absorbed on suspended particle by flocculation and sedimentation (Gibbs, 1977). Sato et al. (2006) found that suspended particles could accumulate metals from water as effectively as biogenic particles. After particle deposition, trace metals are regenerated into water under anaerobic conditions.

In comparison between suspended solids in the surface water and setting particle near the bottom in the wool pool, metal concentrations were lower for suspended solids in the surface water. Settled sediment has to be regularly removed to maintain the hydraulic and technical function of rivers, canals, reservoirs and harbors. When dredged sediment comes into contact with air, chemical and microbial oxidation processes caused acidification, the heavy metals becomes partly soluble, and the material poses an environmental risk. Organic matter in the sediments has been identified as the main component which plays a significant role in the control and transport of heavy metal concentration (Gaiero et al. 1997). Organic matter exists as dissolved and suspended forms and on the bottom sediments. The functional groups of the organic matter interact with heavy metals (Mulligan and Yong, 2005). And also, Carter et al. (2005) showed that organic fractions were the most significant for absorption of metals by sediment. Both the concentrations and speciation of sediment-associated metals exhibited substantial temporal variation. Such variation reflected the accumulation of metals and organic matter on the river bed during the low flows.

Hanoi has experienced a rapid economical growth and urban expansion in the last couple of decades. However, appropriate city planning and wastewater management for both industry and household have not been done, which caused various environmental problems including the heavy metal pollution of surface water and sediment in rivers and lakes (Environmental Information Office, Hanoi, Vietnam, 2001). There are various environmental regulations and standards in Vietnam, but the implementation of these is lacking. In Hanoi City there are a great number of industries which can be the source of pollution: 274 enterprises and factories, 540 service establishments, 450 production cooperations and 3,350 production establishments. Most of them are concentrated in Thuong Dinh industrial zone, Van Dien and Hai Ba Trung areas and some are located in residential areas (Environmental Information Office, Hanoi, Vietnam, 2001). Most manufacturers were established in the 1950s with assistance from China and the former Soviet Union. The plants are old and are not equipped with appropriate wastewater treatment facilities. Exhaust emissions from motor vehicles are also a major source of pollutants.
There are two rivers in Hanoi City, the To Lich and Kim Nguu Rivers, which are the main sources of irrigation water for suburban agricultural land and feed water sources of fish framing pond. Industrial wastewater, including both domestic and production waster, with high organic matter content, discharged into the rivers has degraded the quality of sediments in the river system. This has affected not only farming and fish breeding, but also the health of general public in surrounding areas (Environmental Information Office, Hanoi, Vietnam, 2001). Study from Ho and Egashira (2000) only showed that the sediment were polluted with heavy metals, but did not mention about related factors to retain heavy metal in the sediment. In the present paper, firstly the chemical properties of river sediment including heavy metal concentration are presented. Secondly, the correlation between organic matter and heavy metal concentrations is evaluated to focus the role of organic matter in the sediment. Finally, the mobility of heavy metals in the sediment has been assessed based on selective sequential extraction and leaching tests.

1.1 Brief Description of the Sampling Site Area

Figure 1 shows the location of the To Lich and Kim Nguu Rivers, factories and sampling sites. The To Lich River with 17 km in length originating in West Lake flows through Thuong Dinh industrial zone to Van Dien, joining to the Kim Nguu River. Industrial and non-industrial urban wastewater flowing into the To Lich River amounts to 290,000 m$^3$/day which accounts for two-thirds of the wastewater generated in the city. The industry that discharges wastewater to the two rivers includes 33 plants, and the major ones are the plants for rubber, tobacco, plastic and a soap (table 1), and wastewater from these plants is discharged without appropriate treatments. Irrigation water from the To Lich River is supplied to 1,361 hectares of agricultural land in Yen Hoa, Lang Ha, Nhan Chinh Communes (Cau Giay District), My Dinh Commune (Tứ Liêm District), Thanh Liet Commune (Thanh Xuan District) and Dai Kim Commune (Thanh Tri District) (Environmental Information Office, Hanoi, Vietnam, 2001).

The Kim Nguu River with 11 km length also flows through the densely populated area of Hanoi City. Wastewater from this area with 6 km$^2$, which amounts to 139,000 m$^3$/day and one-third of the wastewater generated in the city, flows into this river. The main industries that discharge wastewater are related to textile, leather, and mechanical engineering (Table 1). Irrigation water from the Kim Nguu River covers the agricultural land in the Trần Phú Commune (Hai Ba Trưng District) and Yen So, Tư Hiep, Tam Hiep and Lien Minh Communes (Thanh Tri District) (Environmental Information Office, Hanoi, Vietnam, 2001).
2. MATERIALS AND METHODS

2.1 Materials and Field Sampling

Sampling in the filed was conducted on December 3 to 6 of 2005. Sediment samples were collected from the surface zone of 0 to 20 cm depth at 6 submerged sites, and 2 from the zone of 0 to 90 cm depth at 2 sites exposed to the air (Fig. 1 and Table 1). The samples were air-dried, ground, passed through a 1-mm sieve, and preserved in...
Table 1. Location of sampling sites, the type of industry and the volume of wastewater

<table>
<thead>
<tr>
<th>Location</th>
<th>Type of industry</th>
<th>Volume of wastewater (m$^3$ day$^{-1}$)</th>
<th>Type of industry</th>
<th>Number in Fig.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Leather factory</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Beer manufactory</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Food and candy factory</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Mechanical</td>
<td>4,907</td>
<td>Mechanical company</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Construction</td>
<td>54</td>
<td>Rubber company</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Textile and shoes</td>
<td>1,015</td>
<td>Soap company</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Foodstuff and tobacco</td>
<td>22,114</td>
<td>Tobacco company</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>other</td>
<td>95</td>
<td>Glass company</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>28,165</strong></td>
<td>Footwear factory</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Plastic factory</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Painting company</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Mechanical</td>
<td>100</td>
<td>Phosphates factory</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Construction</td>
<td>329</td>
<td>Battery factory</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Office</td>
<td>1,003</td>
<td>Mechanical factory</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>1,432</strong></td>
<td>Van Dien cemetery</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>Candy factory</td>
<td>296</td>
<td>Soldering stick factory</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Beer factory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Food factory</td>
<td>18,243</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Leather factory</td>
<td>750</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Textile factory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lock factory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>2,106</strong></td>
<td>Mechanical engineering factory</td>
<td>23</td>
</tr>
</tbody>
</table>

*Sources of information: Environmental Information Office, Hanoi, Vietnam (2001)*
plastic bottles at room temperature.

2.2 Methodology

2.2.1 Chemical and Physical Properties of Sediment

The pH was measured using the soil suspension with soil-to-water ratio of 1:2.5. The organic carbon was determined by Tyurin method, and the organic matter content was calculated by multiplying by the coefficient of 1.724 (Committee of Soil standard methods for Analyses and Measurement, 1986). Cation exchange capacity (CEC) was measured by the method proposed by Muramoto et al. (1992). In the particle-size analysis, 10 g of an air-dried sample was treated with 7% H$_2$O$_2$ to remove organic matter, dispersed by ultrasonic vibration (tank-type; 38 kHz, 250W), and deflocculated by adjusting pH to 10 with addition of 1M NaOH. After sedimentation for a fixed period of time, the clay fraction (<2µm) was siphoned out. With repetition of sonification (50T)-sedimentation-siphoning with intermittent pH adjustment, the whole clay fraction was separated. The silt fraction (2-20µm) was separated by repeated sedimentation and siphoning. The sand (20-200µm) and coarse sand (200-2000µm) fractions were separated by wet sieving. After oven-drying at 105°C, each fraction was weighed to calculate the particle size distribution of a soil.

For total heavy metal concentration, one g of air-dried sediment sample was digested with 5 ml of concentrated HNO$_3$. The mixture was brought to a slow boil by heating the flask at 96°C on a hot plate for an hour. After the mixture was boiled down to about 2ml, the additional 5ml of concentrated HNO$_3$ was added. A reflux cap was placed onto the flask, and the mixture was boiled for approximately 2h. The solution was transferred into 50ml volumetric flask and made up to the mark with distilled water after cooling. The solution was analyzed for Cd, Cr, Cu, Ni, Pb and Zn by atomic absorption spectrometry (SOLAAR m, Nippon Jarrel-ash Co., Ltd., Japan). The determination was made in duplicate and the relative deviation of the duplicate values was usually less than 5%.

2.2.2 Selective Sequential Extraction

The basic utility of selective sequential extraction (SSE) is its use of appropriate reagents to release different heavy metal fractions from soil solids. The SSE is used to investigate partitioning of particulate trace metals and to evaluate their potential mobility. Extraction methods have been adopted from Tessier et al. (1979):

+ Water soluble fraction: One g of air dried sediment sample is extracted with 8 ml of distilled water at room temperature for 1 h with continuous agitation (1000HP Titan Agitator), shaking 1 h
+ Exchangeable fraction: The residual from water soluble fraction is extracted with 8 ml of 1M KNO$_3$ for 1 h at room temperature with continuous agitation.
+ Carbonate-bound fraction: The residual from exchangeable fraction is extracted with 8 ml of 1M \( \text{CH}_3\text{COONa} \) adjusted to pH 5.0 with \( \text{CH}_3\text{COOH} \) for 4 h with continuous agitation.

+ Oxide-bound fraction: The residual from carbonate-bound fraction is extracted with 20 ml of 0.04M hydroxylamine hydrochloride \( \text{NH}_3\text{OH-HCl} \) in 25% (v/v) \( \text{CH}_3\text{COOH} \) heated to 96 ± 3°C with occasional agitation for 6 h.

+ Organic-bound fraction: The residual from oxide-bound fraction is extracted with 3 ml of 0.02M \( \text{HNO}_3 \) and 5 ml of 30% \( \text{H}_2\text{O}_2 \) (adjusted pH 2 with \( \text{HNO}_3 \)). The mixed is heated to 85 ± 2°C for 2 h with occasional agitation. A second 3 ml of aliquot of 30% \( \text{H}_2\text{O}_2 \) (pH 2 with \( \text{HNO}_3 \)) is added and the mixture is heated again to 85°C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2M \( \text{CH}_3\text{OONH}_4 \) in 20% (v/v) \( \text{HNO}_3 \) is added and the mixture is diluted to 20ml and agitated continuously for 30 min.

+ Residual fraction: The residual from organic-bound fraction is digested with 5 ml of concentrated \( \text{HNO}_3 \). The mixed is heated to 96 ± 3°C for 1 h with occasional agitation. An additional 5 ml of concentrated \( \text{HNO}_3 \) was added and the mixture is heated again 96 ± 3°C to for more 2 h with intermittent agitation.

Residues were separated from the supernatant by 30 min centrifugation at 10,000 rpm. The residue was washed with 8 ml of water followed by hand shaking and then followed by 30 min centrifugation (Kubota-KN 70) before the next extraction. Metal content of six fractions in the filtered solution was determined by atomic absorption spectrometry (SOLAAR m, Nippon Jarrel-Ash Co., Ltd., Japan). The determination was made in duplicate and the relative deviation of the duplicate values was usually less than 5%.

2.2.3 Batch leaching test

Batch leaching tests (USEPA, 1987) were used to assess the leachability of heavy metals in the sediment samples. The leaching solutions used were distilled water (pH 5.5), nitric acid (\( \text{HNO}_3 \)) at pH 4, acetic acid (\( \text{CH}_3\text{COOH} \)) at pH 4 and 0.01M ethylene diamino tetra acid (EDTA). The distilled water and acid were used as leaching solutions to simulated normal precipitation and acid rain conditions. Extraction at pH 4 has been chosen to simulate the most adverse exiting environmental conditions likely to be encountered in soils and sediments (Singh et al. 2000). EDTA is the most effective and popular reagent because it is strong, recoverable and relatively chelating agent of low biodegradability that has potential for heavy metal leaching (Wu et al. 2004). Two g of the air-dried sediment sample and 20 ml of the respective leaching solutions above were placed in a 50 ml polypropylene centrifuge tubes. Duplicate samples were prepared for all tests. The samples were shaken continuously at 30 rpm on a mechanical shaker for 24 h, and then centrifuged.
at 3500 rpm for 15 minutes. For each sample, the supernatant was analyzed for Cd, Cr, Cu, Ni, Pb and Zn using an atomic adsorption spectrophotometer (SOLAAR m, Nippon Jarrel-Ash Co., Ltd., Japan). The determination was made in duplicate and the relative deviation of the duplicate values was usually less than 5%.

3. RESULTS AND DISCUSSION

3.1 Sediment Quality

The wastewater of 31,703 m³ per day, is generated by various types of industrial and urban activity, including 28,165 m³ from Thuong Dinh industry zone, 1,432 m³ from Van Dien area and 2,106 m³ from Hai Ba Trung industry zone and is discharged into the To Lich and Kim Nguu Rivers (Environmental Information Office, Hanoi, Vietnam, 2001) (Table 1). Effluents from these industrial zones, containing high levels of organic wastes and various toxic substances such as cuprous salt, chrome salt and cyanides, have degraded the water and sediment quality of this river system including biological, chemical and physical properties (Environmental Information Office, Hanoi, Vietnam, 2001).

The chemical and physical properties of the sediment samples are shown in Table 2. The pH was in the range of 7.10 to 7.80. The organic matter content varied from 3.36 to 7.97%. The highest organic matter content in SD 12 suggests the inflow of organic wastes from the factories of food, candy, and beer, open markets, and residences (Fig. 1). The cation exchange capacity (CEC) ranged between 9.26 and 20.32 cmol/kg. The highest value of CEC in SD 12 can be attributed to the high organic matter content.

All the sediment samples have relatively low clay content, ranging between 3.3 and 10.3%. The predominant fraction was silt for the samples, SD 6, 7, 8, and 9 while it was fine sand for other samples.

The total heavy metal concentrations varied considerably among the samples: 220 to 475 mg/kg for Cu, 260 to 665 mg/kg for Pb, 250 to 535 mg/kg for Zn, 2.5 to 40 mg/kg for Cd, 505 to 655 mg/kg for Cr, and 48 to 165 mg/kg for Ni. The metal concentrations of sediments in the To Lich and Kim Nguu Rivers were also determined by Ho and Egashira (2000). The total metal concentrations in Table 2 were almost the same as their finding, for Ni and Cd while slightly lower for Zn and higher for Cu, Cr and Pb than theirs. In comparison with the maximum permissible level for crop growth, Cr and Cu exhibited the highest pollution where the metal concentrations exceeded the permissible level for all the samples. The Pb and Cd exceeded the permissible level for nine to ten samples while Zn and Ni were below the permissible level in seven to eight samples.
Table 2. Chemical and physical properties of sediments

<table>
<thead>
<tr>
<th>Location</th>
<th>No</th>
<th>Depth (cm)</th>
<th>pH (H₂O)</th>
<th>Organic matter (%)</th>
<th>CEC (cmol, kg⁻¹)</th>
<th>Particle size distribution (%)</th>
<th>Total heavy metal concentration (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Clay (&lt;2 µm)</td>
<td>Silt (2-20 µm)</td>
</tr>
<tr>
<td>SD 1</td>
<td>1</td>
<td>0-30</td>
<td>7.58</td>
<td>4.13</td>
<td>10.5</td>
<td>4.3</td>
<td>24.3</td>
</tr>
<tr>
<td>SD 2</td>
<td>2</td>
<td>30-60</td>
<td>7.71</td>
<td>4.28</td>
<td>11.0</td>
<td>4.0</td>
<td>24.0</td>
</tr>
<tr>
<td>SD 3</td>
<td>3</td>
<td>60-90</td>
<td>7.83</td>
<td>4.45</td>
<td>12.5</td>
<td>4.3</td>
<td>24.3</td>
</tr>
<tr>
<td>SD 4</td>
<td>4</td>
<td>0-20</td>
<td>7.56</td>
<td>6.55</td>
<td>10.9</td>
<td>3.3</td>
<td>25.0</td>
</tr>
<tr>
<td>SD 5</td>
<td>5</td>
<td>0-20</td>
<td>7.45</td>
<td>5.60</td>
<td>12.9</td>
<td>4.0</td>
<td>35.3</td>
</tr>
<tr>
<td>SD 6</td>
<td>6</td>
<td>0-20</td>
<td>7.80</td>
<td>3.54</td>
<td>10.6</td>
<td>7.3</td>
<td>57.3</td>
</tr>
<tr>
<td>SD 7</td>
<td>7</td>
<td>0-30</td>
<td>7.26</td>
<td>3.54</td>
<td>9.5</td>
<td>7.3</td>
<td>53.3</td>
</tr>
<tr>
<td>SD 8</td>
<td>8</td>
<td>30-60</td>
<td>7.26</td>
<td>3.36</td>
<td>9.7</td>
<td>8.5</td>
<td>54.2</td>
</tr>
<tr>
<td>SD 9</td>
<td>9</td>
<td>60-90</td>
<td>7.25</td>
<td>3.84</td>
<td>9.3</td>
<td>10.3</td>
<td>59.0</td>
</tr>
<tr>
<td>SD 10</td>
<td>10</td>
<td>0-20</td>
<td>7.45</td>
<td>4.54</td>
<td>10.5</td>
<td>5.7</td>
<td>25.3</td>
</tr>
<tr>
<td>SD 11</td>
<td>11</td>
<td>0-20</td>
<td>7.14</td>
<td>4.94</td>
<td>12.8</td>
<td>4.3</td>
<td>19.8</td>
</tr>
<tr>
<td>SD 12</td>
<td>12</td>
<td>0-20</td>
<td>7.17</td>
<td>7.97</td>
<td>20.3</td>
<td>5.0</td>
<td>19.3</td>
</tr>
</tbody>
</table>

*ML*: Maximum permissible concentrations of potentially toxic heavy for crop after application of sewage sludge (Steve, 1994)
3.2 Correlation between Organic Matter and Heavy Metal Concentration in Sediment

Fine particles are more capable of adsorbing heavy metals than coarser fractions. There are two main reasons for this: fine particles have a greater surface area, which increases their metal scavenging and absorption capacity, and; greater concentrations of metal adsorbing/binding organic matter and Fe and Mn oxyhydroxides tend to be present in the fine fraction (Kralik, 1999). Though clay fraction percentage in the sediment samples was very small, organic matter content was high in all samples. Hence, assuming that heavy metals are mostly retained by organic matter in the sediment, the correlation between heavy metal concentration and organic matter content in the sediments was determined (Fig. 2). Positive correlations exist between the two parameters for Cu, Pb and Ni while no correlations were found for Cd, Zn and Cr (not shown here). Similar results have been reported by others. Dilek et al. (2001) indicated that heavy metal concentration in sediment was correlated with the organic carbon content of samples rather than with the depth of samples. Senastien et al. (2000) asserted that the organic matter is the most important factor affecting both dissolved and total heavy metals in the sediment.

Fukue et al. (2006) stated that high concentration of heavy metal in sediments is probably due to the high organic content resulting from humus. There is an evidence to suggest that the major functional group of the humid acid with which the metal cations interact is carboxyl group. Humid substances have high affinity with copper, resulting in the formation of stable complexes (Dahrazma and Mulligan, 2006). The mechanisms proposed for the immobilization and consequent reduction in the phytoavailability of metals by organic matter include the enhanced metal adsorption through increased surface charge, increase in the formation of organic and inorganic metal complexes, the precipitation of metals, and the reduction of metals from mobile form with higher valence to immobile form with lower valence (Bolan and Duraisamy, 2003). The complexation of metals with organic ligands is one of the mechanisms that control the availability and mobility of metals. Kamon et al. (2006) showed that heavy metal solubility in marine sediment is enhanced as dissolved organic carbon increases. The formation of soluble organo-metal complexes increases the availability and mobility of trace metals. On the other hand, the formation of metal complexes with solid-phase organics may increase the partitioning of metal toward the solid-phase. Thus the organic matter is an important factor that controls the retention of trace metals by soil (Sudan et al. 1997).

3.3 Distribution of Heavy Metal in Sediment Fractions

The mobility and bioavailability of heavy metals in sediments depend on how the metals are associated with the components of the sediment, and the
Figure 2. Correlation between organic matter content and total heavy metal concentration in sediments (Correlation coefficients are significant at 1% level for Cu, Pb, Ni, Cd and Cr and significant at 5% level for Zn.
measure of mobility of metals serves to predict the fate of heavy metals in the sediment. Heavy metals are bound to the solid components of the sediment through phases such as exchangeable, carbonate, oxides and hydroxides, and organics. The selective sequential extraction of heavy metals provides the detailed insight on how the metals are associated with the components of the sediment.

The sediment samples in Table 2 were analyzed using the selective sequential extraction method, and the concentration of heavy metals associated with the components of the sediment through the phases mentioned above was measured. Figure 3 presents the sequentially fractionated heavy metal concentration for the sediments in all sampling sites. For Cd, the oxide fraction was predominant, ranging from 0.63 to 23.90 mg/kg, followed by the organic matter and residual, carbonate, exchangeable and water soluble fractions. Cr was retained almost equally by all fractions; Cr is the only heavy metal present in the sediment as anion \((\text{Cr}_2\text{O}_7^{2-})\), which may explain why Cr behaved differently from other heavy metals. For Cu, the fraction associated with organic matter exhibited the highest percentage with a range of 142.32 to 365.21 mg/kg. Tessier et al. (1979) indicated that Cu exhibits the highest stability constants for most ligands among the heavy metals considered. Based on this, Ho and Egashira (2000) suggested that the high affinity of organic ligands with heavy metals makes Cu in river sediments more stable. In addition, organic compounds under a reduced condition may be more active to bind with Cu (Tessier et al. 1979). Thus the organic matter plays an important role in the immobilization of Cu. The other fractions associated with Cu were small in percentage in similar to the results obtained by Ho and Egashira (2000). The Pb and Ni, in similar to Cu, were concentrated in the organic matter fraction, ranging from 161.1 to 434.3 mg/kg for Pb and from 25.8 to 98.2 mg/kg for Ni. The oxide fraction was second in proportion for Pb and Ni, followed by the residual, carbonate, exchangeable and water soluble. Ho and Egashira (2000) indicated that Pb and Ni in the sediment of the To Lich and Kim Nguu Rivers were mostly present in oxide fractions. Dahrazma and Mulligan (2006) showed that Ni in the sediment of Lachine Canal in Canada was concentrated in residual fractions. The highest percentage for Zn was found in the oxide fraction, ranging between 146.2 to 346.23 mg/kg. The association of Zn with each fraction decreased in the order of oxide, organic matter, residual, carbonate, exchangeable and water soluble. These results agree with those observed by Ho and Egashira (2000). Ho and Egashira (2000) also indicated that mobilized Zn was adsorbed on Mn, Fe, and Al hydroxides. Dahrazma and Mulligan (2006) showed that more than 60% of Zn in the sediment was sorbed as oxide fraction.
Figure 3. Concentration of heavy metals extracted via selective sequential extraction from sediments at all sampling sites.
3.4 Leachability and Mobility of Heavy Metals in the Sediments

The potential release of heavy metals from the sediment due to changes in water and sediment environment was assessed using the bath leaching tests. Weak acid and strong complexant solutions are commonly used to determine trace-metal mobility in sediment (Sahuquillo et al. 2003). In our tests, nitric acid (pH 4) and acetic acid (pH 4), and 0.01M EDTA were used as the weak acid and a complexing agent, respectively. For the assessment of heavy metal release from the sediment samples, the repeated washings (5 times) of the samples with about solutions based on the bath leaching test were employed. Figure 4 shows the change in the leached metal concentration with the number of washing for the total 5 times leaching of representing sediment sample SD1. The leached metal concentration of all metals increased substantially with increasing the number of washing for all solutions. The leached metal concentration for five washings was in the order: Cr > Ni > Pb > Cu > Zn > Cd for the water and acid treatments and in the order Zn > Cr > Cu > Ni > Pb > Cd for the EDTA treatment. The EDTA treatment gave higher leached metal concentration than the water and acid treatments. After five washings, the leached metal concentration reached almost a plateau for Cd, Cu, Pb and Ni while still tended to increase for Cr and Zn. The leaching tests by repeated washing were also conducted on the sediment samples other than SD1, and similar results were obtained (not shown here).

The leached heavy metal concentration thus determined for all sediment samples were plotted against the total metal concentration for respective leaching solutions. The treatments with water, nitric acid, and acetic acid exhibited similar patterns; for most metals leached metal concentration was almost constant for the change in the total metal concentration. The EDTA treatment gave higher leached concentrations than to the treatments with other solutions.

The ratio of the leached metal concentration to the total metal concentration in Fig. 5 could be a useful index for the leachability of heavy metals in the sediments. The ratio was obtained for the plotted data of the respective heavy metals, and the average of the ratio obtained was calculated. Figure 6 shows the average of the ratio for the respective heavy metals and leaching solutions. The ratio decreased in the order: Cd > Ni > Cr > Cu = Zn > Pb for the treatments with water, nitric acid and acetic acid and in the order: Cd > Ni > Zn > Cu =Cr > Pb for the EDTA treatment.

Such difference in the metal leachability would be related to how metals are associated with the fractions of the sediments (Fig. 3). The Cd with the highest leachability would be released mostly from the oxide-bound fraction as a large proportion of Cd is associated with oxide fraction. The low leachability for Cu and Pb would be attributed to a high proportion of organic fraction for these metals (Fig. 3), since Cu and Pb are capable of forming
Figure 4. Changes in the concentration of heavy metals leached by repeated washings with deionized water, nitric acid, acetic acid and EDTA solutions.
complexes with organic matter and these complexes remain stable even below pH 3 (Brummer, 1986; Lievens, 1991).

The EDTA treatment gave higher leachability than other treatments for all heavy metals (Fig. 5 and Fig. 6). This can be explained by the fact that EDTA extracts organically-bound, oxide-bound and carbonate-bound fractions of metals in the sediments. The ability of EDTA to bind metal ions in extremely stable complexes can be utilized not only for extraction of sorbed ions, but for the dissolution of insoluble metal compound as well (Palma and Ferratelli, 2005). Wu et al. (2004) found that EDTA chelates with heavy metals and enhances the mobility of soil metals in the long term.

As described above, the heavy metal leaching by repeated washings with water, acid and EDTA solutions is capable of releasing metals retained through
exchangeable, carbonate, oxide and organic phases. In order to examine the extent of heavy metal leaching from these phases, the concentration of leached metals with different solutions were compared with the sequentially fractionated heavy metal concentration (Fig. 3) in Fig. 7. The figure represents the average of heavy metal concentrations for all sediment samples. For the water and acid treatments, Cd, Cu, Pb and Ni were released from the exchangeable and carbonate fractions and partly from the oxide fraction, Zn was fully from the exchangeable fraction and partly from the carbonate fraction, and Cr the leaching test results, on the other hand, indicate that a great proportion of heavy metals remain in the sediment solids (Fig. 6), and carbonate, oxide, organic and residual fractions function to retain the heavy metals, and above all the organic matter plays an importance role in retaining Cu, Ni and Pb (Fig. 7). Sediments in the To- Lich and Kim- Nguu Rivers are the source of suspended solids in water phase. Water from these rivers, extremely high suspended solid concentration (Huong et al. 2008), is irrigated to the suburban agricultural land in Hanoi. Through irrigation, the suspended solids retaining heavy metals are transported to the agricultural field and become a part of agricultural soil.

Figure 6. Average percentage of heavy metals leached with deionized water, and nitric acid, acetic acid and EDTA solutions. Variation in the percentage of leached metals is also indicated.
Figure 7. Comparison between the concentrations of metals leached with different solutions and sequentially fractionated metal concentration.
4. SUMMARY AND CONCLUSIONS

The conclusions drawn from this study can be summarized as follows:

1. Sediments in the To Lich and Kim Nguu Rivers are heavily polluted with Pb, Cu, Zn, Cr, Cd and Ni. In comparison with the maximum permissible level for crop growth, most of heavy metals exceeded the permissible level.

2. The total heavy metal concentration in the sediment was correlated with organic matter content for Cu, Pb and Ni while no correlation was found for Cd, Zn and Cr.

3. The percentage of heavy metals retained by each fraction in the sediment was different according to the metal type: different from metal to metal Cu, Pb and Ni, and Zn and Cd were retained predominantly by the organic matter and the oxide, respectively, while Cr was retained almost equally by all fractions.

4. The EDTA caused a high heavy metal extractability compared to water, acetic acid and nitric acid. Average potential leachability decreased in the order: Cd > Ni > Cr > Cu = Zn > Pb. To reduce the pollutants discharged from plants, countermeasures by the government and the technological improvement of wastewater treatment in manufacturing processes are needed. In these cases, EDTA should be used to remove or minimize heavy metals from contaminated sediments.

5. REFERENCES


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