Organic matter composition variability in road sediment and its role in binding heavy metals

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Key Words: Road sediment, organic matter, heavy metals

ABSTRACT

Organic matter is one of the most important factors in heavy metals mobility in soil and sediment. This study investigated the organic matter composition and metallic elements in the road sediment particles of four sizes < 75 µm, 75 to 180, 180 to 800 µm and 800 to 2000 µm collected from fine land-use types in Ulsan, which is the largest industrial city, in South Korea. The land use types include a national-scale industrial complex, industrial vicinity, a heavy trafficked area, as well as residential and rural areas. Organic matter composition using a fluorescence technique coupled with fluorescence regional integration revealed variation in specific organic matter in road sediment fractions. The concentrations of metals were high in the finer fractions. The relationship between organic matter and heavy metals was investigated by correlating specific organic matter and individual heavy metal species. Among the metals measured, Zn showed positive correlation with aromatic protein type, humic type and microbial by-products and Cd showed negative correlation with fulvic acid. The result showed that the nature of specific organic matter varies with particle sizes and its binding strength may result in accumulation of specific metals.

INTRODUCTION

Road sediment has received much attention over the last few decades due to a wide range of organic and inorganic pollutants and potential health risk to human and the environment [1]. Among the pollutants found in road sediment heavy metals have been the subject of much attention over the last few decades due to their prolonged existence and acute and chronic toxicity to human and ecological health [2,3]. Metals are usually non-degradable and become toxic if they exceed their threshold level which poses a threat to biological life [4]. Metals may accumulate in human bodies via direct inhalation, ingestion and dermal contact absorption or via the food chain [5,6] and affect our body in a number of ways [7], or they may act as
of cofactors in other diseases [8]. It has been reported that heavy metal concentrations in urban sediment is not homogeneous in terms of particle size, with finer particles generally containing higher metal concentrations than coarser particles [9-11].

Organic matter derives from plants and animals and their residues. The organic matter associated with soil and sediment is complex chemicals that may range in molecular weight from a few hundred to several thousand Da with potentially different sources, and characteristics [12,13]. It has been reported that organic matter of the finer fraction, such as clay and silt sized fraction, represents more advanced stage of decomposition and consists of less degradable aromatic and aliphatic structures [14,15] whereas the larger particle sizes fraction consist mainly of fresh or slightly decomposed plant material or debris with a higher concentration of easily degradable carbohydrates [13,16]. This suggests that the chemical characteristics of organic matter are also different for different particle sizes.

Adriano et al. [17] reported that the general order of affinity of metal cations complexed by organic matter is Cu > Cd > Fe > Pb > Ni > Co > Mn > Zn. Moreover, organic matter with different functional properties can lead to different binding behavior even with the same heavy metal. This means that a single metal may display different interactive behavior with different organic substances and may attach to the sites where it finds a strong affinity. Boruvka and Drabek [18] found that fulvic acid had stronger binding affinity for heavy metals (Cd, Cu and Zn) than humic acid in polluted soil in Pribram, Czech Republic. It has been reported in the literature [19,20] that the sequence of affinity of soil humic acid to react with selected heavy metals is in the order of Pb > Cu > Cd > Zn > Ca > Mg. Guggenberger et al. [16] observed that Cd had higher binding affinity for hydrophobic fractions than hydrophilic fractions compared to Cu and Cr in an aquatic dissolved organic matter study. A few investigations have investigated the correlation between heavy metals and organic carbons in road sediment [21,22]. However, there has been no study on the chemical variability of organic matter present in road sediment and its role in metal bindings has yet been given little attention.

Fluorescent fingerprinting commonly known as the excitation emission matrix (EEM) method has been widely used to identify the nature of organic matter in water and wastewater [23,24]. EEM fluorescence is an effective tool for analysing organic matter in road sediment, and for differentiating the nature of organic matter and its abundance. However, application of EEM for studying organic matter in road sediment of various sizes has received little attention. This study extends the application of fluorescence spectroscopy to identify the composition of organic matter in sediment particles based on fluorescence regional integration (FRI) [25]. The FRI technique is used to calculate the area of five delimited regions (noted by region I-V). Region I (Ex:Em 200-250:280-330) represents the low molecular weight amino acid type organic matter such as tyrosin. Region II (Ex:Em 200-250:330-380) represents higher molecular weight aromatic amino acids (including heteroatoms) such as tryptophan and oxidizing organic matter (BOD). Region III (Ex:Em 200-250:380-500) represents fulvic acid type substances. Region IV (Ex:Em 250-500:380-500) represents humic type substances. Region V represents the by-products of microorganisms (Ex:Em 250-340:280-380).

In this paper we have focused on the study of heavy metals and organic matter deposited on road sediment particles of various sizes collected from five different land use areas (industrial sites, areas close to industrial sites, heavy traffic areas, urban residential areas and background areas). The aims were to investigate: i) the distribution of five heavy metals Cd, Cu, Ni, Pb and Zn in road sediment particles of various sizes, ii) the abundance and distribution and nature of organic matter in sediment particles of various sizes, and iii) the role of different organic matter in the binding of heavy metals in particles of various sizes.

MATERIALS AND METHODS

1. Sample Collection and Sample Fractionation

Road sediment samples were collected from 12 sampling sites with different land use and traffic activities in Ulsan, South Korea (Fig. 1). Two to three samples were collected from each site for better representation of contamination of that location. The representative samples were collected at least 5 m apart from one another. The 12 sampling sites were broadly categorized into five groups (national-scale industrial complex; industrial vicinity; heavy traffic; residential and background) based on the nature of land-use activities, as shown in Table 1. The samples were collected in late March 2007. This time of year was chosen because in Ulsan there is a dry weather period between late winter and early spring. A vacuum cleaner (LG V-C349T), attached to a sediment collection filter (VPF-300 filter, 15 x 15 x 15 cm filter pack) was used from the road curb over an area of approximately 120 m² from both sides. Several previous studies have used vacuum cleaners to collect road deposited sediments with high efficiency [21,26]. The vacuum cleaner was tested in the laboratory for its efficiency to collect particles. Sediment samples of size < 20, 20-75, 75-180, 180-250 and 250-1000 μm were mixed and placed on a confined floor area (1 m by 2 m) in the laboratory and the vacuum was applied. A vacuum efficiency of 91-95% was recorded. The collected road sediment samples were naturally dried in a conditioned room with a relative humidity of 40 ±
5% and a temperature of 20 ± 1 °C for 7 d [27]. Samples were then placed in a desiccator for 2 d to minimize moisture effects for relative humidity of 50 ± 3%. The dried samples were then fractionated into four different particle sizes (850-2000, 180-850, 180-75 and < 75 µm) using stainless steel mesh sieves under dry conditions with a manual shaking method for 30 min. The fractionated samples were homogenized by

Table 1. Sampling sites, their characteristics and number of samples (n = 34)

<table>
<thead>
<tr>
<th>Group</th>
<th>Area</th>
<th>Specific road site information</th>
<th>Sample notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>National-scale industrial complex (IC)</td>
<td>i) Non-ferrous metal IC, n = 3</td>
<td>NF1, NF2, NF3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ii) Petrochemical IC, n = 3</td>
<td>PC1, PC2, PC3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>iii) Mechanical and shipbuilding IC, n = 3</td>
<td>MS1, MS2, MS3</td>
</tr>
<tr>
<td>2</td>
<td>Industrial vicinity</td>
<td>i) Non-ferrous metal IC vicinity, n = 3</td>
<td>NFVC1, NFVC2, NFVC3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ii) Petrochemical IC vicinity, n = 3</td>
<td>PCVC1, PCVC2, PCVC3</td>
</tr>
<tr>
<td>3</td>
<td>Heavy traffic</td>
<td>i) Traffic roundabout areas, n = 3</td>
<td>RO1, RO2, RO3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ii) Downtown area, n = 3</td>
<td>DT1, DT2, DT3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>iii) Road with high number of heavy duty diesel vehicles, n = 3</td>
<td>DR1, DR2, DR3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>iv) Concrete highway, n = 2</td>
<td>CH1, CH2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>v) Circulation road with high number of gasoline vehicles, n = 3</td>
<td>CR1, CR2, CR3</td>
</tr>
<tr>
<td>4</td>
<td>Residential</td>
<td>i) Typical downtown residential areas, n = 3</td>
<td>RA1, RA2, RA3</td>
</tr>
<tr>
<td>5</td>
<td>Background</td>
<td>i) University campus remote from IC, n = 2</td>
<td>BG1, BG2</td>
</tr>
</tbody>
</table>
repeated, according to the Korean regulations for representative soil samples, and were then stored in a desiccator until further chemical analysis.

2. Heavy Metals Analysis

Approximately 3 g of dry sediment sample were added to 14.4 mL of a mixture of pure nitric acid and hydrochloric acid in 1:3 volume ratios and 15.6 mL of deionized water. The digestion for extraction of heavy metals was carried out in a water bath at 70 °C for 1 h. The extracted solutions were filtered through a glass fiber filter (Advantec 5B). The heavy metals in the filtrate were quantified using Atomic Absorption Spectroscopy (Varian AA 240). Five heavy metals (Cd, Cu, Pb, Zn and Ni) were quantified using standard solutions (Kanto Chemical). The concentrations of these solution standards were verified by Inductively Coupled Plasma Spectroscopy and are traceable to NIST standard reference materials, SRM 3168a. The detection limit of Cd, Cu, Pb, Zn and Ni were 1.5, 1.2, 14, 1.6 and 5.8 µg L⁻¹, respectively. The average extraction efficiency was 85-120% (Cd 82-87%, Cu 97-112%, Pb 88-92%, Zn 104-118%, Ni 89-94%). The heavy metal sample measurement was carried out in triplicate to minimize error and the relative standard deviation of the elements was within the range of 10%. The differences in the measurement of concentration of the heavy metals among triplicate samples were also less than 5%.

3. Contamination Factor and Degree of Contamination

The degree of contamination by heavy metals was calculated by using a modified contamination factor (Cᵢ) to evaluate the contamination of road dust by the analysed heavy metals [28]. The Cᵢ was defined as:

\[ Cᵢ = \frac{Cᵢ_{n-1}}{Cᵢ_n} \]  

where \( Cᵢ_{n-1} \) is the mean content of metal and \( Cᵢ_n \) is the concentration of individual metal at a relatively clean background site.

Hakanson [28] suggested four classes of \( Cᵢ \) to evaluate the metal contamination levels as follows: low \( (Cᵢ < 3) \), moderate \( (1 < Cᵢ < 3, 3 < Cᵢ < 6) \), considerable \( (3 < Cᵢ < 10) \) and very high \( (Cᵢ > 10) \) contamination.

The degree of contamination is the sum of \( Cᵢ \) for all the elements. Abrahim [29] presented a modified and generalized form of Hakanson [28] equation for the calculation of overall degree of contamination as below.

\[ \sum_i Cᵢ = \frac{\sum_i Cᵢ}{5} \]  

In this study, four categories of \( Cᵢ \) were used to evaluate metal contamination levels as follows: low \( (Cᵢ < 5) \), moderate \( (5 < Cᵢ < 10) \), considerable \( (10 < Cᵢ < 20) \), and very high degree of contamination as \( Cᵢ > 20 \). If \( Cᵢ \) values exceed 20, then it is necessary to take immediate countermeasures to reduce heavy metal contamination in the road dust.

4. Organic Analysis

4.1. Total organics analysis

Approximately 1 g from each sediment fraction was heated overnight at 105 °C, reweighed and then ignited in an electric muffle furnace (Sub Kwang Instrument, Korea) at 550 °C for 20 min and cooled in a conditioned desiccator with a relative humidity of 50 ± 3% and a temperature of 20 ± 1°C. Then the cooled dry sediment sample was weighed and the total organic content was measured as ignition loss. The value of loss on ignition at 550 °C was then expressed as the percentage of weight loss after the 105 °C oven drying. Triplicate measurements were carried out in each case and the error was less than 5%.

4.2. Fluorescence data analysis

Approximately 1 g of each sediment fraction sample was treated with NaOH solution (0.1 M, 40 mL) and shaken in a hand to hand shaker for 18 h [30]. The extract was centrifuged at 3,400 rpm for 20 min and then filtered through a glass fiber filter GF/C (1.2 µm, Whatmann USA). The filtrate was analyzed using a spectrophuorometer (Hitachi F4500) with a wavelength range of 200 to 600 nm by increasing the wavelength by 5 nm for both excitation and emission. All slit widths were set to 5 nm. The fluorescence intensity was corrected by blank subtraction and was expressed in quinine sulfate units (QSU), where 10 QSU was equivalent to the 450 nm fluorescence intensity of 10 µg L⁻¹ quinine sulfate solution with an excitation wavelength of 345 nm [31]. A FRI technique was used to quantify the contribution of EEM spectra of the five delimited region shown in Table 2.

Peak volumes and ratios between volumes of the 5 EEM regions were calculated following the equations described previously [25] using 'R' software. The volume of fluorescence intensity (\( \Phi_i \)) of each region 'i' was calculated and normalized 'n' (\( \Phi_i \)) with a multiplication factor (MF) specific to each region 'i' (Eqs. 3 and 4) which is equal to the inverse of the fraction projected excitation-emission area volumes. The cumulative volume 'T' of normalized \( \Phi \) (\( \Phi_i \)) was calculated using Eq. 5. Finally, the total regional volumes were summed and the percentage fluorescence response of each region 'i' (\( P_i = \Phi_i \)) was calculated using Eq. 6.

\[ MF_i = \frac{(\Delta \lambda ex \Delta \lambda em)_i}{(\Delta \lambda ex \Delta \lambda em)_T} \]  

where \( \Delta \lambda ex \) and \( \Delta \lambda em \) are the interval of the excitation and emission wavelength respectively.
Table 2. Representative chemicals in EEM spectra in five excitation:emission regions

<table>
<thead>
<tr>
<th>Region</th>
<th>Chemical composition of organic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>I: λexcitation:emission 200-250:280-330</td>
<td>lower molecular weight tyrosine-like aromatic amino acids</td>
</tr>
<tr>
<td>II: λexcitation:emission 200-250:330-380</td>
<td>low molecular weight aromatic proteins and BOD-type substances</td>
</tr>
<tr>
<td>III: λexcitation:emission 200-250:380-500</td>
<td>fulvic acid type substances</td>
</tr>
<tr>
<td>IV: λexcitation:emission 250-500:380-500</td>
<td>humic acid type substances</td>
</tr>
<tr>
<td>V: λexcitation:emission 250-340:280-380</td>
<td>Large molecular weight peptides and proteins (microbial related by-products)</td>
</tr>
</tbody>
</table>

5. Statistical Analysis

Due to the large variation in concentration of metals and organic in sediment fractions, standardized score data (also called standardized form of data) were used to assess the relationship among metals and also the relationship between metals and specific organics [32]. The standardization was calculated using the following equations:

\[ \Phi_{i,n} = MF_{i} \Phi_{i} \]  

(4)

\[ \Phi_{T,n} = \sum_{i=1}^{n} \Phi_{i,n} \]  

(5)

\[ P_{i,n} = \frac{\Phi_{i,n}}{\Phi_{T,n}} 	imes 100 \]  

(6)

where, \( \bar{x} \) is the mean of the samples and \( \sigma \) is the standard deviation of the samples. The absolute value of \( z \) represents the distance between the raw score and the sample mean in units of the \( \sigma \). Standard score \( z \) is negative when the raw score is below the mean, and positive when above the mean.

RESULTS AND DISCUSSION

1. Particle Size Distribution of Road Sediment

Figure 2 shows an overall particle size distribution of road sediment samples collected from the 12 sampling sites. The finer fraction < 75 \( \mu \)m contributed the least, with 1.3-18.5 wt\%, 75-180 \( \mu \)m fraction contributed 7-20 wt\%, the size range 180-850 \( \mu \)m had the largest mass fraction 38-77 wt\%, followed by 850-2000 \( \mu \)m with 7-51 wt\%. Furumai et al. [33] observed sediment mass around 7.2% < 50 \( \mu \)m, 33.5% in 50-125 \( \mu \)m and 59.3% > 125 \( \mu \)m in road sediment in Winterthur Switzerland. Aryal et al. [34] observed sediment mass in between 7-13% for < 75 \( \mu \)m, 26-33% for 75-150 \( \mu \)m and 54-65% for > 150 \( \mu \)m particles in road sediment in Sydney, Australia.

2. Organic Matter and Its Distribution in the Sediment Fractions

Loss-on-ignition is a current common technique to estimate the organic matter in soil and sediment. Ignition at 550 \(^\circ\)C removes organic matter from soil and sediment [35]. The total organic content in the four sediment fractions measured by loss-on-ignition is shown in Fig. 3. The weight fractions of road sediment with particle sizes of < 75, 75-180, 180-800 and 800-2000 \( \mu \)m were between 44-64, 16-33, 9-20 and 4-12 wt\%, respectively, with mean organic content of % in total road sediment samples. The result showed that the particle size had a significant influence on organic carbon enrichment and accumulation was higher on finer fraction. The finer fraction may provide larger surface areas for deposition or coating of organic substances on their surface as compared to the coarser fraction [36,37]. Fergusson and Ryan [38] estimated the organic matter content of road sediment samples from different cities, ranging from 3.5-18.3% by ignition loss at 500 \(^\circ\)C. Xie et al. [39] reported organic matter level ranges from 1 to 10.1% in the road dust in Liverpool, UK.

Figure 4 shows the EEM spectra of organic substances in the two road sediment in four fractions, divided into five regions (I-V) based on the composition of the organic matter [25]. The EEM spectral pattern showed maximum fluorescence in region III and IV for finer particles (< 75 \( \mu \)m). Moreover, the fluorescence intensity in region III decreased with increase of particle sizes. Therefore these five regions

Fig. 2. Size distribution of road dust in the study areas.
were delimited to quantify relative concentration using the FRI technique [25]. The proportion of total fluorescence (%) for each region is presented in Table 3. There was a significant difference between the distributions of fluorescence intensity among the five regions for sediment particles of different sizes. The EEM spectra were similar for all sediment from all locations (data not shown). The result showed that the humic fraction’s contribution to total fluorescence decreased in all particles whereas fulvic acid’s contribution to fluorescence was relatively similar in all particle sizes. The result (Table 3) shows that finer particles probably contained organic matter in advanced stage of decomposition, such as humic substances, while coarser particles contained only slightly decomposed materials. Observations of higher concentration of less degradable material in fine particles and easily degradable material in coarser fractions have been documented in previous studies [13,15]. The share of the total percentage of organic substances varying between sizes indicates that particle size may play an important role in organic matter accumulation.

3. Heavy Metals in Total and Fractionated Sediment

The total average concentration of heavy metals in road sediment at the 12 sampling sites (n = 34) is shown in Table 4. The heavy metal contents ranged from 0.4 to 21 for Cd, 25 to 204 for Cu, 6 to 58 for Ni, 43 to 343 for Pb and 79 to 326 µg g⁻¹ for Zn. In terms of land-use, the heavy metal concentration decreased in the order of industrial complex > industrial vicinity > heavy traffic > residential > background. Among the industrial and industrial vicinity sites, a non-ferrous metal site was the most polluted. In heavy traffic areas, the concrete cement highway produced the highest concentration of heavy metals and this was comparable to the levels from the industrial vicinity. The residential areas had relatively lower concentrations of heavy metals. The observed concentrations were compared to the literature and found to be within the range of reported values [40-43] as shown in Table 4.

Table 5 shows average heavy metal contents in the four sediment fractions. Among the four fractions, the < 75 µm fraction had the highest metal content and this decreased with increase of particle size. The result shows that finer fractions, despite having a smaller fraction in total (1-18%) contribute a significant amount of heavy metals. This is because smaller sizes of sediment have a relatively large surface area and have higher capacity for attachment of organic matter. The influence of particle size and organic matter on heavy metal content in road sediment has been reported earlier [39,44].
Table 3. Share of total fluorescence (%) of organic matter in 5 regions in road sediment (n = 34) of various sizes based on FRI

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>Tyrosine type (I) (Pmin-max)</th>
<th>Aromatic protein and BOD type (II) (Pmin-max)</th>
<th>Fulvic type (III) (Pmin-max)</th>
<th>Humic type (IV) (Pmin-max)</th>
<th>Microbial by-products type (V) (Pmin-max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 75</td>
<td>2-6</td>
<td>12-23</td>
<td>16-27</td>
<td>27-45</td>
<td>15-29</td>
</tr>
<tr>
<td>75-180</td>
<td>3-8</td>
<td>19-26</td>
<td>17-30</td>
<td>22-34</td>
<td>17-28</td>
</tr>
<tr>
<td>180-850</td>
<td>5-9</td>
<td>21-29</td>
<td>17-32</td>
<td>14-31</td>
<td>18-32</td>
</tr>
<tr>
<td>850-2000</td>
<td>4-11</td>
<td>19-36</td>
<td>13-31</td>
<td>7-28</td>
<td>17-44</td>
</tr>
</tbody>
</table>

Table 4. Concentrations of heavy metals in road dust from this study (n = 34) and other studies

<table>
<thead>
<tr>
<th>Sample site (city)</th>
<th>Concentration of heavy metals (Average ± Standard Deviation), μg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Non-ferrous metal IC (NF)</td>
<td>21 ± 18</td>
</tr>
<tr>
<td>Petrochemical IC (PC)</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>Mechanic/shipbuilding IC (MS)</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td>NF-IC vicinity (VC1)</td>
<td>7.1 ± 1.1</td>
</tr>
<tr>
<td>PC-IC vicinity (VC2)</td>
<td>3.3 ± 0.4</td>
</tr>
<tr>
<td>Traffic roundabout (RO)</td>
<td>1.1 ± 0.6</td>
</tr>
<tr>
<td>Downtown (DT)</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>Diesel vehicle road (DR)</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>Circulation road with high number of gasoline vehicles (CR)</td>
<td>0.8 ± 0.03</td>
</tr>
<tr>
<td>Concrete cement highway (CH)</td>
<td>4.6 ± 0.4</td>
</tr>
<tr>
<td>Residential at downtown (RA)</td>
<td>1.5 ± 1.6</td>
</tr>
<tr>
<td>Background (BG)</td>
<td>0.4 ± 0.07</td>
</tr>
</tbody>
</table>

Table 5. Heavy metal concentrations (μg g⁻¹) in road dust in different fractions

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 75</td>
<td>24 ± 16</td>
<td>243 ± 87</td>
<td>97 ± 43</td>
<td>370 ± 185</td>
<td>149 ± 26</td>
</tr>
<tr>
<td>75-180</td>
<td>18 ± 12</td>
<td>191 ± 69</td>
<td>80 ± 31</td>
<td>300 ± 208</td>
<td>140 ± 26</td>
</tr>
<tr>
<td>180-850</td>
<td>6 ± 5</td>
<td>132 ± 43</td>
<td>52 ± 30</td>
<td>209 ± 201</td>
<td>128 ± 28</td>
</tr>
<tr>
<td>850-2000</td>
<td>3 ± 3</td>
<td>97 ± 63</td>
<td>30 ± 21</td>
<td>129 ± 124</td>
<td>117 ± 27</td>
</tr>
</tbody>
</table>

4. \( C_f \) and \( \alpha C_s \)

The results show the \( \alpha C_s \) by individual metal and in four road sediment fractions based on the \( C_f \) and \( \alpha C_s \), as suggested by Hakanson [28] and Abrahim [29]. The \( \alpha C_s \) for four sediment sizes < 75, 75-180, 180-850 and 850-2000 μm based on background soil (0.3-1.0) were 1.8-13.3, 1.6-16.3, 1.9-15.5 and 1.4-14.2, respectively. The similar ranges in all sizes indicate that the sediments were contaminated in a similar fashion and were less dependent on particle sizes. Of the five areas, the non-ferrous industrial site was the most contaminated with \( C_f \) in the range of 10.8-15.3. This is followed by cemented traffic road 5.3-7.1 and non-ferrous industrial vicinity 4.4-8.4.

5. Relationship among Heavy Metals and with Organic Matter
The interrelationships between the tested heavy metals were estimated by measuring the correlation coefficient \( r \), as shown in Table 6. The relationship was considered to be good if \( r > 0.4 \). All heavy metals showed a good relationship with one another in three fractions (< 75, 75-180 and 180-850 \( \mu \)m), except for Zn. A similar relationship between Cd and Pb was observed by Nadal et al. [45] in an industrialized/petrochemical area in Catalonia, Spain. A few previous studies have shown an exceptional behavior of Zn in urban area [46,47].

The relationship between the heavy metals and the specific organic matter was investigated statistically by comparing \( r \) obtained from standardized score data (Table 7). Among the metals, Zn showed relatively good positive correlation with aromatic protein type (II), humic type (IV) and microbial by-products (V) for fractions up to 850 \( \mu \)m. Cadmium showed negative correlation with fulvic acid in all fractions up to 850 \( \mu \)m. Other metals did not show any correlation trend. The relationships between Zn and specific organic or Cd and fulvic acid indicates that the presence of these metals in sediment is influenced by organic matter.

### Table 6. Correlation coefficient (r) among heavy metals

<table>
<thead>
<tr>
<th>Particle size (( \mu )m)</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 850</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180-850</td>
<td>0.461</td>
<td>0.537</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75-180</td>
<td>0.417</td>
<td>0.567</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 75</td>
<td>0.376</td>
<td>0.565</td>
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<td>0.862</td>
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<td>0.626</td>
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<tr>
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### CONCLUSIONS

Road sediment collected from the industrial city of Ulsan in Korea was segregated into four fractions, namely < 75, 75 to 180, 180 to 800 and 800 to 2000 \( \mu \)m and analyzed for organic matter and heavy metals. Organic matter analysis showed that organic content decreased with increase of particle size. Organic matter composition showed variation in chemistry in different sizes. The smaller particles (< 75 \( \mu \)m) had more humic type fraction whereas the larger particles had more aromatic protein/BOD/microbial related by-products fraction. The relative contribution (fraction) of fulvic acid type substances was similar in all sizes. The heavy metal distribution in road sediment was higher in industrial areas and close by vicinities and this was followed by high traffic areas. Application of \( C_{\text{so}} \) and modified \( C_{\text{so}} \) with background soil for Cd, Cu, Pb, Zn and Ni showed a moderate \( C_{\text{so}} \) in overall but was high in the non-ferrous industrial site, the cement road area and in the vicinity of the non-ferrous industrial area. Among the metals, Zn showed the least correlation with other metals. Good relationships between aromatic protein type, humic type and microbial by-products and fulvic acid and Cd were observed.

### REFERENCES

1. Luo, H., M. Li, R. Xu, X. Fu, G. Huang and X.
Table 7. Correlation coefficient (r) between heavy metals and specific organic matter

<table>
<thead>
<tr>
<th>Specific organic and region of spectra</th>
<th>Particle size (µm)</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
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<td>Tyrosine type (I)</td>
<td>&gt; 850</td>
<td>-0.128</td>
<td>-0.089</td>
<td>-0.133</td>
<td>-0.359</td>
<td>-0.348</td>
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<td>0.023</td>
<td>0.731</td>
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<td>75-180</td>
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<td>0.404</td>
<td>0.218</td>
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<td>0.557</td>
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<td>-0.119</td>
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<td>Aromatic protein type (II)</td>
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</tbody>
</table>


Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

*Manuscript Received: April 9, 2013 Revision Received: August 26, 2013 and Accepted: October 15, 2013*