Heavy metal speciation in various grain sizes of industrially contaminated street dust using multivariate statistical analysis

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ABSTRACT

A total of 36 street dust samples were collected from the streets of the Organised Industrial District in Kayseri, Turkey. This region includes a total of 818 work places in various industrial areas. The modified BCR (the European Community Bureau of Reference) sequential extraction procedure was applied to evaluate the mobility and bioavailability of trace elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in street dusts of the study area. The BCR was classified into three steps: water/acid soluble fraction, reducible and oxidesal fraction. The remaining residue was dissolved by using aqua regia. The concentrations of the metals in street dust samples were determined by flame atomic absorption spectrometry. Also the effect of the different grain sizes (≤38 m, 38–53 m and 53–74 m) of the 36 street dust samples on the mobility of the metals was investigated using the modified BCR procedure. The mobility sequence based on the sum of the first three phases (for <74 m grain size) was: Cd (71.3)> Cu (48.9)> Pb (42.8)> Cr (42.1)> Ni (41.4)> Zn (40.9)> Co (36.6)>Mn (36.3)> Fe (3.1). No significant difference was observed among metal partitioning for the three particle sizes. Correlation, principal component and cluster analysis were applied to identify probable natural and anthropogenic sources in the region. The principal component analysis results showed that this industrial district was influenced by traffic, industrial activities, airborne emissions and natural sources. The accuracy of the results was checked by analysis of both the BCR-701 certified reference material and by recovery studies in street dust samples.

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1. Introduction

Heavy metals in street dust may originate from anthropogenic sources such as petroleum, diesel and coal combustion, as well as from industrial activities and natural geochemical processes such as weathering (Saeedi et al., 2012). They are often not decomposed by microorganisms, and may become enriched through the food chain and can be harmful to human health (Wang et al., 2012). Heavy metal species and solubilities significantly affect their mobility, bioavailability and toxicity (Zhang et al., 2014).

Street dust often becomes a sink for both industrial and vehicle-generated pollutants (Wang et al., 2012). It is an important environmental indicator of heavy metal contamination from atmospheric deposition. Street dust receives varying inputs of anthropogenic heavy metals from various mobile and stationary sources, such as vehicular traffic (lubricating oil residues, tire dust, brake dust, body rust and tail pipe exhaust), industrial plants, power generation facilities, residential fossil fuel burning and construction (asphalt, concrete and road paint) (Lu et al., 2010; Tokaloğlu and Kartal, 2006). Street dust can be a particular risk to humans due to small particle size and inherent mobility in windy weather conditions leading to the possibility of direct and indirect exposure: direct exposure from dust can occur by inhalation and ingestion while indirect exposure results from contact with exposed skin and outer clothing which in turn can be accidentally ingested (Lu et al., 2010; Cook et al., 2005; Okorie et al., 2012; Abrahams, 2002).

The determination of the total concentrations of metals in samples such as soil, sediment, street dust, and sludge is not sufficient to be able to predict the capacity for mobilisation of these elements (Passos et al., 2010). The toxicity and mobility of heavy metals in soils depend not only on their concentrations, but also on both their associations, and chemical properties, and on some surrounding environmental conditions such as pH, redox potential, and biological action of the roots and the formation of chelates (Guillén et al., 2012). Consequently, there is considerable interest in understanding the association of these elements with the solid phase. Single extractants are usually chosen to evaluate a particular release controlling mechanism such as desorption by increasing salinity or complexing by competing organic agents. Generally, fractions can be isolated more specifically by using sequential extraction schemes (Rauret, 1998). Sequential chemical
extraction is an example of operational speciation. Although time-consuming, the use of sequential extraction provides detailed information on the distribution of the various elements in soils/ sediments, and has implications for metal mobility and bioavailability potential. A series of reagent is applied to the sample which increases the strength of the extraction at each step to dissolve the trace metals present in different sediment phases (Passos et al., 2010; Guillén et al., 2012; Tokaloglu et al., 2000).

Many of the sequential extraction schemes employed are based on the five-stage procedure of Tessier et al. (1979) (Tessier et al., 1979). In the late 1980s, the European Community Bureau of Reference (BCR), now the Standards, Measurements and Testing Program, initiated a project to explore the possibilities of developing a standardized sequential extraction procedure with the goal of producing certified reference materials for metal fractionation (Sutherland and Tack, 2003). Three operationally defined fractions are isolated using the BCR procedure: acid extractable (i.e. bound to carbonates), reducible (bound to Fe/Mn oxides), and oxidisable (bound to organic matter and sulphides). The BCR method is faster and simpler than the other sequential extraction methods, because it consists of three stages (Tokaloglu and Kartal, 2006; Rauret et al., 1999).

Up to now, many studies have been carried out on heavy metal pollution using the BCR sequential extraction method in samples such as soils (Li and Feng, 2012; Tokaloglu and Kartal, 2005; Pueyo et al., 2008), sediments (Passos et al., 2010; Tokaloglu et al., 2000; Nemati et al., 2011; Sundaray et al., 2011; Morillo et al., 2002; Cuong and Obbard, 2006; Dundar et al., 2012), sewage sludge (Nemati et al., 2009), street dusts (Saeedi et al., 2012; Tokaloglu and Kartal, 2006; Lu et al., 2010; Banerjee, 2003; Tokaloglu et al., 2003a; Altundag et al., 2013), fly ash (Smeda and Zyrnicki, 2002; Petit and Rucandio, 1999) and air-borne particulate matter (Dabek-Zlotorzynska et al., 2003).

It is well known that sediment grain size is an important factor controlling entrainment and transport thresholds. Also grain size distribution of street sediment affects metal sorption, mobility, biotic ingestion, and thus bioavailability (Sutherland et al., 2012). Some studies have been focused on heavy metal analyses of road sediments in different grain sizes (Qiang et al., 2015; Wang et al., 2006; Bian and Zhu, 2009). Few data are available for trace metal concentrations in terms of the grain sizes of street sediments by using sequential extraction method (Sutherland, 2003; Xiang et al., 2010). Sutherland et al., (2012) examined loading of Al, Cu, Pb and Zn in individual grain size classes (< 63 m to 1000–2000 m) of road sediment samples by using BCR sequential extraction method (Sutherland et al., 2012). It was found that the < 63 m grain size had the highest loading for these elements for each of the four geochemical fractions. Xiang et al. (2010) investigated total and labile heavy metal concentrations in street dusts with different size ranges from different seasons.

The major objectives of this work are (a) to investigate the effect of different grain sizes (< 38 m, 38–53 m and 53–74 m) on the mobility of the metals by using the modified BCR sequential extraction method in 36 street sediment samples and (b) to assess the potential sources of pollutants using multivariate statistical analyses such as principal component analysis (PCA), and cluster analysis (CA).

PCA with varimax rotation was applied to the data matrix (36 cases × 9 metals) of metal concentrations found by BCR 3-step plus aqua regia sequential extraction procedure. Hierarchical CA was performed using the following settings: Ward’s method was used to form the clusters and squared Euclidean distance was used as the similarity measure. Before CA, the variables were standardised by means of z-scores; then Euclidean distances for similarities in the variables were calculated.

2. Materials and methods

2.1. Area of study

The Organised Industrial District (OID) is the biggest industrial region in Kayseri and in Turkey. It is located about 14 km south of Kayseri. It developed after 1980 and its area covers about 24 km². This region includes 818 work places in the following areas: packaging and plastic (52), dye and chemistry (13), glass products (9), electric-electronic (29), home supplies (46), food (32), construction building materials (32), paper (5), mining (8), machine (55), printing and advertisement (18), metal products (158), furnitures (216), forest products (37), automotive (9), textiles (80) and other (19). In our previous work (Tokaloglu and Kartal, 2006), the number of work places in the region has increased from 509 to 818. In this study we also investigated the effect on heavy metal fractionation of the different grain sizes of 36 street dust samples.

2.2. Sample collection and pre-treatment

Thirty six street dust samples were collected from both sides of the OID streets in June 2012 by sweeping using a plastic brush and were placed in polyethylene plastic bags. Site locations are illustrated in Fig. 1. All the samples were air-dried, ground and sieved through 38, 53 and 74 m sieves. Because the loading of heavy metals in street sediments is adversely related to sediment grain sizes, these grain sizes were used. It is well known that finer grains: (a) adsorb more heavy metals due to their high surface area; (b) comprise a more serious threat to health; (c) are more soluble than coarser ones (Wang et al., 2006; Bian and Zhu, 2009).

2.3. Reagents

All reagents used were of analytical grade (Merck, Germany). Ultrapure water (18.2 MΩ cm) was supplied from a Millipore Milli-Q system. Acetic acid, hydroxyammonium chloride, hydrogen peroxide, and ammonium acetate were used in the sequential extraction procedure. Concentrated HCl and HNO₃ were used for the pseudo total digestion. Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn stock standard solutions (1000 g mL⁻¹) were prepared from their nitrate salts. Working standard solutions of the metals were prepared daily by dilution of their stock solutions. All the plastic and glassware were soaked for 24 h in an acid bath containing 10% (v/v) HNO₃ and then rinsed with ultrapure water.

2.4. Apparatus

Analyses of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in street dust samples were carried out by using a PerkinElmer Analyst 800 model (Waltham, MA, USA) flame atomic absorption spectrometer in an air-acetylene flame. The operating parameters for metals were set as recommended by the manufacturer. A Mettler Toledo 320 pH metre equipped with a combined pH electrode for checking the pH of solutions, a Clifton model shaker with end-over-end shaking, and an Anita ALC PK120 centrifuge were used throughout the work.

2.5. The modified BCR sequential extraction procedure

The extractants used and extraction conditions of the modified BCR sequential extraction procedure are outlined in Table S1. The method was applied to 1.00 g of all air dried street dust samples for each grain size of < 38 m, 38–53 m and 53–74 m. Details of the
A modified BCR extraction procedure can be found elsewhere (Tokalıoğlu and Kartal, 2006; Rauret et al., 1999; Nemati et al., 2009). The extractants obtained from each step of the BCR scheme were firstly evaporated to near dryness and then completed to 5 mL with 1 M HNO₃, except for third step. The final volume for third step is 6 mL. The sample and blank analyses were performed in triplicate throughout all the analysis.

2.6. Statistical analysis

Statistical analyses were performed by SPSS v11.5. Pearson’s correlation coefficient analysis, PCA and CA were used to evaluate the relationship among heavy metals in street sediment samples and to identify their pollution sources.

Pearson’s correlation reflects the degree of linear relationship between two variables (Wang and Jiao, 2014). PCA is a multivariate technique widely used to reduce data and to extract a smaller number of independent factors for analysing the relationships among observed variables (Lu et al., 2010). Data reduction is accomplished by transforming the data into a new set of variables, which are derived from linear combinations of the original variables (Matiatos et al., 2014). Variables and factor loading correlations with absolute values between ±0.75 and ±1.0 are described here as strong; those between ±0.5 and ±0.75 as moderate, and those between ±0.5 and ±0.3 as weak (Bošnjak et al., 2012). The most common PCA type producing more interpretable components, is varimax rotation, which was applied in the current study (Idris, 2008).

CA classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables (Lu et al., 2010). Hierarchical CA (HCA), as the most commonly applied CA method for environmental analysis, looks...
for groups of samples according to their similarities (Idris, 2008). In clustering, the objects are grouped so that ‘similar’ objects fall into the same class. Multivariate statistical techniques (PCA and CA) have been widely applied to environmental samples such as sediments (Passos et al., 2010; Idris, 2008; Danielsson et al., 1999; Tokaloglu and Kartal, 2002a), soil (Guillén et al., 2012; Tokaloglu et al., 2004; Tokaloglu et al., 2003b), dust (Saeedi et al., 2012; Zhang et al., 2014; Tokaloglu and Kartal, 2006; Lu et al., 2010) and water (Zhao et al., 2012; Muhammad et al., 2010; Tokaloglu and Kartal, 2002b).

2.7. Detection limits

The detection limit (DL) was determined for each extraction step of the BCR sequential extraction procedure including the residual phase. Ten analytical blanks were analysed for each step. In calculation of the DLs, the 3s/b equation was taken into consideration, where s is the standard deviation of absorbances of the blank solutions and b is the slope of the calibration graph for each element. DL values (in g mL\(^{-1}\)) changed from 0.005 (F1) to 0.008 (R) for Cd; from 0.009 (F3) to 0.026 (R) for Co; from 0.010 (F2) to 0.026 (R) for Zn.

2.8. Accuracy of the method

To evaluate the accuracy of the method, both a BCR-701 certified sediment reference material analysis and the pseudo total digestion of some samples were conducted. They are as follows.

2.8.1. Pseudo total metal digestion

Aqua regia digestion was used for the determination of the pseudo total metal contents of the street dusts #5, 9, 14, 21, 25 and 33 (< 74 m). One gram of each sample was weighed into a 100 mL beaker. Ten millilitres of aqua regia was added to the beaker. Ten millilitres of aqua regia was added to the beaker. The temperature of the mixture was slowly raised and it was evaporated to near dryness. After that 10 mL of aqua regia was added to the beaker again. The evaporation procedure was repeated. The obtained clear solution was made up to 5 mL with 1 mol L\(^{-1}\) HNO\(_3\). Each sample was analysed in triplicate. The total amount of metals extracted from each step of the sequential extraction of the samples was compared with their pseudo total contents. The recovery values of the metals (see Table S2) changed between 92% and 108% for six street dust samples.

2.8.2. Analysis of certified reference material

The modified BCR sequential extraction procedure was applied for the BCR-701 certified reference material. The obtained results were compared with certified element concentrations of the BCR-701. Table 1 shows that there is a good agreement between the certified and obtained metal concentrations. The recovery values changed between 95% and 115%.

3. Results and discussion

3.1. Heavy metal concentration

The mean concentrations and standard deviations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in each extraction step of the BCR procedure for the different grain sizes (<38 m, 38–53 m and 53–74 m) of the 36 samples are shown in Table 2. As can be seen, there was a good consistency among the metal concentrations found in each extraction step using the BCR sequential extraction procedure in different grain sizes. The mean total Cd, Cu, Pb and Zn concentrations for three grain sizes were found to be higher than the upper limits of their typical soil concentrations (Grishaw et al., 1989), 0.3, 80, 20 and 300 mg kg\(^{-1}\), respectively. These concentrations are higher than the limit values by about 40-fold for Cd, 10-fold for Pb, 2.7-fold for Zn and 1.25-fold for Cu. This means that this region is affected by anthropogenic metal pollution sources such as traffic and industry.

3.2. Chemical partitioning of metals

The first fraction of the BCR sequential extraction procedure shows the amount of weakly bound metals which are readily soluble in water or a slightly acidic medium. The second and third fraction, associated with oxides and hydroxides of Fe and Mn, and sulphides and organic matter, respectively, are susceptible to releasing those metals present in its structure depending on variations that occur with potential changes or pH (Guillén et al., 2012).

The percentages of metals in the street dusts of three grain sizes extracted from each extraction step are illustrated in Fig. 2. When the percentages of metals extracted in the most labile fractions (F1 + F2 + F3) are considered, the order of mobility of the metals is as follows:

Cd (71.3%) > Cu (48.9%) > Pb (42.8%) > Cr (42.1%) > Ni (41.4%) > Zn (40.9%) > Co (36.6%) = Mn (36.3%) > Fe (3.1%) for < 74 μm.

Cd (71.5%) > Cu (49.5%) > Ni (42.8%) = Pb (42.4%) > Cr (41.7%) > Co (37.6%) = Zn (37.3%) > Mn (36.7%) > Fe (2.9%) for 38 – 53 μm.

Cd (71.1%) > Cu (49.4%) > Pb (43.2%) > Ni(42.8%) > Cr (40.3%) > Zn (38.0%) = Co (38.0%) > Mn (36.9%) > Fe (2.8%) for < 38 μm.

As can be seen, the partitioning of the metals for each three

<table>
<thead>
<tr>
<th>Element</th>
<th>Fraction</th>
<th>(\text{Found (mg/kg)})</th>
<th>(\text{Certified (mg/kg)})</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>F1</td>
<td>7.0 ± 0.1</td>
<td>7.3 ± 0.4</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>3.88 ± 0.30</td>
<td>3.77 ± 0.28</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>0.31 ± 0.04</td>
<td>0.27 ± 0.06</td>
<td>115</td>
</tr>
<tr>
<td>Cr</td>
<td>F1</td>
<td>2.23 ± 0.03</td>
<td>2.26 ± 0.16</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>48.5 ± 1.6</td>
<td>45.7 ± 2.0</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>145 ± 5</td>
<td>143 ± 7</td>
<td>101</td>
</tr>
<tr>
<td>Cu</td>
<td>F1</td>
<td>46.9 ± 1.3</td>
<td>49.3 ± 1.7</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>125 ± 2</td>
<td>124 ± 3</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>56 ± 1</td>
<td>55 ± 4</td>
<td>102</td>
</tr>
<tr>
<td>Ni</td>
<td>F1</td>
<td>15.3 ± 0.6</td>
<td>15.4 ± 0.9</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>25.0 ± 1.1</td>
<td>26.6 ± 1.3</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>16.8 ± 0.4</td>
<td>15.3 ± 0.9</td>
<td>110</td>
</tr>
<tr>
<td>Pb</td>
<td>F1</td>
<td>3.55 ± 0.13</td>
<td>3.18 ± 0.21</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>128 ± 3</td>
<td>126 ± 3</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>9.2 ± 1.7</td>
<td>9.3 ± 2.0</td>
<td>99</td>
</tr>
<tr>
<td>Zn</td>
<td>F1</td>
<td>196 ± 6</td>
<td>205 ± 6</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>121 ± 5</td>
<td>114 ± 5</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>52 ± 3</td>
<td>46 ± 4</td>
<td>113</td>
</tr>
</tbody>
</table>

Table 1

Analysis results of certified reference material (BCR-701).
grain sizes was found to be very similar to each other. When the results obtained from the samples with a grain size < 74 m were taken into consideration, Cd was the most mobile element. The concentrations of Cd in the exchangeable and bound to carbonates, reducible, oxidisable and residual fractions were found to be 21.6%, 23.6%, 26.1%, and 28.7%, respectively. Approximately 71% of its total concentration was extracted in the first three extraction stages.

Copper showed highest concentrations in the residual (51%) and bound to organic matter and sulphide fractions (42%). The proportions of Cu present in the first and second fractions changed from 3.1% to 3.9%, respectively. The presence of Cu in the organic fraction is supported by the high formation constants of Cu-organic complexes (Banerjee, 2003). The high concentration of Cu in the organic fraction (42%) is in good agreement with other studies in soils (Guilén et al., 2012), estuarine sediments (Passos et al., 2010), lake sediments (Tokalioglu et al., 2000), river sediments (Cuong and Obbard, 2006), aquaculture sludge (Morillo et al., 2002) and street dusts (Tokalioglu and Kartal, 2006; Banerjee, 2003).

<table>
<thead>
<tr>
<th>Grain size (m)</th>
<th>Step</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>53–74</td>
<td>F1</td>
<td>2.59 ± 0.22</td>
<td>1.51 ± 1.09</td>
<td>nd³</td>
<td>3.11 ± 1.49</td>
<td>79.7 ± 50.3</td>
<td>39.1 ± 13.7</td>
<td>4.45 ± 1.73</td>
<td>12.2 ± 7.2</td>
<td>87.0 ± 43.6</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>2.83 ± 0.31</td>
<td>1.43 ± 1.26</td>
<td>nd³</td>
<td>3.87 ± 1.90</td>
<td>230 ± 88</td>
<td>54.9 ± 17.9</td>
<td>4.67 ± 1.75</td>
<td>16.6 ± 6.7</td>
<td>112 ± 34</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>3.14 ± 0.56</td>
<td>3.25 ± 1.76</td>
<td>7.15 ± 2.33</td>
<td>41.6 ± 16.7</td>
<td>320 ± 103</td>
<td>59.4 ± 25.9</td>
<td>7.46 ± 2.46</td>
<td>56.8 ± 12.6</td>
<td>119 ± 57</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>3.44 ± 0.67</td>
<td>10.7 ± 3.18</td>
<td>9.85 ± 3.60</td>
<td>50.8 ± 17.8</td>
<td>10754 ± 6014</td>
<td>269 ± 94</td>
<td>23.5 ± 8.4</td>
<td>114 ± 35.3</td>
<td>468 ± 126</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>12.0 ± 1.3</td>
<td>18.9 ± 5.68</td>
<td>17.0 ± 4.6</td>
<td>99.3 ± 29.6</td>
<td>20385 ± 6046</td>
<td>422 ± 125</td>
<td>40.0 ± 11.9</td>
<td>200 ± 44</td>
<td>778 ± 133</td>
</tr>
<tr>
<td>38–53</td>
<td>F1</td>
<td>2.52 ± 0.21</td>
<td>1.62 ± 1.08</td>
<td>0.05 ± 0.14</td>
<td>3.42 ± 1.79</td>
<td>84.2 ± 35.1</td>
<td>40.4 ± 13.7</td>
<td>4.29 ± 1.93</td>
<td>118 ± 7.1</td>
<td>73.4 ± 34.4</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>2.80 ± 0.32</td>
<td>1.54 ± 1.26</td>
<td>0.17 ± 0.43</td>
<td>4.34 ± 2.19</td>
<td>227 ± 48</td>
<td>56.1 ± 18.2</td>
<td>4.47 ± 2.47</td>
<td>16.3 ± 6.9</td>
<td>101 ± 24</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>3.11 ± 0.56</td>
<td>3.37 ± 1.76</td>
<td>6.98 ± 2.48</td>
<td>42.4 ± 16.6</td>
<td>329 ± 103</td>
<td>60.2 ± 25.6</td>
<td>7.52 ± 2.66</td>
<td>56.3 ± 12.4</td>
<td>117 ± 46</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>3.35 ± 0.68</td>
<td>10.8 ± 3.18</td>
<td>10.1 ± 3.20</td>
<td>51.2 ± 14.6</td>
<td>21787 ± 5722</td>
<td>270 ± 94</td>
<td>21.8 ± 7.4</td>
<td>115 ± 35</td>
<td>488 ± 144</td>
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<tr>
<td></td>
<td>Total</td>
<td>11.8 ± 1.3</td>
<td>17.4 ± 5.7</td>
<td>17.3 ± 4.4</td>
<td>101 ± 27</td>
<td>22427 ± 5778</td>
<td>427 ± 125</td>
<td>38.1 ± 11.6</td>
<td>199 ± 44</td>
<td>792 ± 188</td>
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<tr>
<td>&lt; 38</td>
<td>F1</td>
<td>2.64 ± 0.21</td>
<td>1.66 ± 1.08</td>
<td>nd³</td>
<td>3.32 ± 1.73</td>
<td>99 ± 87</td>
<td>41.3 ± 14.7</td>
<td>4.32 ± 1.93</td>
<td>12.6 ± 7.2</td>
<td>76.9 ± 34.3</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>2.91 ± 0.32</td>
<td>1.58 ± 1.26</td>
<td>nd³</td>
<td>4.23 ± 2.23</td>
<td>229 ± 48</td>
<td>57 ± 17.8</td>
<td>4.50 ± 2.47</td>
<td>17.2 ± 6.8</td>
<td>104 ± 24</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>3.22 ± 0.56</td>
<td>3.40 ± 1.76</td>
<td>7.52 ± 2.59</td>
<td>43.5 ± 17.3</td>
<td>333 ± 102</td>
<td>61.4 ± 25.1</td>
<td>7.55 ± 2.66</td>
<td>57.6 ± 12.6</td>
<td>120 ± 46</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>3.56 ± 0.68</td>
<td>10.9 ± 3.2</td>
<td>11.1 ± 3.6</td>
<td>52.2 ± 14.7</td>
<td>22992 ± 6000</td>
<td>273 ± 96</td>
<td>21.9 ± 7.35</td>
<td>115 ± 35</td>
<td>492 ± 144</td>
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<tr>
<td></td>
<td>Total</td>
<td>12.3 ± 1.3</td>
<td>17.5 ± 5.7</td>
<td>18.7 ± 4.9</td>
<td>103 ± 27</td>
<td>23652 ± 6074</td>
<td>433 ± 126</td>
<td>38.3 ± 11.6</td>
<td>202 ± 45</td>
<td>792 ± 188</td>
</tr>
</tbody>
</table>

Table 2
The mean concentrations (mg/kg) and standard deviations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in each extraction step of the BCR procedure for the different grain sizes of the 36 samples (n = 3).

* Not detected.
* TSC: Typical soil contents, source: Grimshaw.

Fig. 2. The chemical fractionation patterns of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the 36 street sediments to grain sizes: (a) < 74 m, (b) 38–53 m and (c) < 38 m.
Table 3
Varimax rotated loadings and communalities for the street dust samples (n=36, only those larger than 0.10 are shown).

<table>
<thead>
<tr>
<th>Element</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Co</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu</td>
<td>0.18</td>
</tr>
<tr>
<td>Mn</td>
<td>0.81</td>
</tr>
<tr>
<td>Ni</td>
<td>0.88</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.86</td>
</tr>
<tr>
<td>Fe</td>
<td>0.85</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Explained variance (%) 18.52 16.57 15.81 15.51 14.31


Lead had the highest percentage in the residual fraction (57%). This fraction was followed by the oxidisable fraction (28%), reducible fraction (8.3%) and exchangeable and bound to carbonates fraction (6.1%). Pb in the oxidisable fraction is strongly complexed with organic matter in street dusts and is released into the environment following degradation of the organic matter or oxidation of sulphides to sulphates (Passos et al., 2010). The high Pb concentration in the residual fraction has been reported by other authors (Passos et al., 2010; Banerjee, 2003; Tokalioglu et al., 2003).

Chromium concentration was found only in the oxidisable and residual fraction in all the samples. Cr had the highest percentage in the residual fraction (58%). The remaining Cr (42%) was partitioned in the oxidisable fraction. The high Cr concentration in the residual fraction showed that the metal is bound to resistant components of the street dust matrix. The high Cr concentration in the residual fraction results in agreement with those reported in the literature (Passos et al., 2010; Tokalioglu et al., 2000; Banerjee, 2003).

Ni was partitioned as 59% in the residual fraction, 19% in the oxidisable fraction, 11% in the reducible fraction and 11% in the exchangeable and bound to carbonates fraction. The residual fraction was the most important fraction for Ni in street dust samples. Banerjee (2003), Tokalioglu and Kartal (2006) and Passos et al. (2010) have reported this fraction as 71%, 40%, and 36%, respectively. The fraction distributions of Zn were found to be similar to Ni. The zinc in the street dust was associated with the residue in a proportion of 59%, while 15%, 14% and 11% levels of Zn were present in forms bound to organic matter and sulphides, bound to Fe and Mn oxides and in exchangeable and bound to carbonates form, respectively.

The highest concentration of Co was found in the residual fraction (63%) followed by oxidisable fraction (19%). Co was partitioned almost equally between the exchangeable and bound to carbonates (9.0%) and reducible fractions (8.5%). Manganese fractionation in the street dust was as follows: residual (64%) > oxidisable (14%) > reducible (13%) > exchangeable and bound to carbonates (9.3%). About 97% of the total Fe was found in the residual fraction. In the non-residual fraction, the percent Fe concentration ≤ 1.6. The high Fe concentration in the residual fraction showed that the metal was associated with the crystalline structures of the minerals. It is not easy to extract the metals in this fraction.

3.3. Correlation coefficient analysis

The Pearson’s correlation matrix for metal concentrations in street dusts collected from the OID in Kayseri, Turkey are presented in Table S3. Inter-element relationships provide important informations on their sources. The high correlation coefficients found between metals show that sources of pollution could be same. Significant positive correlations at 99% confidence level were observed between only Cd–Fe (0.461), whereas significant negative correlations at the same confidence level were found between Pb–Mn (–0.453) and Cd–Cr (–0.425). Cr is uncorrelated with all the other metals, except for Cd. The pairs of Ni–Co (0.348), Zn–Cu (0.367), and Cd–Pb (0.348) were significant and positively correlated at 95% confidence level. The correlations between the other metal pairs which changed from −0.018 to 0.285 were not significant. The positive correlations between Cd–Fe, Cu–Zn and Co–Ni show a common origin for the metal pairs (probably several anthropogenic activities) whereas negative correlation between Pb–Mn represents that its source is different. These results are consistent with the following PCA and CA interpretations.

3.4. Multivariate analysis results

3.4.1. Principal component analysis

PCA was applied to identify the sources of heavy metals in street dusts with a grain size fraction < 74 μm by applying varimax rotation with Kaiser normalisation. The number of significant factors and the percent of variance explained by each of them were calculated by using the SPSS v11.5 software package. Table S4 shows that there are four eigenvalues higher than 1.00 and these four factors explain 66% of the total variance. The fifth eigenvalue of 0.82 explains 14.3% of the total variance. The first five eigenvalues explain 81% of the total variance.

The rotated component matrix (grain size < 74 μm) is given in Table S5. PCA loadings ≥ 0.61 are shown in bold. The PCA loadings ≥ 0.61 are shown in Table S5. PCA loadings ≥ 0.61 are shown in bold. The first factor explains 18.5% of the total variance. It contains Fe and Cd with loading values of 0.85 and 0.81, respectively. This factor for Fe may be related to corrosion of the steel parts of vehicles, etc., Cd is widely used to protect the alloy surface and in building materials. It is also used in galvanization, batteries, plastic, and appliance machines. Therefore, corrosion of alloy and building materials, galvanization, batteries, and plastic may produce large amounts of Cd (Wei et al., 2010). Moreover, abrasion of tires may also be a source of Cd (Saeedi et al., 2012). Lead (0.86) and Mn (–0.81) which appear in the second factor, account for 16.6% of the total variance. Mn is of soil origin. However the Pb mainly come from the historical use of leaded petrol. Moreover the other source of Pb may be zinc smelter emissions which are about 16 km from the OID. Negative loading values between Pb and Mn probably shows an antagonistic effect for these metals. Factor 3 is loaded primarily by Ni and Cr which have ≥ 0.61 loading values and this explains 15.8% of the total variance. This factor is most probably industrial because of the presence of various metal processing industries in the area. Factor 4 is dominated by Cu and Zn accounting for 15.5% of the total variance. It appears that this factor may be due to air-borne emissions from various sources containing zinc smelter. Cobalt has a high loading value (0.92) in Factor 5 and it explains 14.3% of the total variance. It originates in the soil. Fig. 3 shows the 3-D plot of the PCA loadings.

3.4.2. Cluster analysis

The variables were standardised by z-scores before HCA. Hierarchical clustering by the Ward’s method was performed with this data set. The Euclidean distances for similarities in the variables/samples were calculated. The results of the HCA are presented in Fig. 4(a) for variables and in Fig. 4(b) for samples as a dendrogram.
Elements belonging to the same cluster had strong correlations among themselves and may originate from a common source. As can be seen from Fig. 4(a), the results indicate three clusters: (1) Fe–Cd–Pb; (2) Cu–Zn–Mn; (3) Co–Ni–Cr. However, cluster 1 is moderately associated with cluster 2 and cluster 3. In this case, cluster 1 includes Fe–Cd–Pb, whereas cluster 2 includes the other metals (Cu–Zn–Mn–Co–Ni–Cr). In general, the results of CA agreed very well with those of PCA analysis. Fig. 4(b) shows two distinct clusters. Cluster I contains the first 15 samples and also sample 17 and 28 (includes three sub-clusters: samples #6–10, samples #1, 2, 5, 4, 17 and 28 and samples #11, 12, 13, 14, 3 and 15). Cluster II contains the following samples: 16, and those between 18 and 36, except for sample 28 (includes three sub-clusters: samples #29, 30, 25, 20, 31, 23, 16 and 24, samples #21, 36 and samples #19, 22, 18, 32, 35, 27, 34, 26 and 33).

4. Conclusion

In this study, the concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in a total of 36 street dust samples from the streets of the OID for three different grain sizes (< 38 m, 38–53 m and 53–74 m) were determined by FAAS after application of a modified sequential extraction procedure. There was very good consistency among the metal concentrations found in each extraction step for different grain sizes. The mean total Cd, Cu, Pb and Zn concentrations for three grain sizes were found to be higher than the upper limits of their typical soil concentrations by about 40-fold for Cd, 10-fold for Pb, 2.7-fold for Zn and 1.25-fold for Cu. The mobility sequence based on the sum of the first three step metal concentrations (for < 74 m grain size) was as follows: Cd (71.3) > Cu (48.9) > Pb (42.8) = Cr (42.1) > Ni (41.4) > Zn (40.9) > Co (36.6) = Mn (36.3) > Fe (3.1). Cd is the most mobile metal in this region. The multivariate statistical analysis results show that the sources of metals in this region are industrial, traffic, airborne emissions and natural. The CA results indicate three clusters: (1) Fe–Cd–Pb; (2) Cu–Zn–Mn; (3) Co–Ni–Cr. In general, correlation analysis, PCA and CA results are consistent with each other.

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Appendix A. Supplementary material