Environmental impact assessment of industrial activities on heavy metals distribution in street dust and soil

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Abstract

Street dust and soil are important materials for evaluating the contaminants level in industrial areas. Detailed size-resolved distribution of metal(loid)s in street dusts and soils influenced by industrial activities has rarely been investigated. This study was carried out to understand how industrialization might affect the size distribution of metal(loid)s concentration and contamination level in the street dust and soil from Murcia, southern Spain. An industrial and a natural areas were selected and surface soil and street dust samples were taken. They were fractionated into eleven size classes and total concentrations of Pb, Zn, Cu, Cd, Cr, Ni, As and Fe were determined in both the bulk samples and their fractions. Enrichment factor, geoaccumulation index, and mass loading of different heavy metal(loids) were calculated. The results indicated that the street dust from natural and industrial areas had almost the same particle size distribution, both containing higher percentage of coarse-sized particles than the soil. Industrialization seems to have only slightly affected the concentration of most elements studied in the soil. In contrast, the concentrations of the heavy elements in bulk industrial dust samples and all their size fractions were extremely higher than those from the natural area. This means that the industrial activities only affected the size dependency of the concentration (contamination level) of certain elements (Pb, Zn, Cu, Cd, and Cr) in the street dust, but not in the soil.

Keywords: Particle size, Heavy metal(loid)s geochemistry, Street dust, Industrial activity, Enrichment factor, Geoaccumulation index

1. Introduction

It is generally believed that industrialization has been a key factor and an integral part of the economic growth (Jan et al., 2010; Antoci et al., 2018). Numerous studies, however, have indicated the negative impact of industrial activities on major components of the environment including soil, water, and air. A great deal of concern has been recently expressed over issues of dust and soil contamination with metals and metalloids due to rapid industrialization (Loska et al., 2004; Al-Khashman and Shavabkeh, 2006; Rawat et al., 2009; Jan et al., 2010; Panagopoulos et al., 2015; Mathur et al., 2016; Lu et al., 2017; Ayoubi et al., 2018).

Metal(loid)s can be transferred from soil and dust and accumulate in plants, animals, and water bodies, and finally making their pathways to humans through the food chain (Govil et al., 2018). Heavy metals and metalloids, accumulated in street dust and soils, are known to adversely influence human health through several pathways including direct contact with skin, inhalation, and inadvertent ingestion (Bi et al., 2013; Han et al., 2016). Therefore, it is important to assess the risk posed by the contamination of soils and street dusts with heavy metal(loid)s derived from industrial and other anthropogenic activities.

Heavy metal(loid)s in the street dust and soil should be kept at their minimum level possible since they are both toxic and non-degradable. When the soil and dust particles containing these elements enter the human body, elements can be either deposited in the circulatory system or be accumulated in different tissues (Han et al.,

2016). These, in turn, may interfere with the normal functions of internal organs creating various diseases (Christoforidis and Stamatis, 2009).

Among the major solids carrying environmental pollutants including heavy metals and metalloids (dust, soil, and sediment), dust appears to be the most important factor affecting human health (Al-Khashman, 2004; Lu et al., 2017). Street dust acts as both sink to receive heavy elements from various anthropogenic sources and also as source from which heavy metals could be transferred to air and water (Wang et al., 2006; Zhao et al., 2010; Han et al., 2016; Jayarathne et al., 2017; Padoan et al., 2017). Besides, street dust has been reported to be a valuable archive of environmental information because it is widespread ubiquitously, it is easy to sample, and its composition could be used for source identification (Sutherland, 2003).

In the last few decades, a number of investigations have been carried out on the concentration, source, distribution pattern, degree of pollution, and the risk assessment of heavy elements in the street dusts or soils affected by industrial activities (Ordonez et al., 2003; Loska et al., 2004; Al-Khashman and Shawabkeh, 2006; Govil et al., 2008; Rawat et al., 2009; Jan et al., 2010; Yaylali-Abanuz, 2011; Pathak et al., 2013; Wang et al., 2014; Panagopoulos et al., 2015; Peña-Fernández et al., 2015; Benhaddya et al., 2016; Mathur et al., 2016; Yildirim and Tokalioğlu, 2016; Gabarrón et al., 2017a; Jiang et al., 2017; Lu et el., 2017; Antoci et al., 2018). However, in almost all of these studies, bulk soil/dust samples have been examined with no or minimum attention paid to the size distribution of metals and metalloids. Only a few recent studies (Wang et al., 2006; Acosta et al., 2009; Zhao et al., 2010; Fujiwara et al., 2011; Cao et al., 2012; Yildirim and Tokalioğlu, 2016; Kang et al., 2017; Ayoubi et al., 2018)have indicated that if size distribution of

contaminants in soils or sediments is not studied, the risk assessment results would be neither comparable nor accurate.

In addition, little information is available on metal(loid)s pollution of rapidly industrializing urban areas of small to medium size. Therefore, the objectives of this study were to: (i) determine the concentrations of major heavy metal(loid)s in street dusts and soils in an industrial area, (ii) understand the effect of industrialization on size distribution of heavy elements in soil and street dust, and (iii) evaluate the level of contamination of different sized particles of street dust and soil with heavy elements as affected by the industrial activities in Murcia city, southeastern Spain.

2. Material and methods

2.1. Study area and sample collection

An industrial area (P.I. Oeste) and a natural site were chosen for our investigation. The industrial area is located in the outskirt of Murcia city (SE Spain). Its major activities are related to service industry including manufacturing paints, steel products, chemicals, electrical materials, etc. Metals associated with this type of industry include Zn, Pb and Cd (Fakayode and Onianwa, 2002, Acosta et al., 2010). In addition, the natural area selected as a control site is located 5 km south of the industrial area in a natural park where no population is recorded and there is no industrial activity (Fig. 1).

Climate of the Region of Murcia is Mediterranean semiarid with mean annual temperature of 18 ºC and average annual rainfall of 350 mm. Both industrial and natural areas have the same soil parent materials. Lithology of this area consist of limestones, marls, sandstones, and clays (Arana, 2007).

Data on metals concentration in the soil horizons from this industrial area has indicated that the highest metal concentrations are found in the topsoil (0-5 cm) (Gabarrón et al., 2017b). Metals in different soil layers are non-degradable and persistent (Selene et al., 2003). Tha is why five topsoil samples (0-5 cm) and five street dust samples were collected from each sampling area (Fig. 1). Difficulties to find appropriate sites for soil sampling limited the number of samples. The soil samples were collected using a soil spade while road dust was swept directly into a plastic bag to avoid resuspension (Acosta et al., 2011a; Zhang et al., 2012; Du et al., 2013; Acosta et al., 2015).

2.2. Laboratory analysis

Soil and dust samples were dried for 48 h at 45 ºC and passed through a 2 mm sieve. A split of each sample was ground using an agate mortar (RetschRM 100) for total metal(loid)s determination.

Physical fractionation of the soil and street dust samples was carried out to obtain eleven particle size fractions, including 2000-850 µm (F1), 850-425 µm (F2), 425-180 µm (F3), 180-150 µm (F4), 150-106 µm (F5), 106-75 µm (F6), 75-50 µm (F7), 50-20 µm (F8), 20-10 µm (F9), 10-2 µm (F10) and < 2 µm (F11). A stack of sieves was used to separate F1 to F7 from the bulk soil or dust samples. To separate F8, F9, F10 and F11, 50 g of soil/street dust was dispersed with Na-polyphosphate for 8 h by horizontal shaking at 250 rpm. The mixture was then transferred to a 1000 mL glass cylinder, bulked up with distilled water. Fractions were separated by repeated sedimentation and decanting based on the Stokes' law (Ljung et al., 2008; Boisa et al., 2014; Li et al., 2017) and then oven-dried.

To extract the total metal(lod)s content in the soil and street dust samples and their fractions, 0.5 g of ground sample was placed into microwave vessel and 10 mL of concentrated HNO_3 (65% pure, Panreac) was added and digested using a microwave digester (Mars 6, 240/50 CEM company) following the USEPA method 3051a (Environmental Protection Agency, 2007). Extract obtained was diluted with deionised water in a 50 mL volumetric flask. The concentration of Pb, Zn, Cu, Cd, Cr, Ni, As, and Fe was measured in the extract using an ICP-MS (Agilent 7500CE). For quality assurance, reagent blanks as well as certified reference materials (BAM-U110), available from the Federal Institute for Materials Research and Testing Research and Testing were also run with the samples. Recoveries obtained for BAM-U110 were: 87% for Pb; 95% for Cu; 95% for Ni; 86% for Cr; 89% for Zn; 97% for Cd; 93% for Fe and 81% for As.

2.3. Enrichment factor, geoaccumulation index and grain size fraction loading

The level of anthropogenic addition of heavy elements in bulk and different particle size fractions of both the soil and street dust samples from industrial andnatural areas was assessed using enrichment factor (EF) and geoaccumulation indices. EF values were calculated using the following equation:

$$EF = (C_m/C_{Fe})_{Sample} / (C_m/C_{Fe})_{Background} \qquad \text{(Equation 1)}$$

where, $(C_m/C_{Fe})_{Sample}$ is the ratio of concentration of metal to that of Fe in either industrial soil or street dust and $(C_m/C_{Fe})_{Background}$ is the same ratio in the natural soils studied. EF values are generally categorized as (i) no enrichment to minimal enrichment (EF<2), (ii) moderate enrichment (2<EF<5), (iii) significant enrichment (5<EF<20), (iv) very

significant enrichment (20<EF<40), and (v) extremely significant enrichment (EF>40) (Gope et al., 2018).

The geoaccumulation index (I_{geo}) could also be used to evaluate the level of contamination by comparing the current concentration of elements in the soil or dust samples with that of preindustrial time. This index was initially used for bottom sediments (Müller, 1981), but could also be employed for assessing soil and dust contamination (Loska et al., 2004; Yaylali-Abanuz, 2011; Pathak et al., 2013; Wang et al., 2014; Li et al., 2015; Qiang et al., 2015; Benhaddya et al., 2016; Han et al., 2016; Mathur et al., 2016; Jiang et al., 2017; Lu et al., 2017). I_{geo} was computed using the following equation:

$$I_{geo} = \mathrm{Log}_2 (C_i/1.5B_i) \qquad \text{(Equation 2)}$$

where C_i is the measured concentration of the element i and B_i is the geochemical background value of the same element. In this study, average concentrations of elements in upper continental crust were used as the geochemical background for Pb, Zn, Cu, Cr, and Co (Taylor and McLennan, 1985) and also for Cd and As (Kabata-Pendias and Mukherjee, 2007). Based on the I_{geo} values, the contamination level is classified into 7 categories (Müller, 1981) including: class 0, practically uncontaminated (I_{geo}<0); class 1, uncontaminated to moderately contaminated (0<I_{geo}<1); class 2, moderately contaminated (1<I_{geo}<2); class 3, moderately to heavily contaminated (2<I_{geo}<3); class 4, heavily contaminated (3<I_{geo}<4); class 5, heavily to extremely contaminated (4<I_{geo}<5); and class 6, extremely contaminated (5<I_{geo}).

To determine the relative contribution of different size fractions to the overall contamination of soils and street dusts, the grain size fraction loading ($GSF_{loading}$) was

computed for each sample using the concentration of metal in each fraction and the mass size percentage. The following equation was employed (Acosta et al., 2011b):

$$GSF_{loading} = 100 \times \left[\frac{\boldsymbol{Xi} \times GSi}{\sum_{i=1}^{11} Xi \times GSi} \right] \qquad \text{(Equation 3)}$$

where X_i is the metal concentration in a given grain size fraction, considering 11 classes for each sample, and GS_i is the mass percentage of that fraction in the sample. The summation of the $GSF_{loading}$ for each sample is always 100 %.

2.4. Statistical treatment

Descriptive statistics (mean and standard deviation) of physic-chemical properties and metal(loid)s concentration on soil, dust and their fractions were performed applying the Excel for Windows software package. The relationship among enrichment factors and geoaccumulation indexes were studied by Pearson correlations at $p<0.01$, this statistical analysis was performed with the software IBM SPSS Statistics 23.

3. Results and Discussion

3.1. Particle size distribution and chemical properties

Table 1 shows the distribution of 11 different size fractions of the soil and street dust in natural and industrial areas. In both natural and industrial soils, F10 (2-10 μm) is the most dominant fraction. Coarse size fractions having a diameter bigger than 106 μm (F1(850-2000 μm), F2 (425-850 μm), F3 (180-425 μm), F4 (150-180 μm), and F5 (106-150 μm)) are the least abundant size fractions, totally making less than 25% of both the natural and industrial soils. In contrast, finer sized particles with a diameter of less than

50 µm including fractions F8 (20-50 µm), F9 (10-20 µm), F10 (2-10 µm), and F11(< 2 µm) comprise more than 70% and 60% of natural and industrial soils, respectively.

Table 1 further indicates that street dust samples taken from both natural and industrial areas are very much identical, both having higher percentage of coarse-sized (F1-F6) and lower quantity of fine-sized particles (F8-F11) as compared to their corresponding soils. Fraction F10 (2-10 µm) is the most dominant fraction in the street dust from both natural and industrial areas. Great attention seems needed to be paid to control more than 20% of particles smaller than 10 µm in the street dust of the industrial area, commonly referred to as PM_{10} and considered environmentally more hazardous (Kjelgaard et al., 2004).

Great similarity in the particle size distribution of the natural and industrial soils might indicate that they derived from almost identical parent materials and also exposed to the similar pedogenic processes they both experienced during the soil formation. It seems that during the generation of street dust from soil, a portion of fine sized materials have been transported to areas further away.

While ample information is available on the particle size distribution of the soil and street dust (e.g. Wang et al., 2006; Zhao et al., 2010; Acosta et al., 2011a; Cao et al., 2011; Luo et al., 2011; Sutherland et al., 2012; Bi et al., 2013; Li et al., 2015; Qiang et al., 2015; Padoan et al., 2017), in industrial areas there is a lack in this type of information. Only few studies have evaluated the particle size distribution of heavy metals in the soil and dust from industrial areas (e.g. Ayoubi et al., 2018), but they have not provided detail explanation on the distribution of different size fractions.

Selected physic-chemical properties of the soil and street dust from industrial and natural areas are given in Table 2. All the samples are alkaline but industrial street dust has a slightly lower pH than industrial soil, natural soil, and street dust (Soil Survey Division Staff, 1993). This might be attributed to the acid producing materials which have been added to the street dust in the industrial area, such as the case of waste from the steel and chemical industries, and atmospheric deposition of nitrogen and sulphur compounds (Duan *et al*., 2016). The soil and street dust are highly calcareous with the carbonate content of 35 to 40 % and have a very low electrical conductivity, just the same as other data reported for the Murcia soil (Acosta et al., 2015). Industrial street dust has considerably higher quantity of organic carbon than the industrial soil and soil and street dust from natural area, which could be attributed to the anthropogenic addition of materials having high content of organic carbon such as smoke, oil, etc. (Stone et al., 2010; Acosta et al., 2011a).

3.2. Metal(loid)s concentration

The concentrations of seven heavy metal(loid)s including Pb, Zn, Cu, Cd, Cr, Ni, and As in all samples as well as in eleven different size fractions of soil and street dust from natural and industrial areas are shown in Fig. 2. There are no significant differences between the concentration of Pb, Zn, and Cu in bulk natural and industrial soils as well as in almost all their size fractions. These likely indicate an anthropogenic inputs derived from industrial activities have not been high enough to make considerable changes in the soil, a relatively big sink. In contrast, the concentrations of these heavy elements in bulk industrial street dust samples as well as in all their size fractions are extremely higher than those from the natural area. This indicates that street dust, as a much smaller size

sink receiving contaminants, is more easily influenced by the negative impact of industrially derived pollutants than the soil. The behavior of Cd is almost the same as that of Pb, Zn, and Cu but with a very low concentration, particularly in the soil.

Chromium concentration in the bulk industrial soil and all its size fractions is even less than that in the natural area. Just like the other elements, however, the concentration of Cr in the street dust samples and their fractions is much higher in industrial area as compared to the natural site. Concentrations of Ni and As in industrial soil and also in industrial street dust and all their size fractions are higher than those in the natural area. Relatively low concentration of Ni and As and also their inconsistent size distribution in both the soil and dust seem to confirm their non-anthropogenic sources.

Results also clearly indicate that the response of elemental concentration to size fraction varies depending on the type of element, the concentration level, the type of material (soil or dust), and degree of industrialization. Lead, Zn, Cu, Cd, and Cr show higher concentrations in finer sized fractions, particularly in the street dust samples from the industrial area. In contrast the concentrations of Pb, Zn, Cu, Cd, Cr, Ni, and As in soil (excluding Zn in F11) and also in dust samples from natural area are mostly size independent.

Acosta et al. (2011) investigated the heavy metal concentrations in different particle size fractions from street dust of Murcia city. They found higher concentrations of metals in the fine-sized fractions. They also reported that the accumulation of metals in the fine-sized fractions were higher when the heavy metals were derived from anthropogenic sources. Han et al. (2016) studied the particle size distribution of selected heavy metals in street dust of Baotou, China, and reported the large accumulation of most elements (except for Co and Ba) in the particles less than 50 μm. In contrast, Yildirim

and Tokalioğlu (2016) found no significant difference among metal partitioning for three particle size classes of industrially polluted street dust from Kayseri, Turkey.

3.3. Enrichment factor

Values of enrichment factor (EF) for all the seven heavy elements calculated for the eleven different size fractions of the industrial soils and street dusts are depicted in Fig. 3. Metal(loid)s investigated could be grouped into three somehow different categories based on their degree of enrichment which will be further discussed.

The first category includes Pb, Zn, and Cu with highest degree of enrichment among the elements studied, particularly in the street dust of the industrial area. This is agreed with the results reported by Gabarrón et al. (2017b), who concluded that industrial soils from Murcia were moderately contaminated by Zn, Pb and Cu, and suggested that some remediation actions, such as phytoremediation (Lam et al., 2018), should be carried out in order to reduce the risk for human health and the environment. Different size fractions of the industrial soil and street dust are non-enriched to moderately enriched in Pb. In this category, Zn and Cu even show higher enrichment.

While different size fractions of industrial soil are mostly non-enriched to moderately enriched in Zn, most fractions of industrial street dust are significantly enriched in Zn, excluding F11 fraction which is even very significantly enriched in Zn. Also, different fractions of the industrial soil are moderately to strongly enriched in Cu, whereas all the fractions of the industrial street dust are strongly enriched with this heavy metal. Acosta et al. (2011) reported that finest fraction from an industrial area of Murcia are more sensible for Pb, Zn and Cu enrichment that coarse fraction.

Cadmium, Cr, and As with minimum enrichment in both the soil and street dust of the industrial area fall into the 2nd category. Almost all the fractions of the industrial soil are not enriched in Cd and As, but street dust fractions are moderately enriched in both elements. Also, none of the industrial soil or street dust fractions are enriched in Cr. In contrast, according to calculated enrichment factor, Jiang et al. (2017) reported moderate pollution of Cr and Cd in street dust from Lanzhou (China), which indicates that the different industrial activities, climatic condition and management of industrial area among other aspects are key factors determining the final metal(lod)s concentration in soil and dust

Nickel, as the only element in the 3rd category, shows a different and somehow unexpected behavior in terms of its concentration and enrichment. In contrast to other elements, street dust fractions are not enriched in Ni while industrial soil fractions are all moderately enriched. Nickel has been usually considered as a geogenic element, mostly associated strongly to crystalline net of primary minerals (Acosta et al., 2010), therefore its transfer through weathering from parent material to soil and from soil to dust is slower that the other metal(lod)s, which explains the higher concentration reported in soil than dust.

3.4. Geoaccumulation index

Mean values of geoaccumulation index for the different elements in the natural and industrial soil and street dust samples are given in Table 3. Results indicate that bulk sample and almost all the different fractions of the natural soil are practically uncontaminated with Zn, Cu, Ni, and As, but uncontaminated to moderately contaminated

with Pb, Cd, and Cr. Natural street dust is lightly different from the natural soil showing more contamination with As and Ni.

Table 3 further indicates that the industrial soil is also practically uncontaminated with the heavy elements investigated, except for Cd, which shows moderately contaminated in some fractions. Based on the geoaccumulation index, however; industrial street dust is much more contaminated than the industrial soil and both natural soil and street dust. Almost all the different size fractions of the industrial street dust are only uncontaminated with Ni, but moderately to heavily contaminated with Zn, Cu, and Cd, and uncontaminated to moderately contaminated with Pb, As, and Cr.

Previous investigations have also indicated the negative impact of industrialization on heavy metal(loid)s content of urban and agricultural soils and street dust, although mostly on bulk samples, not on the size fractions. Ordoñez et al. (2003) reported elevated concentrations of Zn, Cd, and Hg in the street dusts and soils of Avilés, an industrial city in Northern Spain. Peña-Fernández et al. (2015) indicated that the soils of the industrial area of Alcalá de Henares (Spain) have higher concentrations of heavy metals than the urban area.

The results of an investigation by Loska et al. (2004) showed elevated concentrations of Cd, Pb, As, Sb, and Hg in arable land affected by industrial activities in Southern Poland. Govil et al. (2008) reported that most of the soils in the Katedan industrial development area, India, were heavily polluted by As, Pb, and Zn and those of certain local areas by Cr, Cu, and Ni. High concentrations of As, Cd, Zn, Pb, Cu, Cr, Mn, and Hg were also reported for the surface soils around Gebze industrial area, Turkey (Yaylali-Abanuz, 2011). Wang et al. (2014), Yildirim and Tokalioğlu (2015), and Mathur et al. (2016) also reported high levels of selected heavy metals or metalloids in dust from

Changqing industrial park of Baoji, NW China, different grain sizes of industrially road dust in Kayseri, Turkey, and street dust from industrial areas of Hyderabad, India, respectively.

Table 4 shows correlation coefficients between the two indices for contamination assessment, enrichment factor (EF) and geoaccumulation index (Igeo) for different heavy elements. Very strong correlations found between the two indices for almost all the heavy metal(loid)s, except for Cu and As, further confirm the explanations given above on the level of contamination in the street dust derived from industrial activities.

3.5. Heavy elements mass loadings

In order to assess the heavy metals(loid)s relative contribution in each of the eleven size fractions in the street dusts and soils from both the natural and industrial areas, the mass loadings were computed (Fig. 4). The results showed that almost all the eleven size fractions have notable contribution to the overall loadings of almost all the elements studied in both the natural and industrial soils and dust samples. Acosta et al. (2011) found that about 35% of the concentrations of Cd, Zn, Pb and Cu resided in the particle grain size fraction of 0–10 μm, while the highest contribution to the total metal concentration in bulk dust came from the 50–20 μm size fraction with almost 50% of the metals concentrations in an industrial area of Murcia Region.

In addition, for most elements, the loadings in natural street dust are more similar to those in the natural soil. Similarly, the contribution of different size fractions to the total content of most heavy elements in industrial street dust is more similar to those in the industrial soil. Practically, all the coarse-sized, medium-sized, and fine-sized particles are important to be environmentally evaluated.

4. Conclusions

The concentration and level of contamination of Pb, Zn, Cu, Cd, Cr, Ni, and As in physically fractionated street dusts and the soils from a moderately industrial area and a natural area, both having the same parent materials, were studied.

Particle size distribution analysis indicated that the street dust samples taken from both natural and industrial areas were physically very similar, both containing higher quantity of coarse-sized but less amount of fine-sized particles as compared to their corresponding soils. If we assume that the street dust particles mainly derive from the local soil, a fraction of particles with the dimeter of less than about 100 μm seems to have been preferentially transferred to areas further away during the production of dust and its transfer and deposition as the street dust. Despite this, street dust in the industrial area still contains more than 20% particles smaller than 10 μm which might cause environmental problem.

A moderate rate of industrialization in the study area appears to affect moderately to greatly the levels of heavy elements in the street dust and all the size fractions investigated, while no effect was observed in the surface soils and most of its studied fractions, except for Ni. This may suggest that the street dust is much more easily and, therefore, more highly contaminated with metal(lod)s as compared to the soil. Therefore, since metal(lod)s could be more easily transferred to the food chain from the street dust than the soil, measures need to be taken to keep the contamination levels of pollutants to their lowest levels possible in the street dust of the industrial area.

Both enrichment factor (EF) and geoaccumulation index (I_{geo}) values indicated that industrialization has greatly increased the level of Pb, Zn, and Cu, particularly in the street

dust. In contrast, they suggest that the level of both Cd and As in the street dust fractions have moderately been affected by industrialization. Finally, industrialization has not affected the degree of Cr accumulation in the street dust.

Based on our results, the concentrations (and level of contaminations) of elements are only size dependent in some cases, but not all. Much higher concentrations of Pb, Zn, Cu, Cd, and Cr were found in finer sized fractions, particularly in the street dust samples from the industrial area. In contrast, the concentrations of Pb, Zn, Cu, Cd, Cr, Ni, and As in the soil (excluding Zn in F11) and also in dust samples from natural area were mostly size independent. Therefore, laborious and costly process of size fractionation of soil and dust samples in similar investigations seems to be necessary for moderately to highly contaminated areas, not for all the areas.

Acknowledgments

Authors appreciate the financial support provided by the Fundación Séneca of Comunidad Autónoma de Murcia (15380/PI/10), Spain, to carry out this investigation.

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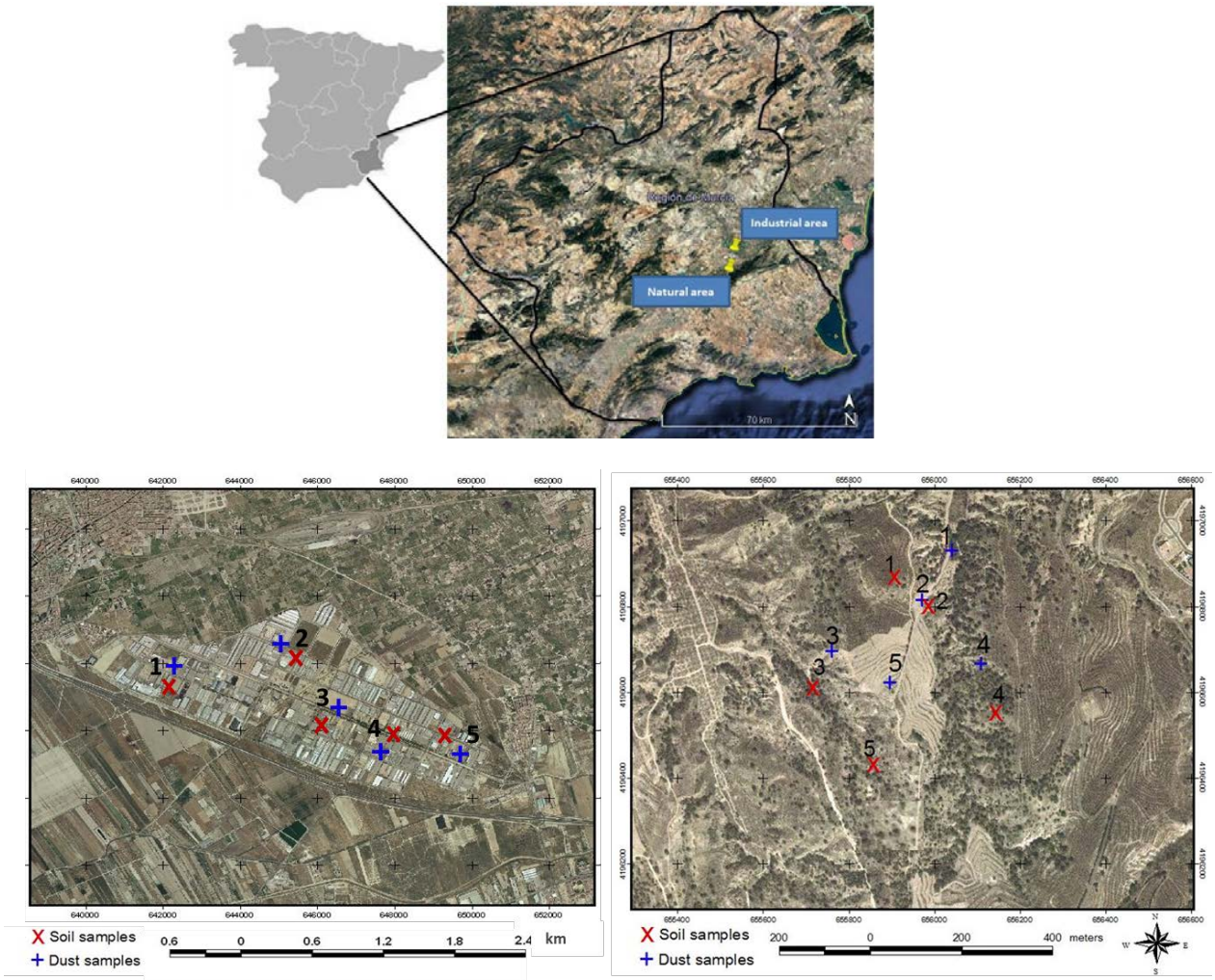
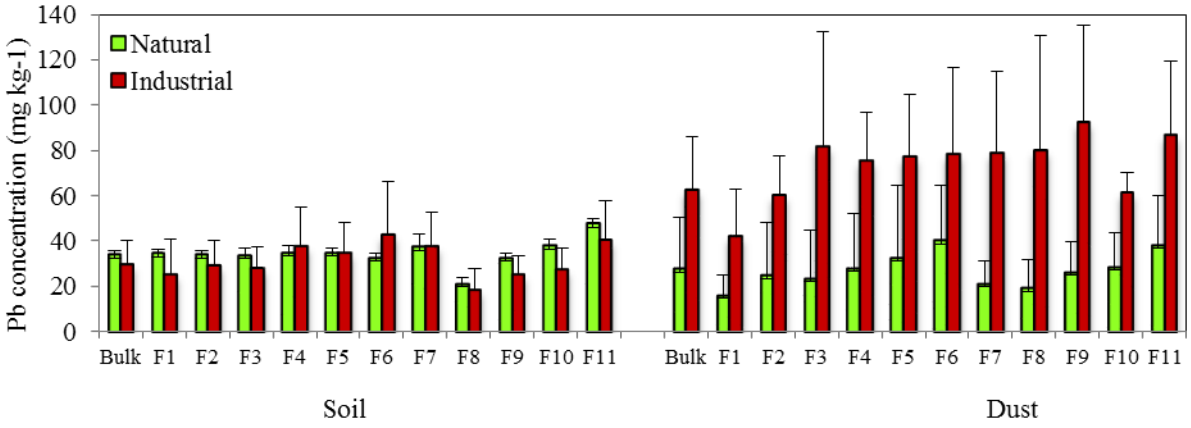
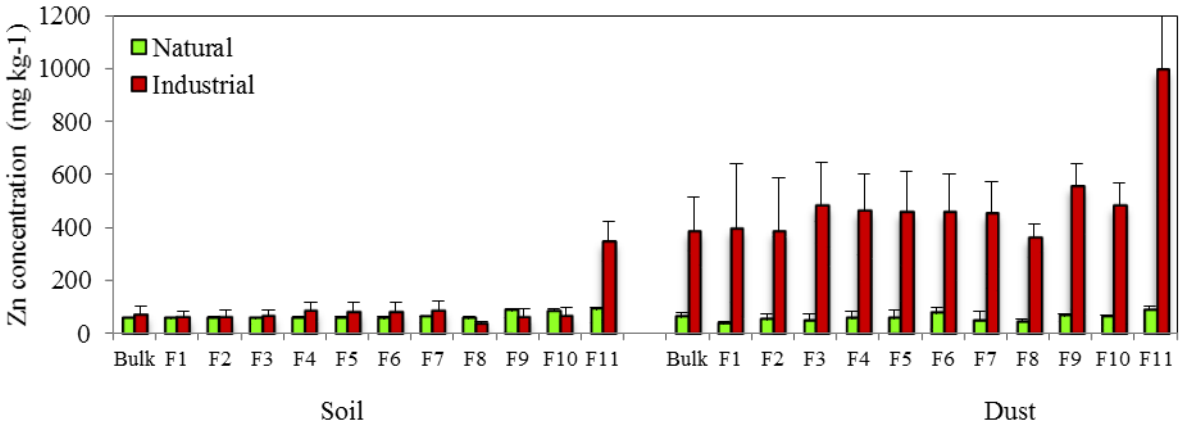
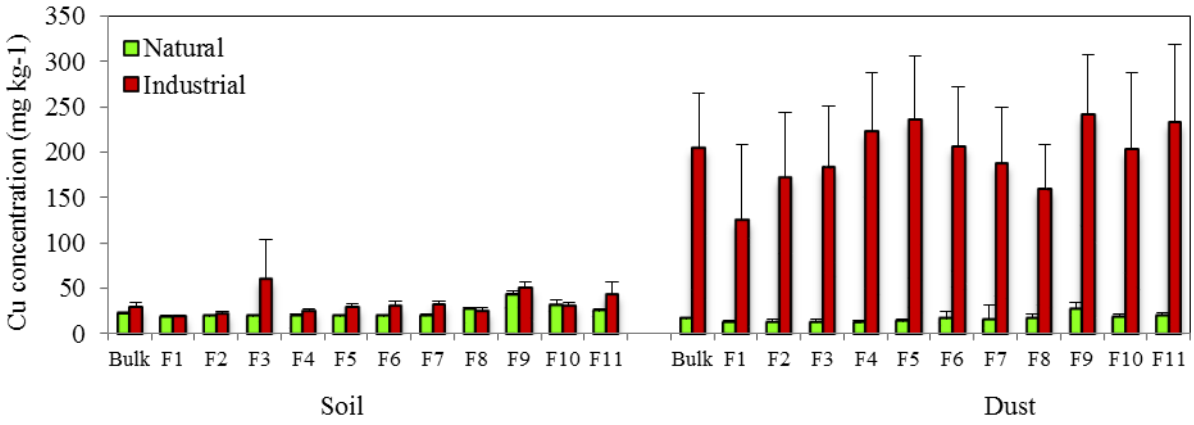
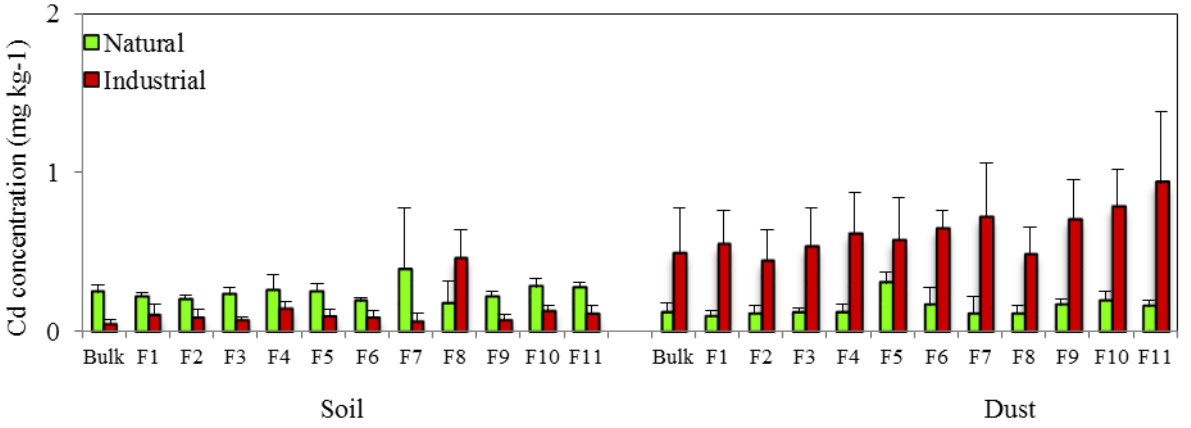


Fig. 1. Locations of study areas in Murcia Province, southeastern Spain. Spatial distribution of the soil and street dust sampling locations in industrial and natural areas studied.


Pb concentration (mg kg-1)
Natural
Industrial
0
20
40
60
80
100
120
140
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Soil
Dust


Zn concentration (mg kg-1)
Natural
Industrial
0
200
400
600
800
1000
1200
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Soil
Dust


Cu concentration (mg kg-1)
Natural
Industrial
0
50
100
150
200
250
300
350
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Soil
Dust


Cd concentration (mg kg-1)
Natural
Industrial
0
1
2
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Bulk F1 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11
Soil
Dust

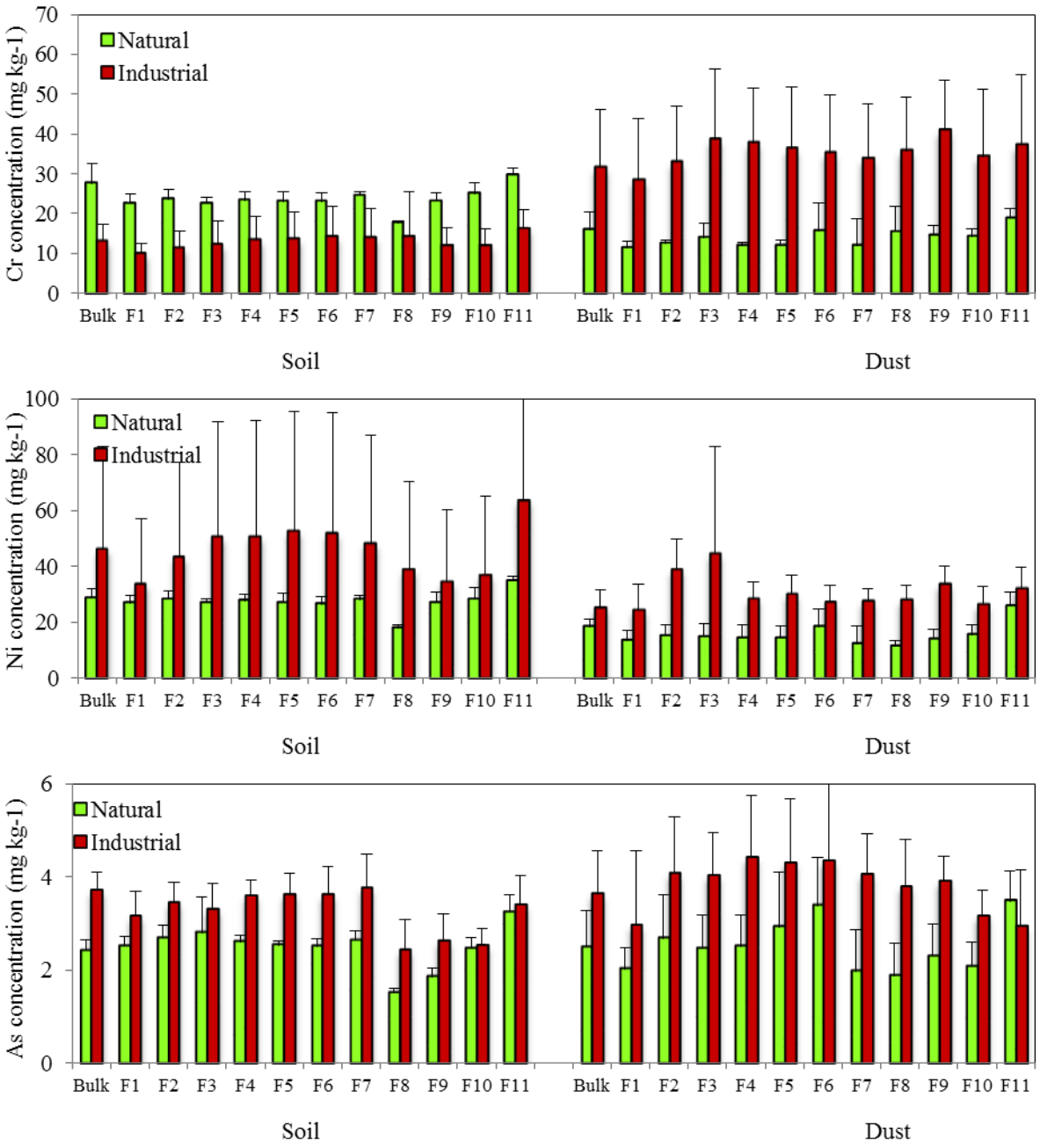


Fig. 2. Mean concentration of different heavy metal(loid)s in bulk samples and different size fractions of soil and street dust samples taken from the industrial and natural areas.

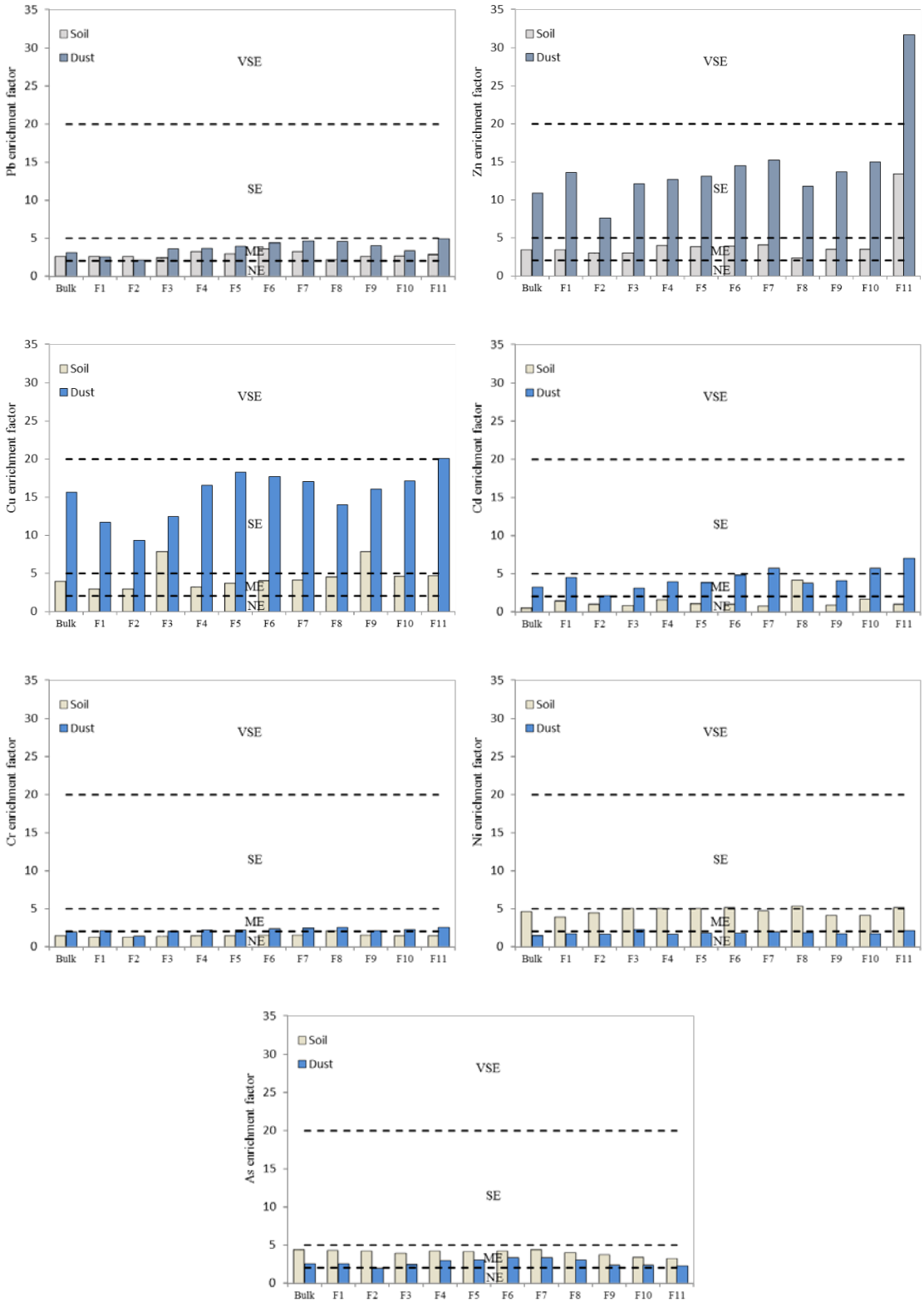


Fig. 3. Mean enrichment factors (EFs) of heavy elements in different particle size fractions and the bulk soil and street dust from industrial area. Dotted lines separate

different classes of enrichment factor including no enrichment (NE), moderate enrichment (ME), significant enrichment (SE), and very significant enrichment (VSE).

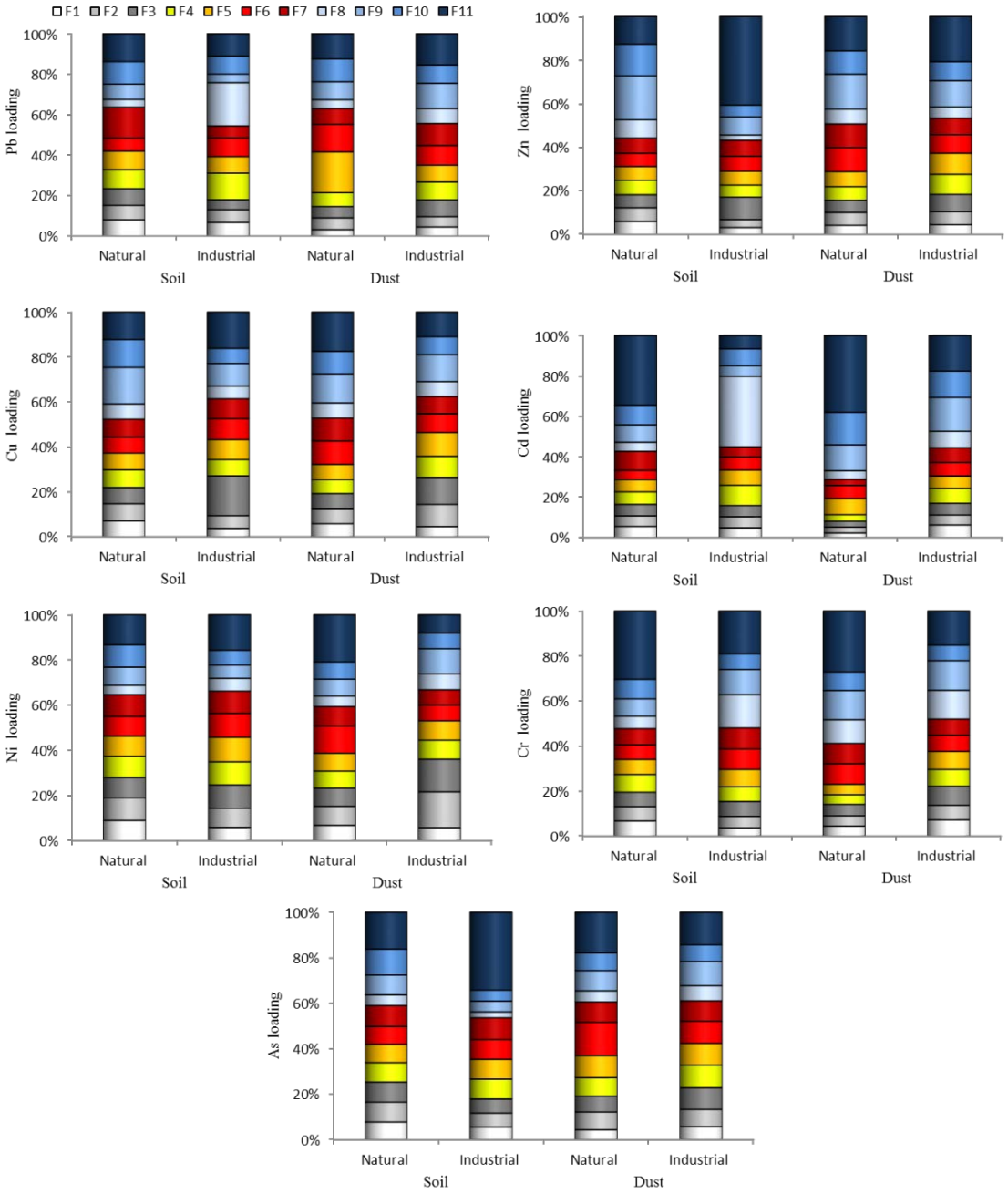


Fig. 4. The loadings of different heavy metal(loid)s in different particle size fractions of the soil and street dust samples taken from industrial and natural areas.

Table 1. Mean values (%) of 11 different size fractions (μm) of soil and street dust samples from industrial and natural areas.

	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**	**F9**	**F10**	**F11**
	850-2000	**425-850**	**180-425**	**150-180**	**106-150**	**75-106**	**50-75**	**20-50**	**10-20**	**2-10**	**<2**
Natural soil	2.67	3.05	4.02	1.30	2.83	3.65	5.19	14.06	12.72	33.72	16.90
Natural street dust	9.38	10.16	12.83	3.42	7.01	6.81	6.56	10.63	8.89	17.83	6.49
Industrial soil	3.03	6.33	9.06	1.89	4.10	4.50	5.70	14.22	12.46	27.79	10.80
Industrial street dust	6.12	10.89	17.21	3.69	6.63	5.79	5.62	11.82	11.03	16.86	4.35

Table 2. Mean values of selected characteristics of soil and street dust from industrial and natural areas.

Sample	pH	EC	Carbonates	Organic carbon	Clay	Silt	Sand
		dS m^{-1}		%			
Natural soil	8.46 (0.42)*	0.11 (0.01)	39.3 (4.02)	1.45 (0.33)	16.9 (1.2)	60.5 (4.3)	22.7 (5.2)
Natural street dust	8.27 (0.28)	0.13 (0.03)	40.4 (5.18)	0.59 (0.64)	6.4 (2.6)	37.3 (6.5)	56.1 (7.9)
Industrial soil	8.14 (0.13)	0.33 (0.08)	35.5 (5.65)	1.62 (0.76)	10.8 (3.4)	54.4 (9.5)	34.6 (12.8)
Industrial street dust	7.82 (0.20)	0.24 (0.06)	39.6 (3.63)	3.74 (0.81)	4.2 (2.0)	37.7 (20.6)	57.9 (22.7)

*Values in parentheses indicate standard deviation (SD).

Table 3: Mean geoaccumulation index of heavy elements calculated for bulk and different fractions of soil and street dust samples from industrial (IA) and natural (NA) areas.

	Pb (20)*		Cd (0.1)		As (1.8)		Zn (71)		Cu (25)		Ni (20)		Cr (10)	
	NA	IA	NA	IA	NA	IA	NA	IA	NA	IA	NA	IA	NA	IA
Soil														
Bulk	0.16	0.00	0.73	-1.74	-0.16	0.47	-0.85	-0.56	-0.78	-0.31	-0.07	0.63	0.88	-0.18
F1	0.19	-0.23	0.55	-0.52	-0.10	0.23	-0.93	-0.80	-0.99	-0.96	-0.16	0.18	0.59	-0.57
F2	0.16	-0.02	0.42	-0.81	-0.01	0.36	-0.85	-0.79	-0.97	-0.75	-0.08	0.54	0.65	-0.38
F3	0.16	-0.09	0.62	-1.08	0.05	0.29	-0.91	-0.72	-0.97	0.70	-0.15	0.76	0.60	-0.28
F4	0.20	0.34	0.78	-0.11	-0.05	0.42	-0.84	-0.33	-0.89	-0.59	-0.12	0.76	0.64	-0.16
F5	0.20	0.21	0.73	-0.66	-0.10	0.43	-0.89	-0.36	-0.93	-0.36	-0.15	0.81	0.62	-0.12
F6	0.09	0.51	0.34	-0.80	-0.10	0.43	-0.92	-0.35	-0.95	-0.27	-0.18	0.80	0.62	-0.07
F7	0.30	0.34	1.38	-1.25	-0.03	0.49	-0.76	-0.28	-0.90	-0.23	-0.09	0.69	0.72	-0.08
F8	-0.52	-0.69	0.22	0.80	-0.82	-0.15	-0.94	-1.55	-0.47	-0.57	-0.73	0.38	0.24	-0.05
F9	0.10	-0.24	0.55	-1.15	-0.54	-0.04	-0.33	-0.77	0.19	0.43	-0.15	0.21	0.63	-0.31
F10	0.32	-0.13	0.90	-0.20	-0.13	-0.08	-0.36	-0.69	-0.25	-0.26	-0.09	0.30	0.73	-0.33
F11	0.65	0.43	0.88	-0.45	0.26	0.34	-0.24	1.71	-0.57	0.24	0.21	1.08	0.99	0.13
Street dust														
Bulk	-0.13	1.07	-0.31	1.71	-0.11	0.43	-0.84	1.86	-1.22	2.45	-0.71	-0.25	0.09	1.08
F1	-0.92	0.50	-0.67	1.88	-0.42	0.14	-1.54	1.90	-1.56	1.75	-1.15	-0.30	-0.38	0.92
F2	-0.29	1.01	-0.39	1.56	-0.01	0.60	-1.09	1.85	-1.51	2.20	-0.97	0.38	-0.26	1.13
F3	-0.37	1.45	-0.35	1.82	-0.13	0.58	-1.15	2.19	-1.52	2.29	-1.01	0.58	-0.10	1.36
F4	-0.11	1.34	-0.33	2.03	-0.10	0.71	-0.95	2.12	-1.55	2.57	-1.05	-0.07	-0.32	1.33
F5	0.10	1.36	1.02	1.92	0.11	0.67	-0.92	2.11	-1.45	2.65	-1.04	0.02	-0.30	1.28
F6	0.41	1.39	0.15	2.10	0.33	0.69	-0.53	2.11	-1.17	2.46	-0.71	-0.12	0.07	1.23
F7	-0.52	1.40	-0.39	2.26	-0.45	0.59	-1.11	2.10	-1.25	2.32	-1.28	-0.11	-0.33	1.18
F8	-0.67	1.41	-0.41	1.69	-0.53	0.49	-1.27	1.77	-1.11	2.09	-1.39	-0.09	0.06	1.26
F9	-0.20	1.63	0.13	2.23	-0.23	0.54	-0.69	2.39	-0.46	2.69	-1.09	0.18	-0.03	1.45
F10	-0.08	1.03	0.38	2.38	-0.38	0.23	-0.74	2.18	-0.99	2.44	-0.94	-0.17	-0.07	1.19
F11	0.33	1.53	0.08	2.64	0.36	0.13	-0.28	3.23	-0.90	2.63	-0.22	0.10	0.33	1.31

* Values in parentheses are world means of the elements in the continental crust (Taylor and McLennan, 1985; Kabata-Pendias and Mukherjee, 2007).

Table 4. Pearson correlation coefficients between enrichment factor (EF) and geoaccumulation index (Igeo) values for different heavy elements in urban soil and street dust of the industrial area.

	Pb	Zn	Cu	Cd	Cr	Ni	As
Urban soil	0.87**	0.90**	0.57	0.95**	0.90**	0.75**	0.45
Street dust	0.77**	0.92**	0.49	0.92**	0.73**	0.53	0.32

** Correlation is statistically significant at the 0.01 level.
ns Correlation is not statistically significant.