DISTRIBUTION OF METAL(LOID)S IN PARTICLE SIZE FRACTION IN URBAN SOIL AND STREET DUST: INFLUENCE OF POPULATION DENSITY

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Abstract

Assessment of street dust is an invaluable approach for monitoring atmospheric pollution. Little information is available on the size distribution of contaminants in street dusts and urban soils and it is not known how the population density would influence them. This research was carried out to assess the size distribution of trace metal(loid)s in street dust and urban soil, and to understand how population density might influence the size-resolved concentration of metal(loid)s. Three urban areas with a high (HD), medium (MD) and low population density (LD) and a natural area (NA) were selected, and urban soil and street dust sampled. They were fractionated into 8 size fractions: 2000-850, 850-180, 180-106, 106-50, 50-20, 20-10, 10-2, and < 2 µm. The concentration of Pb, Zn, Cu, Cd, Cr, Ni, As, and Fe was determined and enrichment factor and grain size fraction loadings were computed. The results indicated that the concentration of Pb, Zn, Cu, Cd, Cr were highly size dependent, particularly for particles < 100 µm, especially for street dust. Low concentrations of Ni and As in street dust and urban soil were size and population density independent. Higher size dependency of the metals concentration and the higher degree of elemental enrichment in the street dust fractions than the urban soils indicate higher contribution of human induced pollution to the dust. Findings also confirm the inevitability of size fractionation when soils or dusts are environmentally assessed, particularly in moderately to highly polluted

areas. Otherwise, higher concentrations of certain pollutants in fine-sized particles might be overlooked leading to inappropriate decisions for environmental remediation.

Keywords: Particle size, metal(loid)s geochemistry, Street deposits, Population density, Enrichment factor

1. Introduction

The term “Street dust”, which is alternatively used with “Road dust” or “Road deposited sediment”, is referred to as the solid particulates deposited on outdoor ground areas, mainly during the dry weather conditions (Tanner et al., 2008; Jayarathne et al., 2017). Dust particles deposited on the street and its surrounding areas are the result of interaction among liquid, solid, and gaseous materials generated by various sources (Fujiwara et al., 2011b). These solid particles include a complex mixture of both inorganic and organic constituents such as metal oxides, different minerals, and organic matter (Gunawardana et al., 2012).

Street dust is believed to be composed of elements that either mainly originate from soil (e.g. K, Na, Al and Ti) or primarily derive from other sources (e.g. Pb, Zn, Cu, and Cd), mostly anthropogenic, including car exhaust emissions, abrasion of the road surface (cement, asphalt) and road paint, industrial activities, and wear of different parts of the vehicles such as tires and brake pads and body rust, leakage of brake and lubricating oil, and residential construction and fuel burning (Fergusson and Ryan, 1984; Al-Khashman, 2007; Tanner et al., 2008; Khanal et al., 2014; Li et al., 2015; Vu et al., 2015; Yildirim and Tokalioğlu, 2016). As an important non-point source of metals (Li et al., 2015), street dust has been widely reported to significantly threaten the human health via particle ingestion, dust inhalation, or even through the dermal contact (Luo et al., 2011; Du et al., 2013). As such, the assessment of street dust is considered a valuable passive tool for monitoring atmospheric pollution in urban and industrial areas (Sutherland, 2003; Ram et al., 2014; Acosta et al., 2015). The advantages of using street dust for evaluating the environmental pollution in urban and industrial areas include its ease of sampling, its ubiquity and nonpoint source nature, and its strong relationship with car emissions (Sutherland, 2003).

Street dust has been reported to remain deposited on the street or the surrounding places only for a short period of time and will soon be resuspended by air and enter the atmosphere (Tanner et al., 2008) or washed by runoff and transferred to other areas (Murakami et al., 2008; Luo et al., 2011) causing environmental problems. In fact, street dust not only acts as a sink to

receive and accumulate environmental contaminants such as metal(loid)s and hazardous organic particles, but also serve as a source which can contaminate the important components of the environment including air, water, and soil (Al-Khashman, 2007; Li et al., 2015; Yildirim and Tokalioğlu, 2016).

Street dust deposition is widespread, particularly in industrial and urban areas (Al-Rajhi et al., 1996). Therefore, the information on the concentration of metal(loid)s in the street dust can serve as a valuable proxy for the environmental contamination assessment (Fujiwara et al., 2011b). That is why many investigations have been carried out in the last few decades on metal(loid)s concentration in street dust in many parts of the world including both developed and developing countries (Fergusson and Ryan, 1984; Li et al., 2001; Ordonez et al., 2003; Manno et al., 2006; Al-Khashman, 2007; Han et al., 2008; Tanner et al., 2008; Zibret and Rokavec, 2010; Acosta et al., 2011; Fujiwara et al., 2011a and 2011b; Shi et al., 2011; Bi et al., 2013; Khanal et al., 2014; Ram et al., 2014; Pan et al., 2015a and 2015b; Bourliva et al., 2016; Han et al., 2016; Yildirim and Tokalioğlu, 2016; Wang, 2016; Jayarathne et al., 2017; Padoan et al., 2017; Alsbou and Al-Khashman, 2018; Gope et al., 2018; Jafari et al., 2018). In most of these studies, the bulk street dust has been assessed with no particular attention to the size distribution of metals.

The size of pollutant bearing particles, such as street dust, is of great importance when evaluating their environmental risk. The rate of bioavailability of metals and their potential ability for biotic ingestion very much depend on the size of particles (Khanal et al., 2014). Besides, the concentration of metals in soil, dust, and sediment is highly size dependent, the finer-sized particles normally having higher concentration than the coarser-sized materials (Fergusson and Ryan, 1984; Al-Rajhi et al., 1996; Lisiewicz et al., 2000; Sutherland, 2003; Acosta et al., 2009, 2011; Fujiwara et al., 2011a, 2011b; Luo et al., 2011; Cao et al., 2012; Bi et al., 2013; Khanal et al., 2014; Pan et al., 2015; Han et al., 2016; Yildirim and Tokalioglu, 2016; Kang et al., 2017). It has even been emphasized that, for more accurate comparisons, international standards should be provided based on the particle size, not based on the bulk analysis of soil or dust samples (Al-Rajhi et al., 1996).

Although most studies were initially focused on the concentration of metal(loid)s in bulk soils and sediments, researchers later shifted their effort toward the size distribution of metals and other pollutants in soils, atmospheric dusts, and sediments (e.g. Al-Rajhi et al., 1996; Lisiewicz et al., 2000; Acosta et al., 2009; Cao et al., 2011, 2012; Luo et al., 2011; Pan et al., 2015; Vu et al., 2015; Zannoni et al., 2016; Kang et al., 2017). However, a few studies have examined the size

distribution of environmental contaminants in street dust (Fergusson and Ryan, 1984; Han et al., 2008; Fujiwara et al., 2011a, 2011b; Bi et al., 2013; Li et al., 2015; Jayarathne et al., 2017; Padoan et al., 2017). In addition, in most of the above listed publications, only a few fractions of the street dust have been evaluated, not the whole range of solid particles. To the best of our knowledge, the influence of population density on the total concentration of metals in street dust has rarely been determined (Acosta et. al., 2015), and the size dependency of metal(loid)s concentration under the influence of population density has yet received no attention. Therefore, the objectives of this study were: (i) to comprehensively assess the contribution of eight different size fractions to the total concentration and also total mass loading of major metal(loid)s and (ii) to understand how population density might influence the size-resolved concentration of metal(loid)s in street dusts and urban soils.

2. Material and methods

2.1. Description of the study area

Three urban areas having different population densities and a natural area (NA) with no settled population (as control), all located in Murcia Region (SE Spain) were chosen (Fig. 1). Murcia city represents high density (HD) population (498 persons km^{-2}), while Totana and Abaran cities are considered medium density (MD) and low density (LD) cities with the population densities of 106 and 27.8 inhabitants per km^{-2}, respectively.

The climate of the study area is Mediterranean semiarid with a mean annual temperature of 18 ºC and an average annual rainfall of 350 mm. Murcia Region is characterized by the presence of sedimentary rocks such as limestones, marls, sandstones, and clays (Arana, 2007). Studied cities are located in corridors and depressions of tectonic origin that divide the surrounding mountainous lines formed by limestones. Therefore, urban and natural soils studied have been developed on eroded betic and sub-betic materials derived from these mountains, with a main composition of limestones (Martínez-Sánchez and Pérez-Sirvent, 2007).

Major activities in the HD city are related to the service sectors, although an intense agriculture, mainly the cultivation of lemon, orange, cereals, and vegetables, has also been traditionally important in surrounding areas of all the 3 cities. Two industrial areas are located 5 km away from the HD city, one in the northwest and the other in the southwest, including paint manufactories, concrete plants, automobile services, and factories producing steel and electrical

materials and parts. Previous studies, however, have indicated that metals generated in these industrial complexes do not really reach HD city (Acosta et al., 2009). Therefore, industrial activities are not expected to have any influence on its urban soils or street dusts in HD city. There is no major pollutant producing manufactory in and around MD and LD cities. Anthropogenic activities in these urban areas include agricultural practices, transportation services, heating and/or cooling systems, and building and road construction.

2.2. Sampling

Because of the difficulties in collecting soil samples in urban areas, the sampling was limited to parks and urban gardens which were selected based on their spatial distribution, size, and the number of users. A total of 36 surface soil samples (0-5 cm) were taken from the three cities and the natural area including18, 8, 4, and 6 samples from HD, MD, LD, and NA soils, respectively. In addition, a total of 14 street dust samples were collected from the three urban areas (3 samples per city) and the natural site (5 samples) by slowly sweeping an area of 1 m^2 using a polyethylene brush and directly transferring into a plastic bag to avoid dust resuspension (Fig. 1).

2.3. Laboratory analysis

Soil and dust samples were dried for 48 h at 45 ºC and passed through a 2 mm sieve to be used for analysis. Physical fractionation of samples was carried out to obtain the following eight particle size fractions: 2000-850 µm (F1), 850-180 µm (F2), 180-106 µm (F3), 106-50 µm (F4), 50-20 µm (F5), 20-10 µm(F6), 10-2 µm (F7), and < 2 µm (F8). A series of sieves were used to separate F1 to F5 from the bulk soil or dust samples. To separate F6, F7, and F8, 50 g of soil/street dust was dispersed with Na-polyphosphate for 8 h by horizontal shaking (250 rpm). The mixture was then transferred to a 1000 ml glass cylinder, bulked up with distilled water, and the 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).

For the total metal extraction from the bulk street dust and urban soil samples and also their different fractions, a split of each sample was ground using an agate mortar (RetchRM 100). 1 g of each ground sample (dry weight) was placed in digesting tubes containing 20 ml of HNO_3-H_3ClO_4 mixture (1:1 v/v) and heated at 210 ºC for 90 minutes (Risser and Baker, 1990). Furthermore, the digested samples were diluted with HCl 0.5N to a final volume of 100 ml. The total concentration of Pb, Zn, Cu, Cd, Cr, Ni, As, and Fe was determined by an Inductively Coupled

Plasma Mass Spectrometer (ICP-MS) model Agilent 7500CE ICP. Certified reference materials (BAM-U110), available from the Federal Institute for Materials Research and Testing, as well as reagent blanks were run to test the quality of analyses, obtaining recoveries of 91% for Pb; 90% for Cr; 102% for Ni; 95% for Cu; 96% for Zn; 114% for Cd and 91% for As

The magnetic susceptibility of dried bulk soil and street dust samples was measured using a Bartington MS2B dual frequency susceptibility meter having a sensitivity in the range of 10^{-8} m^3 kg^{-1}. It was measured at both low and high frequencies (0.46 and 4.6 kHz, respectively). Since there was a very high correlation between the magnetic susceptibility at 0.46 and 4.6 kHz, only the high frequency magnetic susceptibility data was used for correlation analysis with other soil and dust data.

2.4. Enrichment factor and grain size fraction loading

Among different calculation methods being used to evaluate the degree of metals contamination, the level of anthropogenically added metals in different particle size fractions of both soil and street dust samples from 3 urban areas with different population densities was assessed using the index enrichment factor (EF) according to the following equation:

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

where, $(C_m/C_{Fe})_{Sample}$ is the ratio of metal concentration (C_m) to the Fe concentration (C_{Fe}) in either urban soil or street dust; and $(C_m/C_{Fe})_{Background}$ is the same ratio for the natural soils studied (Kartal et al., 2006). 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) (results are showed on supplementary material).

To determine the relative contribution of different size fractions to the overall contamination of urban soils and street dusts, the grain size fraction loading ($GSF_{loading}$) was computed for each sample using both the concentration of metal in each fraction and the mass size percentage. The following equation was employed (Acosta et al., 2011):

$$GSF_{loading} = 100 \times \left[\frac{\mathbf{X}i \times GSi}{\sum_{i=1}^{8} Xi \times GSi} \right] \quad \text{(Equation 2)}$$

where X_i is the metal concentration in a given grain size fraction, considering 8 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 will always be 100% (results are showed on supplementary material).

3. Results and Discussion

3.1. Particle size distribution and chemical properties

Figure 2 illustrates the distribution of eight size fractions in soils and dusts studied, from the largest particles (F1-850 to 2000 μm) to the finest particles (F8-< 2 μm). The second largest fraction (F2-180-850 μm) is dominant in all the street dust samples from the three cities and also in urban soils from MD and LD cities. Together with F5 and F7 fractions, this fraction is also among the dominant fractions in HD urban soil. In contrast, the finest fraction (< 2 μm), which corresponds with the size of clay, is either the least dominant fraction or among the least dominant fractions in both soils and dusts, except in natural soil. Great similarity in the particle size distribution of street dust deposits from 4 different areas, including the natural area, and also 3 urban soils might indicate the natural soil as their identical source. If we assume that all the urban soils (HD, MD, and LD soils) and also all the street dust initially derived from the natural soil (NA soil), it seems that anthropogenic activities could decrease the amount of fine sized particles (clay) and increase the quantity of coarse-sized particles (sand). Such activities could enhance the level of toxic elements which will be discussed in the next subsection.

Previous studies have indicated a high variability in the particle size distribution of the street dust. Shi et al. (2011) investigated urban and suburban street dust in Shanghai, as the most populated city in China. They reported that the distribution patterns of the street dust were characterized by unimodal distribution showing dominant particles in the range of 100 to 400 μm. The research findings of Li et al. (2015) indicated that particles with the size of 300-830, 150-300, and 75-150 μm were the most abundant particles in road-deposited sediments collected from the Beijing Olympic Park. Size distribution of street dust collected from Baotou, China, showed that the particle size fraction of 50-100 μm was the most abundant (59%) followed by the 100-300 μm size fraction (26.4%) (Han et al., 2016). In contrast, Padoan et al. (2017) fractionated the road dust samples taken from the metropolitan area of Turin, Italy, into five different size classes including less than 2.5 μm, 2.5-10 μm, 10-50 μm, 50-200 μm, and 200-2000 μm. They reported the mass percentage of 4, 2, 5, 27, and 62 for the above mentioned size classes, respectively, very much similar to the distribution pattern of the street dust reported here.

Fine particles, particularly those with the mean aerodynamic diameter of 10 μm or less, referred to as PM_{10}, have been reported to be more hazardous to human health since such particles

could more easily penetrate pulmonary defenses and also lodge deep in the lung (Kjelgaard et al., 2004). The mean values of PM_{10} quantity, which corresponds to the sum of F7 and F8, in the street dust from HD, MD, LD, and NA are 11.3, 13.6, 8.0, and 24.3%, respectively. This value in the urban soils from HD, MD, and LD cities, and the natural area (NA) is 27.8, 21.7, 24.1, and 51.9%, respectively. Besides, the particles less than 100 μm in diameter (roughly corresponding to the sum of F4 to F8), account for 35.2, 44.1, 34.3 and 57.2% of the street dust in HD, MD, LD, and NA, respectively. Although these particles are not as hazardous as the PM_{10}, but they are believed to be easily suspended in the atmosphere and move to other areas in the wind stream (Han et al., 2016). Considering the higher concentration of toxic metals in fine-sized fractions, which will be discussed in the next subsection, the rate of generation and transfer of the street dust should be minimized in the area in order to protect the environmental quality.

The mean pH values of the urban soils and street dusts are about 7.9 with no statistically significant difference. Both urban soils and street dusts are non-saline with a mean EC value of less than 1 dS m^{-1}. Besides, soil and dust samples are highly calcareous with about 35 to 40% calcium carbonate equivalent. They also have 2.5 and 2.0% organic carbon content, respectively (Acosta et al., 2015).

3.2. Concentration of metal(loid)s in different size fractions and bulk samples

The concentrations of six metals (Pb, Zn, Cu, Cd, Cr, and Ni) and a metalloid (As) in bulk samples as well as in eight different size fractions of both urban soils and street dusts from three differently populated areas and also from the natural area are shown in Fig. 3. The metal(loid)s investigated could be grouped into two distinctive categories based on their concentrations in urban soils and street dusts. The first category includes Pb, Zn, Cu, Cd and Cr whose concentrations in the bulk street dusts and also in almost all their size fractions are higher to extremely higher than those in the bulk urban soils and almost all their size fractions. In contrast, the concentrations of the 2nd category elements including Ni and As in both bulk urban soils and street dusts and also those in their size fractions are almost identical. It is also important to note that the concentrations of Ni and As in soils and dusts and their size factions are generally low and comparable to those in non-polluted soils and sediments. Whereas, the high to extremely high concentrations of the first category elements in urban soils and street dusts and their size fractions clearly indicate how anthropogenic activities have greatly increased the level of these metals, particularly in the street

dust. Ordoñez et al., (2003) investigated the elemental composition of street dust and soils in Avilés, northern Spain. They reported that the concentrations of such metals as Zn, Cd, Hg, and Pb in urban deposits were very high in comparison with their average concentrations found in urban soils.

Figure 3 also clearly shows the influence of population density on the concentrations of different metals in urban soils and street dusts and their size fractions. In contrast to different responses of urban soils and their size fractions to the population density in terms of metals concentrations, the concentrations of most metal(loid)s, except As and Ni, in the street dust and their individual size fractions mostly follow the order HD>MD>LD>NA. This might firstly indicate that street dust is more highly influenced, than the urban soils, by those anthropogenic sources such as car emissions and asphalt abrasion whose rate of influence is population dependent. Secondly, this shows that environmental assessment based on the analysis of street dust is more reliable than the urban soil. In addition to the low concentration of As and Ni in bulk urban soils and street dusts and their fractions, their inconsistent response to population density seems to further corroborate their natural source.

The concentration of most elements in both urban soils and street dusts is size dependent (Fig. 3). As the size decreases from F1 (850-2000 μm) to F8 (< 2 μm), the concentration of most elements increases in all the three urban areas with different population densities. The degree of the size dependency of the concentration of elements (the concentration ratio of F8 to F1 fractions) is much higher in the street dust than the urban soils. This is also both element dependent and also a function of the population density which would be further discussed later. The widely reported association of higher quantities of elements with finer particles in soils, dusts, and sediments has been attributed to the relatively higher adsorption capacity and surface area of finer particles (e.g. Fergusson and Ryan, 1984; Lisiewicz et al., 2000; Acosta et al., 2009, 2011; Bi et al., 2013; Li et al., 2015; Han et al., 2016; Jayarathne et al., 2017; Padoan et al., 2017; Ayoubi et al., 2018). The high variability of the concentration of toxic metals in different size fractions well corroborates the significance of particle size fractionation when studies on risk assessment of human exposure to different contaminants in soils and dusts are to be carried out, as also emphasized by other researchers (Acosta et al., 2009, 2011; Cao et al., 2012; Kang et al., 2017; Padoan et al., 2017; Ayoubi et al., 2018).

Among the elements studied, the concentration of As in urban soils and street dusts is size independent, further confirming non-anthropogenic source of this element. It is also interesting to note that the concentration of all the elements in both soil and dust samples from natural area is not only much less than that from the 3 differently populated urban areas (as expected), but is also size independent. This suggests that human induced additions of toxic elements are mostly accumulated in fine sized fractions while naturally derived elements are almost equally distributed in different sized particles in soils and dusts.

Table 1 shows the correlation coefficients between the magnetic susceptibility at low frequency and the concentration of different metal(loid)s in the bulk soils and dusts. While there was no relationship between the two parameters in the bulk soil samples, there were very strong correlations between these two parameters in the street dust samples, except for As. Since magnetic susceptibility is much easier to measure as compared to the concentration of metals, investigators may use it to estimate the concentration of metals in future studies as also recommended by others (Wang et el., 2012; Ayoubi et al., 2018)

3.3. Enrichment factor

The enrichment factor (EF) values of all toxic metals computed for eight size fractions of urban soils and street dusts relative to the background concentrations of the natural soil are showed in Fig. S1 (supplementary material). Comparison of the values for soils and dusts indicates that almost all the fractions of the dust samples collected from HD, MD, and LD cities are more enriched in Pb, Zn, and Cu than their corresponding urban soils. This also shows that Cd and Cr are slightly more enriched in dust fractions than the soil fractions, particularly in medium to fine sized fractions from HD and MD areas. Whereas, neither urban soils fractions nor street dust fractions exhibited any enrichment in Ni and As. Most fractions of the urban soils from the 3 differently populated cities are either not detectably enriched with elements or only their fine sized fractions are slightly to moderately enriched of Pb, Zn, and Cu. In contrast, different size fractions of the street dusts are moderately to significantly (Pb, Zn, Cu, Cd and Cr) and even extremely significantly (Cu in F5 fraction of the HD city) enriched with metals. Street dusts and their size fractions studied are also much more enriched in metals as compared to the soil samples and their fractions from Murcia playground reported by Acosta et al. (2009). Considering that urban soils are more contaminated, with respect to metals, than the non-urban soils such as natural soils

(Acosta et al., 2011), street dusts investigated have been moderately to extremely influenced by anthropogenic activities.

Enrichment factor has not been widely reported for the street dust fractions. Han et al. (2016) investigated the grain-size contamination characteristics of metals in the street dust of Baotou, China. They reported that most dust samples were uncontaminated to moderately contaminated. Heavy metals were determined in bulk samples of household dust and street sediment from Celje city, Slovenia (Zibret and Rokavec, 2010). The results showed an increasing trend in Fe, Cr, Mn, Co, Mo, and Ni enrichment in both street sediment and household dust from the non-contaminated area to the most contaminated one. This research also indicated that the street sediment was more highly enriched with metals than the household dust.

There is no clear relationship between the population density and the degree of metals enrichment in the bulk urban soils and their fractions studied. In contrast, the influence of population density on metals enrichment in urban dust samples and their size fractions is obvious. In most cases, particularly with respect to more enriched metals (Pb, Zn, and Cu), the higher the population density, the higher the rate of enrichment. This definitely confirms that, among different human activities generating environmental contaminants, the population dependent ones, such as traffic and buildings heating systems, more significantly affect the level of toxic metals in the street dust.

Higher rates of metal enrichment are found in smaller sized fractions (Fig. S1 supplementary material). This is particularly true for metals with higher degree of enrichment such as Pb, Zn, and Cu. It is also interesting to note that all the 4 fractions smaller than 106 μm (F1, F2, F3, and F4) are distinctly less enriched with all elements, except for As which is not enriched at all, than the 4 fractions coarser than 106 μm (F5, F6, F7, and F8). Therefore, we suggest the cutoff value of about 100 μm for future studies when not all the fractions are to be investigated due to financial and/or time limitations.

Our results clearly show how important the fractionation of soil and dust samples could be, when their enrichment with different contaminants are evaluated. For example, our data indicates that the bulk street dust in the LD area is only moderately enriched in Pb, while F5, F6, and F7 fractions are significantly enriched with this toxic element. Bulk analysis of street dust also indicates the non-enriched status with respect to Cd in MD area, but the analysis of size fractions shows that particles < 50 μm in diameter are moderately enriched in Cd. Thus, if the risk

assessment is only based on the bulk analysis, the risk will be underestimated, as also discussed by Acosta et al. (2011) and Cao et al. (2012).

3.4. Metals mass loadings

The mass loadings were calculated in order to evaluate the relative contribution of each size fraction to the total concentration of elements in urban soils and street dusts in HD, MD, and LD cities and natural area (Fig S2. supplementary material). In general, grain size loadings of all the 7 elements appear to follow the same trend. In average, the top three fractions with the highest contribution to the total concentration of almost all the elements in soils (more than 50) are F5, F6, and F7 in HD city, F2, F4, and F7 in both MD and LD cities, and F6, F7, and F8 in NA site. Grain size loadings of the dust samples are slightly different from those of the soil samples. The top three fractions totally contributing more than 55% to the concentration of almost all the elements in urban and natural dusts include F2, F4, and F7 in HD and natural areas and F2, F3, and F4 in both MD and LD cities. Contrary to our results, Han et al. (2016) reported that more than half of the concentrations of all the metals they studied in the street dust was contributed by the grain size fraction of 50 -100 μm, almost the same size of our F4 fraction.

The grain size loadings of different elements presented in this paper are mostly controlled by the particle size mass percentage, and not very much by the element concentration. This seems to be due to the fact that either the magnitude of changes in concentration of the elements with size is not high enough or the changes in the concentration of all the elements with size occur simultaneously.

4. Conclusions

Heavy metal(loid)s geochemistry of physically fractionated street dusts and urban soils from 3 differently populated cities and a non-settled area in Murcia Region, Spain, provided great insight into their environmental quality and assessment. Such insight would never be achieved if only the bulk samples were examined.

Urban street dusts and the dust from natural area are medium to coarse textured and so are the 3 urban soils. The natural soil, however, is much finer in texture having more than 50% particles less than 10 μm in diameter. If urban soils and also all the street dusts are considered to have originated from the natural soil, it seems that anthropogenic activities as well as aeolian

processes during the detachment and transport have resulted in decreasing the amount of clay-sized and increasing the quantity of sand-sized particles. Besides, population density does not seem to control the particle size distribution of street dust and urban soil.

Two distinctive categories of metal(loid)s were recognized based on their concentrations. In the first category, the size dependent concentrations of Pb, Zn, Cu, Cd and Cr in bulk urban soils and also in almost all their size fractions are higher to significantly higher than those in the bulk street dusts and almost all their size fractions. In contrast, the concentrations of the 2nd category elements (Ni and As) in bulk soils and road dusts and also those in their size fractions are very low and also size independent. In addition, population density has great positive influence on the concentration of the 1st group of elements, particularly in the street dusts. High size dependency of the concentrations of most elements studied, particularly those with high level of contamination in both street dusts and urban soils, indicates the necessity of physical fractionation in environmental monitoring and assessment of soils and sediments.

EF values indicate that different size fractions of urban dust samples are very much more enriched in Pb, Zn, and Cu, but only slightly more enriched in Cd and Cr as compared to urban soil fractions. No enrichment with either Ni or As was recognized in urban soil and street dust fractions. The influence of population density on metals enrichment was observed in urban dusts but not found in urban soils, suggesting the more contribution of anthropogenic inputs to the street dust as compared to the urban soil.

Environmental assessment based on the bulk sample analysis appears to be misleading in most cases, if not all. This is mainly due to the fact that different sized particles of soils, dusts, and similar materials do not directly enter human body and/or food chain proportional to their relative abundance. Besides, particles having different sizes normally carry various quantities of environmentally hazardous metals or other contaminant. In general, fine-sized particulates are more enriched with contaminants and also more easily enter the target tissues in human body. On the other hand, the fractionation of soil, dust, and similar deposits is a very time consuming and, therefore, expensive process. Besides, size-resolved environmental assessment of soils and dusts undoubtedly needs substantially higher number of samples to be extracted and instrumentally analyzed. Therefore, researchers need to know how critical and necessary the fractionation really would be for environmental assessment of hazardous pollutants in soils and sediments. If research fund and/or time are not limited, fractionation of samples and analysis of as many fractions as

possible would certainly provide more information and better assessment. If such limitations exist, which is often the case, the reconnaissance survey of the bulk samples would be needed before the decision is made on whether or not the researcher should proceed with the fractionation. Analysis of bulk samples appears to be enough when no or minimum enrichment of the samples is expected. But, environmental assessment of bulk samples for moderately to highly contaminated soils, dusts, and similar materials would often provide misleading interpretation, and should be avoided. Furthermore, fractionation of samples into two size classes using 100 μm as cutoff diameter is proposed to obtain a more reliable evaluation with the minimum cost possible.

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Table 1. Pearson correlation coefficients between the concentration of metal(loid)s and magnetic susceptibility at low frequency in the bulk urban soil (n=36) and bulk street dust samples (n=14)

	Pb	Zn	Cu	Cd	Cr	Ni	As
Urban soil	0.16^{ns}	0.02^{ns}	-0.12^{ns}	-0.15^{ns}	0.07^{ns}	0.10^{ns}	0.30^{ns}
Urban dust	0.84**	0.67**	0.75**	0.73**	0.73**	0.67**	-0.15^{ns}

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

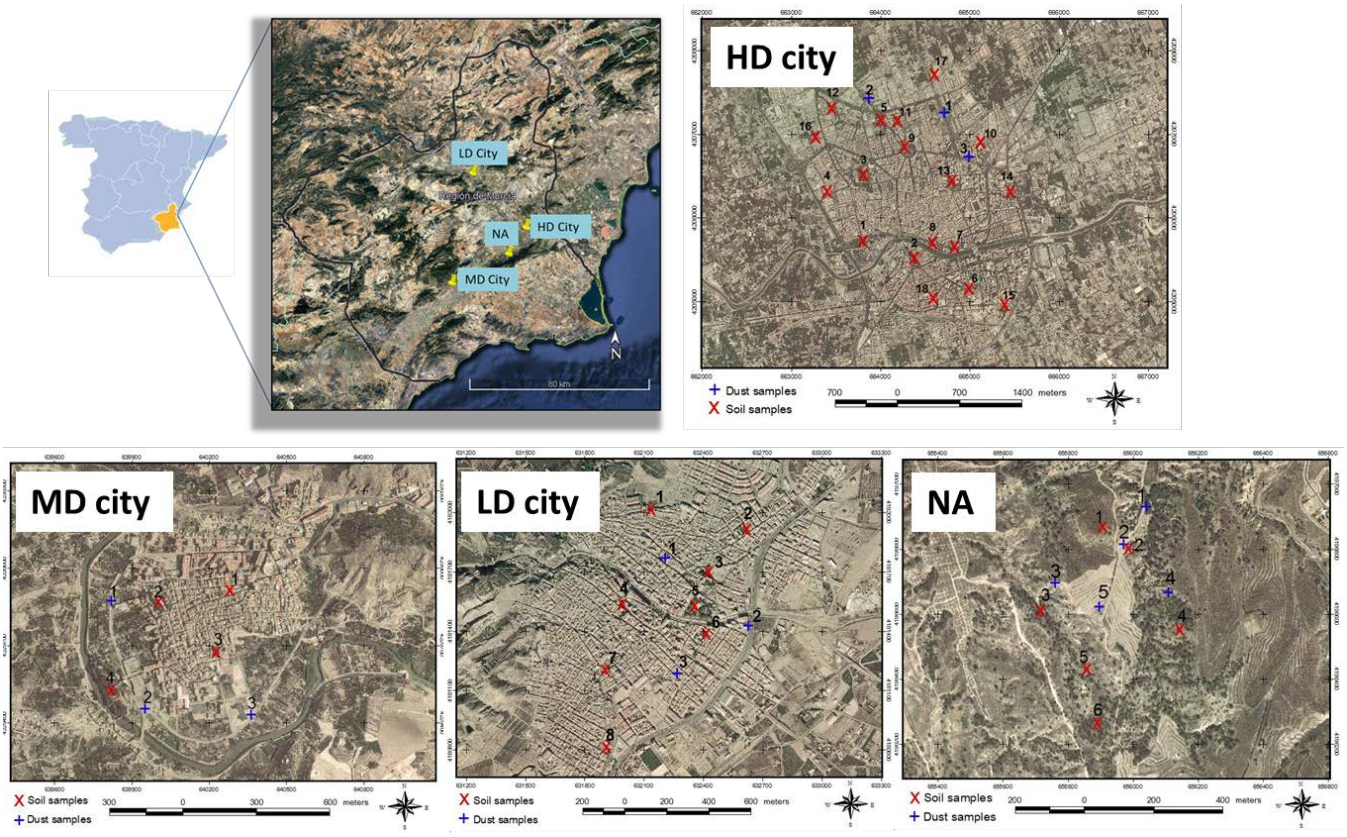


Fig. 1: Locations of urban areas with different population densities (HD, MD, and LD) and the natural area (NA) studied in Murcia Province, southeastern Spain, and spatial distribution of soil and dust sampling

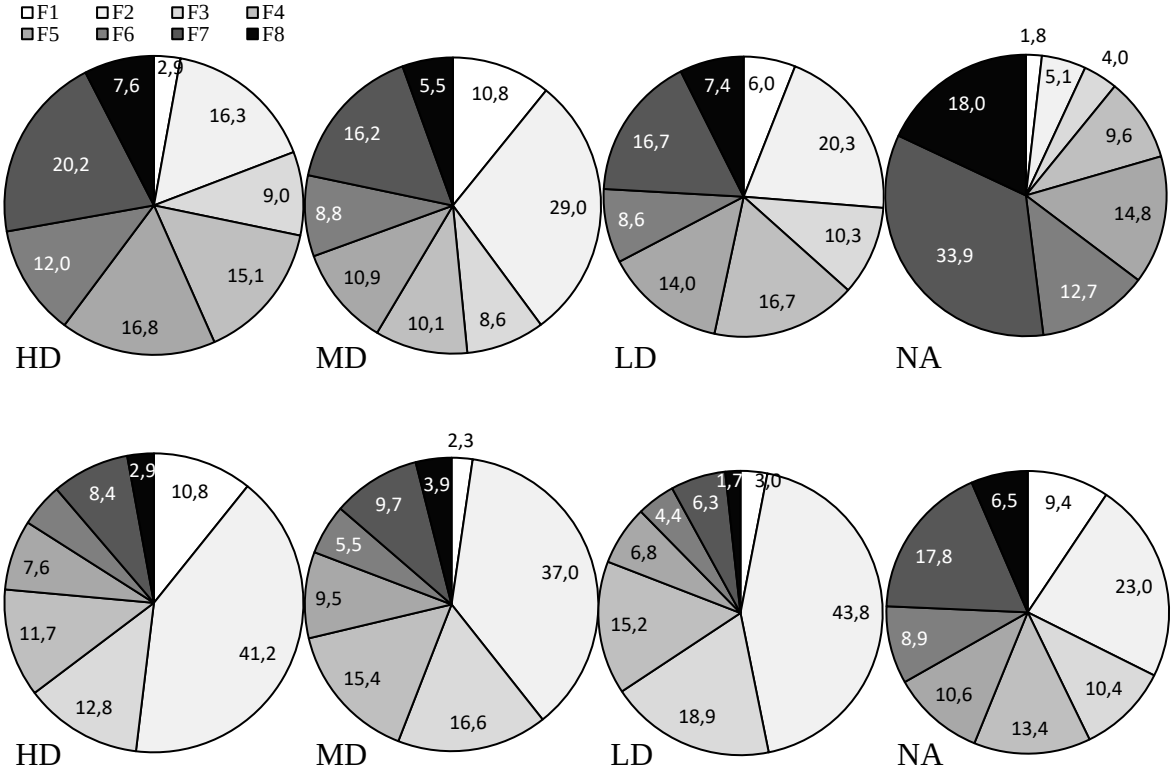
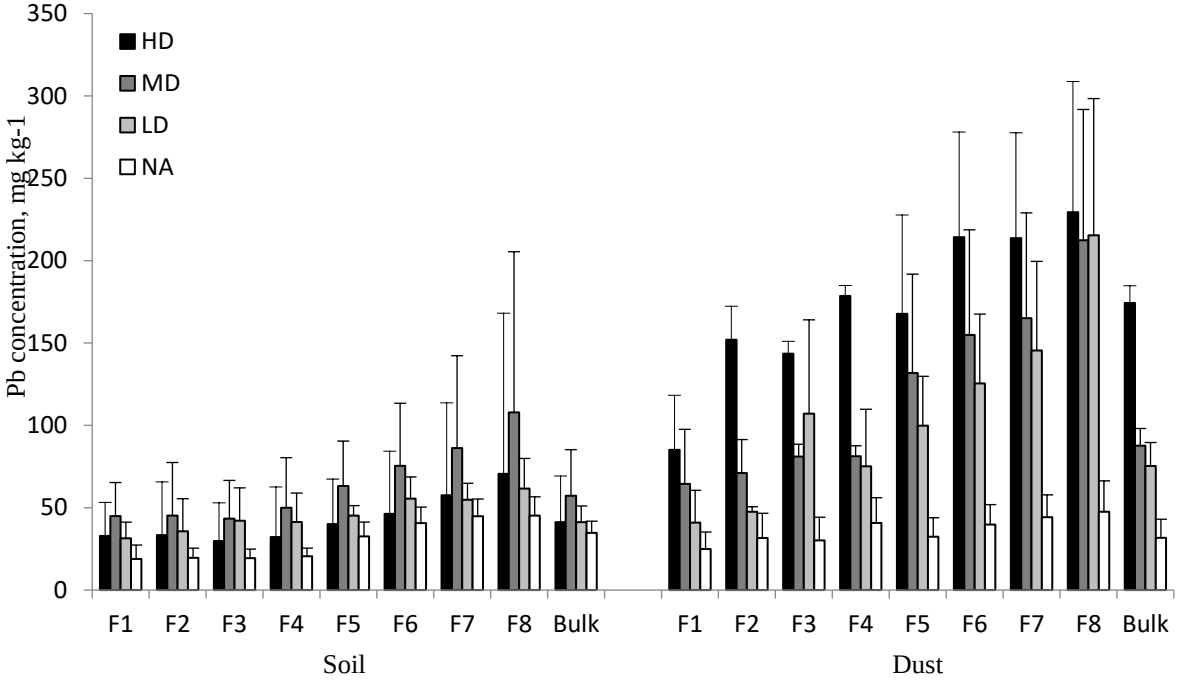
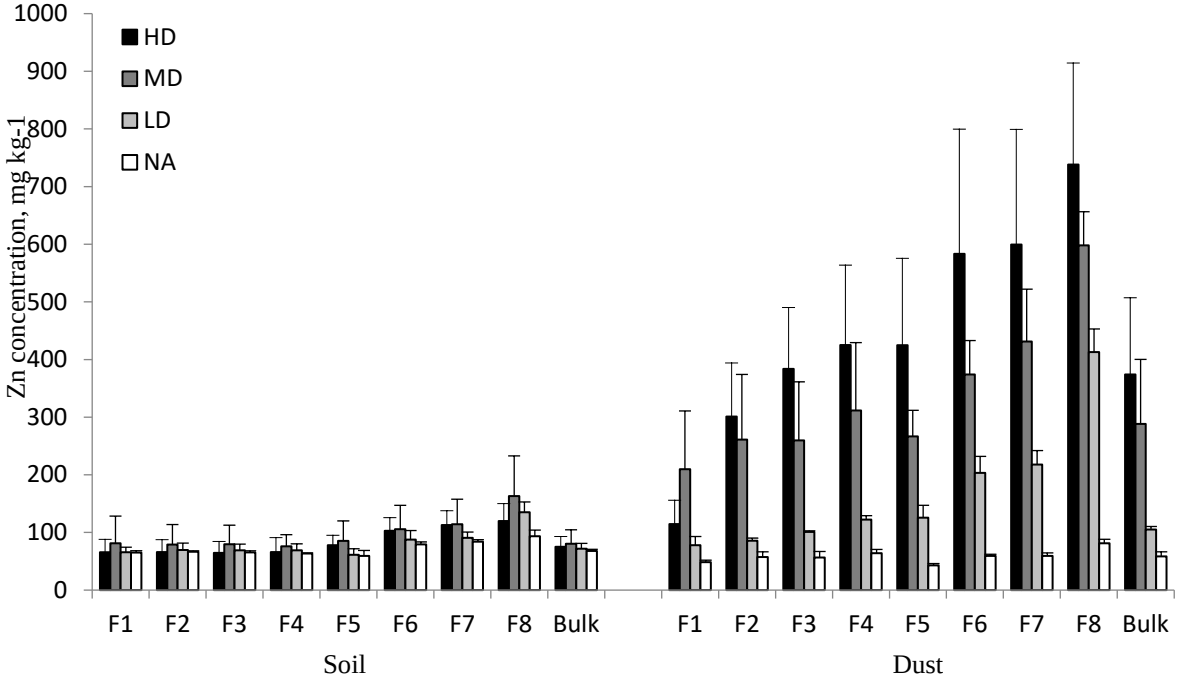
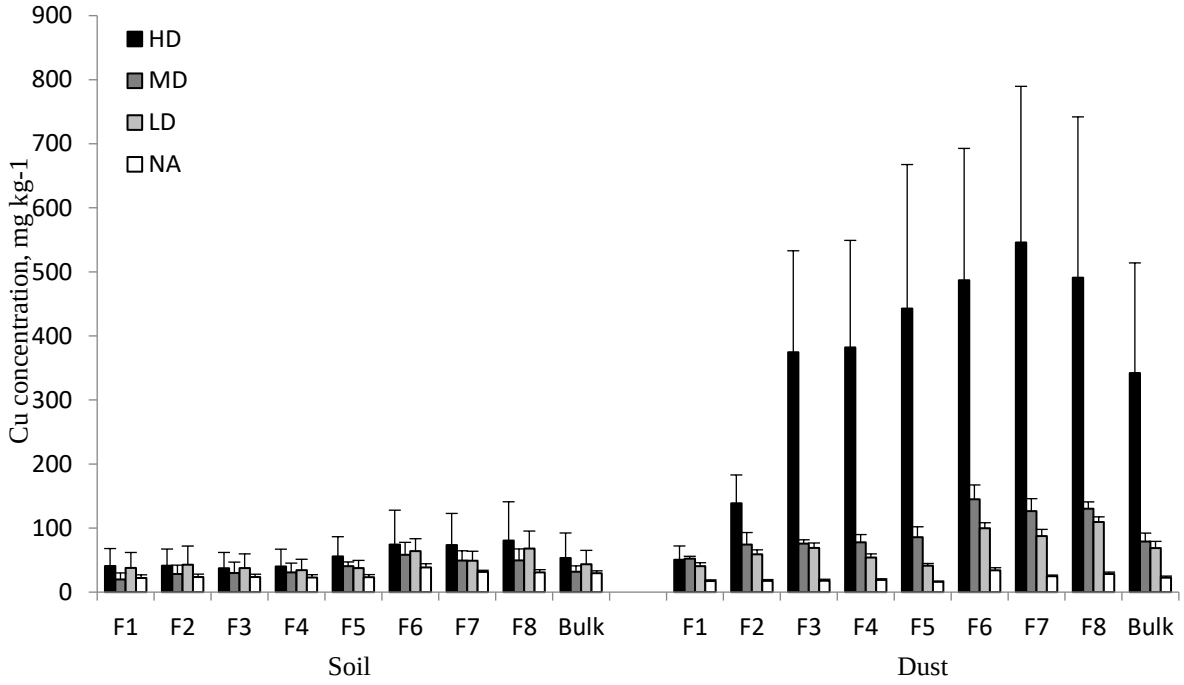
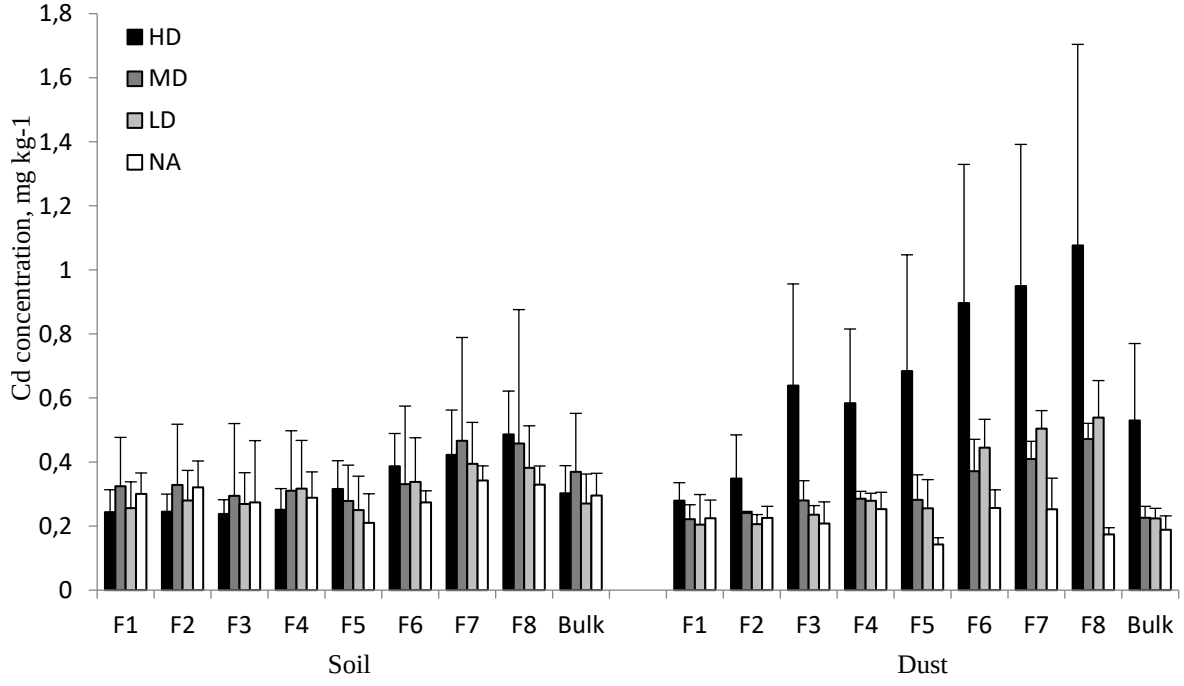


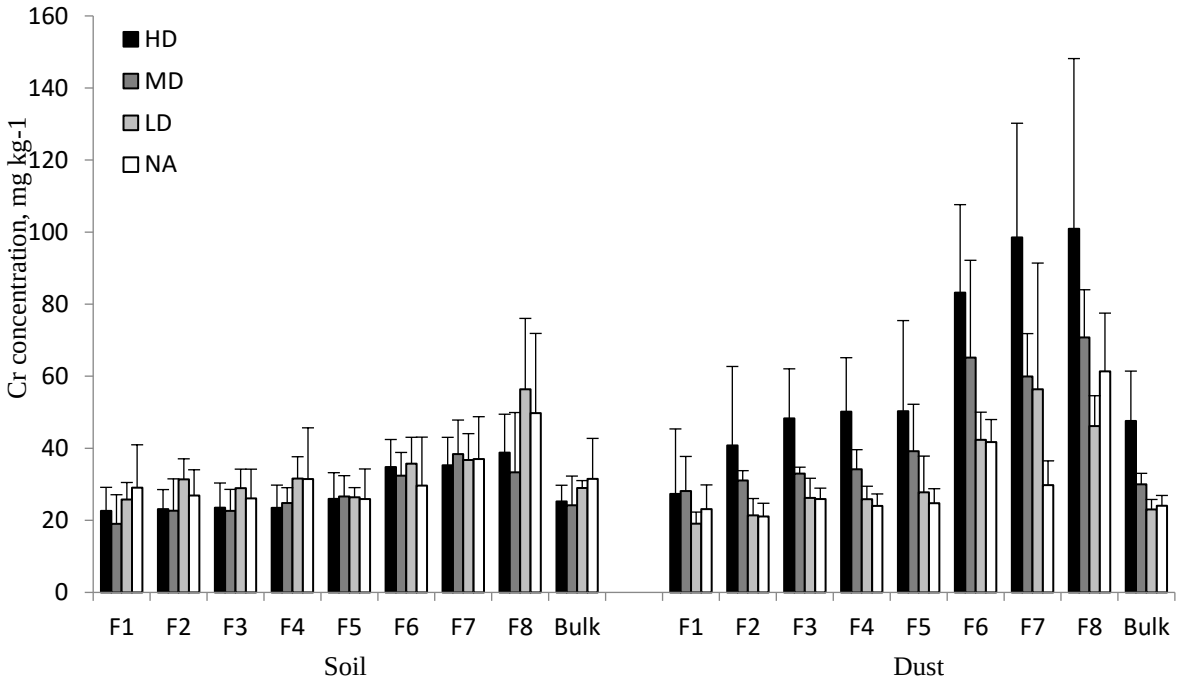
Fig. 2: Average particle size distribution of soils (top) and road dusts (bottom) in the three cities (HD, MD, and LD) and the natural area (NA) studied.

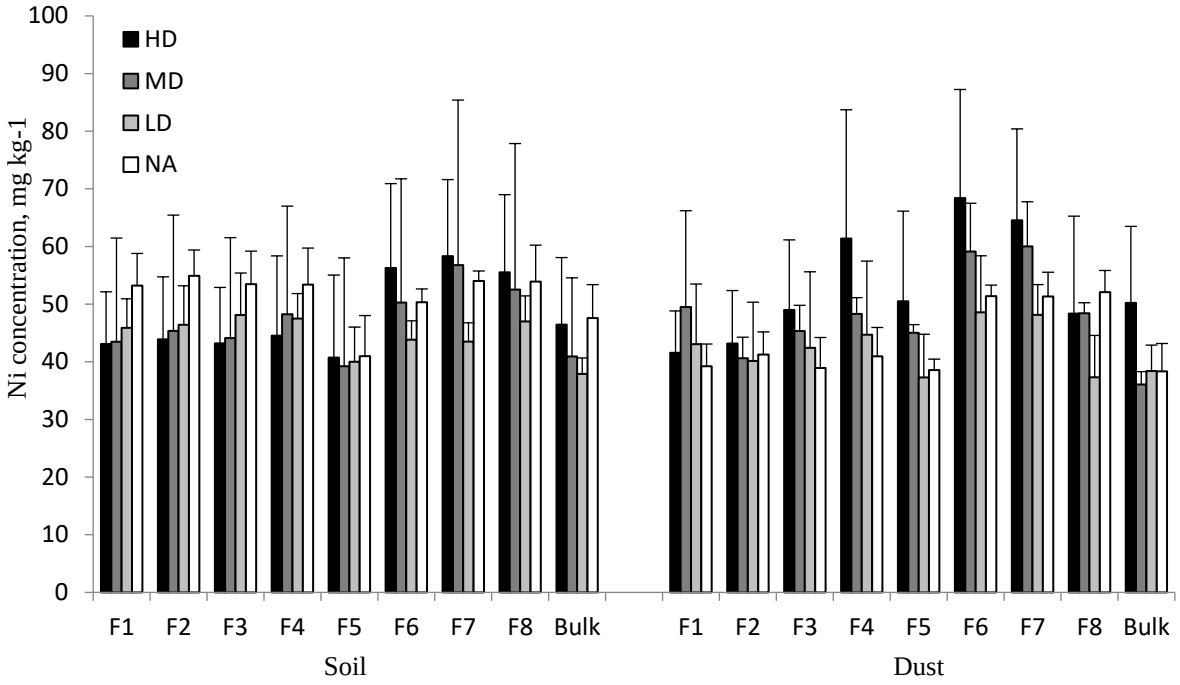

HD
MD
LD
NA
Pb concentration, mg kg-1
350
300
250
200
150
100
50
0
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Soil
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Dust


HD
MD
LD
NA
Zn concentration, mg kg-1
1000
900
800
700
600
500
400
300
200
100
0
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Soil
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Dust


HD
MD
LD
NA
Cu concentration, mg kg-1
900
800
700
600
500
400
300
200
100
0
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Soil
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Dust


HD
MD
LD
NA
Cd concentration, mg kg-1
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Soil
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Dust


HD
MD
LD
NA
Cr concentration, mg kg-1
160
140
120
100
80
60
40
20
0
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Soil
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Dust


HD
MD
LD
NA
Ni concentration, mg kg-1
100
90
80
70
60
50
40
30
20
10
0
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Soil
F1 F2 F3 F4 F5 F6 F7 F8 Bulk
Dust

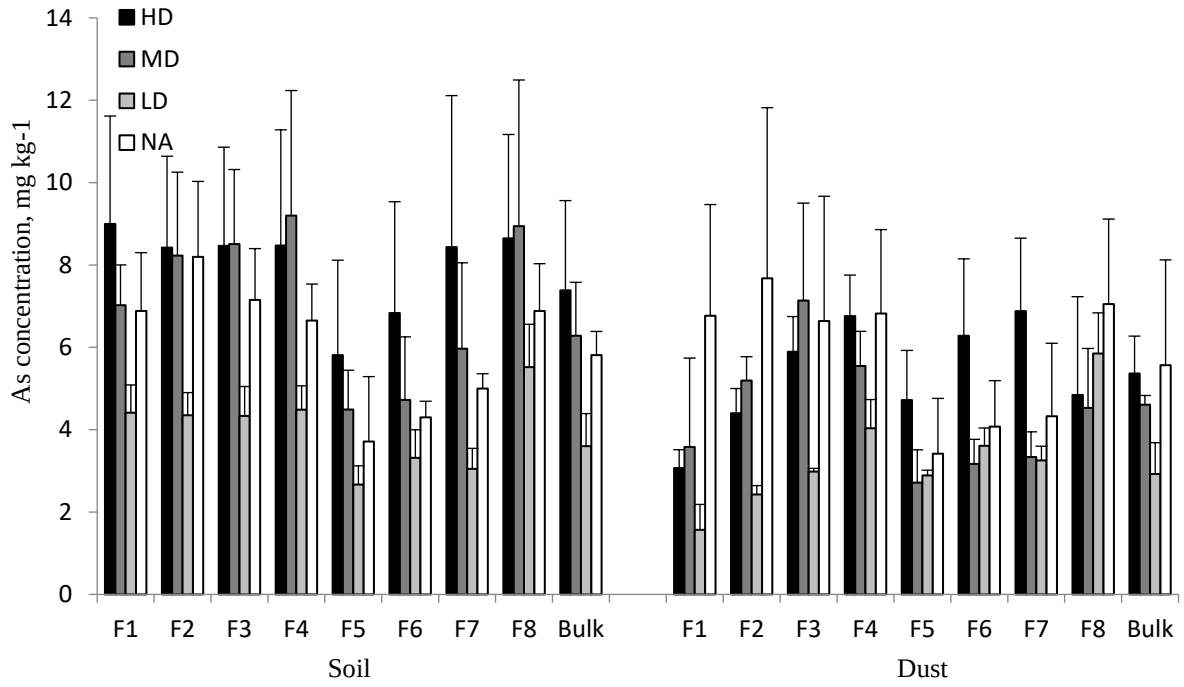


Fig. 3: Mean concentration of different metal(loid)s in different particle size fractions and the bulk sample of the urban soils and street dusts affected by population density.