A comparative study between the fluxes of trace elements in bulk atmospheric deposition at industrial, urban, traffic and rural sites

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ABSTRACT

The input of trace elements via atmospheric deposition towards industrial, urban, traffic and rural areas is quite different and depends on the intensity of the anthropogenic activity. A comparative study between the element deposition fluxes in four sampling sites (industrial, urban, traffic and rural) of the Cantabria region (northern Spain) has been performed. Sampling was carried out monthly using a bulk (funnel-bottle) sampler. The trace elements As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, Zn and V were determined in the water soluble and insoluble fractions of bulk deposition samples. The element deposition fluxes at the rural, urban and traffic sites followed a similar order (Zn>Mn>>Cu≈Ti>Pb>V≈Cr>Ni>>As≈Mo>Cd). The most enriched elements were Cd, Zn and Cu, while V, Ni and Cr were less enriched. An extremely high deposition of Mn was found at the industrial site, leading to high enrichment factor values, resulting from the presence of a ferro-manganese/silico-manganese production plant in the vicinity of the sampling site. Important differences were found in the element solubilities in the studied sites; the element solubilities were higher at the traffic and rural sites, and lower at the urban and industrial sites. For all sites, Zn and Cd were the most soluble elements, whereas Cr and Ti were less soluble. The inter-site correlation coefficients for each element were calculated to assess the differences between the sites. The rural and traffic sites showed some similarities in the sources of trace elements; however, the sources of these elements at the industrial and rural sites were quite different. Additionally, the element fluxes measured in the insoluble fraction of the bulk atmospheric deposition exhibited a good correlation with the daily traffic volume at the traffic site.

Keywords

Atmospheric deposition; trace elements; deposition variability; element enrichment

INTRODUCTION

Total atmospheric deposition of trace elements can be considered a good indicator of the influences of anthropogenic activities on the environment. Moreover, the analysis of atmospheric fall-out is useful for identifying the variability, fluxes and sources of air pollutants (Bermudez et al. 2012). As a consequence of human activity, the emission of trace elements into the atmosphere strongly depends on the land use and anthropogenic intensity (Styers and Chappelka 2009); therefore, the input of such elements into the environment via atmospheric deposition varies widely among industrial, urban, sub-urban, rural and remote areas (Shi et al. 2012). However, the contribution of long-range transport of trace metals to total deposition should not be neglected.

Some trace elements have a natural origin; e.g. Al, Ca, Fe, Mg and Ti usually originate from soil dust whereas Na, K, Mg and Ca are associated to sea salt aerosols (Hovmand and Kystol, 2013). However, many trace elements that can potentially affect the human health are mainly emitted by anthropogenic activities, such as road traffic (vehicle exhaust gases and particles, wearing of brakes and tires, asphalt abrasion) (Thorpe and Harrison 2008); other modes of transportation, such as shipping (Viana et al. 2009); domestic combustion (Kemp 2002); and industrial activities, such as large combustion facilities (Petaloti et al. 2006), iron and steel production, non-ferrous metallurgy, ceramic industries, or petrochemical plants (Querol et al. 2007). An important amount of particulate matter-bound metals is also emitted from fugitive sources, such as harbor and industrial estates (Castillo et al. 2013).

Atmospheric deposition is typically studied in regional, rural and remote areas, with the objective of determining the regional and transboundary transport of pollutants toward these ecosystems (Sweet et al. 1998; Kyllönen et al. 2009; Deboudt et al. 2004; Hovmand and Kystol 2013). However, studies on urban and industrial-influenced inputs are relatively abundant in the literature (Azimi et al. 2003, 2004, 2005a,b; Motelay-Massei et al. 2005; Sharma et al. 2008; Mijic et al. 2010; Usero and Gracia 1986a,b; Wong et al. 2003; Jeffries and Snyder 1981; Tate and Bates 1984; Rossini et al. 2005, 2010; Soriano et al. 2012; Castillo et al. 2013). The input of trace metals via atmospheric deposition is usually much higher in urban and industrial environments; therefore, higher elemental concentrations in soils and plant tissues are found at those sites compared to rural environments (Styers and Chappelka 2009). In these areas, the contribution of dry deposition (mainly sedimenting particles from local point sources) to the total deposition may be of significant importance (Aas et al. 2009). Some studies have focused their investigations on the soluble fraction of the atmospheric deposition of metals (Tate and Bates 1984, Usero and Gracia 1986a). Because heavy metals in their soluble forms transfer faster towards the plants and the ground water, they represent a greater hazard to the environment than metals from insoluble fraction.

Atmospheric deposition is one of the main pathways by which trace elements (metals and metalloids) reach soils, surface waters and seawater environments (Soriano et al. 2012; Okubo et al. 2013; Castillo et al. 2013). Metal deposition is an important source of soil contamination; metals have a relatively short period of life in the atmosphere, mainly metals associated with sedimenting particles, but once incorporated into soils, the water insoluble fraction of these elements tends to accumulate and can alter biogeochemical cycles (Pouyat and McDonnell

1991). The metal enrichment of soils may affect the growth of vegetation and may disturb photosynthesis (Li et al. 2010). Furthermore, depending on the mobility of the deposited metals and the physico-chemical characteristics of the soil, the ground and surface waters may also become polluted, causing potential detrimental effects to human health and the environment.

Several recent studies have reported the relationships between atmospheric deposition of trace elements and soil pollution. For example, Soriano et al. (2012) studied the input of toxic metals into soils via deposition in an industrial area of Castellon (Spain). They reported that the implementation of correction measures has reduced the levels of metals in settled dust and has led to a lower intake of heavy metals into the soil. Herndon et al. (2011) concluded that atmospheric transport of manganese led to soil contamination in an industrial area of Pennsylvania (USA); the study revealed that approximately 53 % of Mn in ridge soils was attributed to atmospheric deposition from anthropogenic sources. High concentrations of Mn in soils were also observed in Northern Italy (Vallecamonica), where ferroalloys plants worked for over a century until 2001 (Borgese et al. 2013). Bermudez et al. (2010) identified the levels and sources of heavy metals and trace elements in topsoils from industrial (cement plant and a former open-cast uranium mine), agricultural and residential areas in the region of Cordoba (Argentina). Later, Bermudez et al. (2012) reported the relationship between atmospheric deposition of these elements and their levels in topsoils and wheat in this region of Argentina. They concluded that the input of heavy metals from the atmosphere may lead to potential health hazards of wheat consumption.

Cantabria is a small region in northern Spain that combines different land uses with different anthropogenic intensities; urban, industrial and rural areas are present in a relatively small total area (5300 km^2). Previous studies have shown great differences between the metal levels in particulate matter (PM10) in urban (Santander) and rural (Los Tojos) areas in this region (Arruti et al. 2010; 2011). Furthermore, higher metal levels were identified in Cantabrian towns in the vicinities of industrial point sources (Ruiz et al. 2014). Considering these previous findings, the present study aims to investigate the variability of trace elements in bulk atmospheric deposition in urban, industrial, traffic and rural areas of the Cantabria region. Both the water soluble and the insoluble fractions were taken into consideration. In addition, using a report regarding the background levels of heavy metals and trace elements in soils in the Cantabria region (Gobierno de Cantabria, Consejería de Medio Ambiente 2011), we performed an analysis of the levels of the studied elements in local soils in comparison with the input of these elements by bulk deposition.

EXPERIMENTAL METHODS

Study area

This study was performed in the Cantabria region (593,121 inhabitants, 2011) located in northern Spain. This small region (5300 km^2) has a formidable array of landscapes and environments, such as coasts (approximately 135 km in front of Cantabrian Sea), high mountains (Picos de Europa) and deep valleys, but it also accommodates urban areas (Santander Bay and Torrelavega) and some industrial estates, mainly related to chemical and metallurgical activities. So, the heterogeneity of this small region allows the comparison of the deposition rates of some trace elements based on different land uses. Four sampling sites representing urban, industrial, traffic and rural environments were selected for this study. The location of the sampling sites is shown in Figure 1, and a brief description of the sampling points is given below.

Santander (SANT) is a medium-sized coastal city (179,921 inhabitants, 2011) that extends over a wide bay. It is mainly commercial and residential in nature with a low-middle pollution level. However, some industrial areas (with mostly iron, steel and ferroalloy manufacturing plants) are located in the Santander suburbs (5-10 km SW) upwind of the city. The SANT sampling site (43°28'22.33"N, 3°47'52.67"W, 23 m a.s.l.) is located on the campus of the University of Cantabria, on the rooftop of the building "E.T.S. de Ingenieros Industriales y de Telecomunicación" (30 m above ground). The sampling point is representative of an urban background site.

Maliaño (MAL) (9,609 inhabitants, 2011) is a small town located in the southern part of Santander Bay. Maliaño is highly influenced by close industrial areas, mainly by a ferro-manganese alloy plant located 0.66 Km SSE of the monitoring station. The MAL sampling site (43º25'12.35"N, 3º50'30.13"W, 5 m a.s.l.) is situated on the rooftop of a municipal building "Casa El Botiquín" (3 m above ground). Although MAL is also influenced by urban and traffic activities, this site is considered an industrial site.

Bárcena Mayor (BAR) (434 inhabitants, 2011) is a small village at the heart of Cantabria located in the Nature Reserve of Saja-Besaya. The BAR sampling site (43°09'25.86" N, 4°14'21.44" W, 431 m a.s.l.) is situated between Bárcena Mayor and Los Tojos villages in a plot surrounded by woodland area and close to a cottage and a low traffic road, 50 km SW of Santander. This site is considered to be rural.

The fourth site was located in a place very close to the main motorway that crosses the Cantabria region (A8). This site (43°19'13.46"N, 4°13'53.03"W, 201 m a.s.l.) was located 1.3 km NNW of Cabezón de la Sal (CAB). Although the location of this roadside site (kilometer mark 248) does not represent the maximum traffic intensity on this motorway, this site receives metal inputs from only traffic sources; thus, this allows us to consider it a traffic site.

Figure 1 also shows the wind roses calculated from data registered in meteorological stations that were located close to Bárcena Mayor/Cabezón de la Sal and Maliaño/Santander sites respectively. The prevailing wind directions in the area of Bárcena Mayor/Cabezón de la Sal are S and SW. The highest wind speeds are found when NW wind is blowing. In the Santander bay

SW and NE are the directions of the predominant winds; this pattern has been previously shown in the literature (Ruiz et al., 2014): light winds blow predominantly from the SW in the morning but, in the afternoon, they reversed direction to become NE onshore moderate breezes, mainly in the summer.

Sampling

Bulk atmospheric deposition sampling was performed using the surrogate surface approach, with a collector made with a high density polyethylene bottle (10 L) connected to a funnel of 0.0779 m^2 collection area. The collector was placed on a steel chassis with a protective ring on the top to prevent bird nesting.

The device was based on the standard EN 15841:2009 (Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition). Although some errors in assessing atmospheric deposition with the surrogate approach could result from poor sampling properties and defective sampling strategies (Dämmgen et al., 2005), the European Committee for Standardization (CEN) recommends bulk (bottle/funnel) samplers to collect and assess the atmospheric deposition of metals. Aas et al. (2009) evaluated sampler uncertainties of different collectors (wet only, bulk, Bergerhoff and bulk bottle/funnel); the authors showed that the lowest uncertainty was found for the bulk bottle/funnel sampler. This sampler is recommended to measure total atmospheric deposition at industrial and urban sites, mainly when total deposition is not only due to precipitation events (Aas et al. 2009). The funnel was 1.7 m above the ground to avoid the collection of re-suspended soil particles. The sampling was carried out monthly. At the end of each sampling period, the funnel was rinsed with 250 ml of Milli-Q water and all equipment was replaced with a clean one. At the SANT site, sampling was performed from September 2009 to February 2013. At the MAL and CAB sites, the sampling period was from January 2012 to February 2013. At the BAR site, sampling was conducted from November 2011 to February 2013. In summary, 40 samples were collected at the SANT site, 16 at the BAR site, and 13 at the CAB and MAL sites.

The levels of heavy metals and trace elements in the soil of Cantabria were available for several sites of the region, some of them close to the deposition sampling sites (Gobierno de Cantabria, Consejería de Medio Ambiente 2011). The average distances between the deposition sites and the soil sampling points were 2.3, 2.7, 6.3 and 3.6 km in SANT, MAL, BAR and CAB sites, respectively. The averaged trace element levels at each site were used in the present work for comparison purposes.

Sample treatment and chemical analysis

Bulk atmospheric deposition samples were transported to the laboratory at the end of each sampling period. The precipitation amount was determined via gravimetry, and pH was measured in some samples to determine their acidity. The pH ranged from 5.4 to 7.2 at the MAL site; from 4.5 to 6.4 at the CAB site; from 4.6 to 7.6 at the BAR site; and from 5.9 to 6.9 at the SANT site. Subsequently, samples were filtered through 0.45 µm membrane filters (mixed cellulose esters, Millipore, 47 mm i.d.) to separate the soluble and insoluble fractions. The water soluble fraction was then acidified with nitric acid to pH=1 and stored at 4°C prior to analysis.

The sample treatment for the analysis of trace elements in the insoluble fraction from the bulk atmospheric deposition was in accordance with the standard EN-UNE 14902:2005 (Standard method for the measurements of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter). A microwave-assisted acid digestion of filters was performed for 1 h, during which time the temperature was slowly increased to 185 °C. The acid mixture was 8 ml of 65% HNO_3 (Suprapur®, Merck) and 2 ml of 30% H_2O_2 (Suprapur®, Merck). Arsenic, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, Zn and V were determined using an Agilent 7500 CE collision/reaction cell inductively coupled plasma mass-spectrometer (CRC-ICP-MS) operating in hydrogen mode to avoid matrix interferences. Rhenium was used as internal standard and a multi-element standard solution was used for the external calibration. To minimize the contamination of samples, the ICP-MS was operated in a clean room. Due to the relatively low Ti recovery from NIST 1649 reference material (68 %), the Ti level in the insoluble fraction of the atmospheric deposition was corrected, as it was previously reported in Fernández-Olmo et al (2014). Further details regarding the procedure for the trace metals analysis and quality assurance were also described in the later paper.

RESULTS AND DISCUSSION

1. Levels of trace elements in bulk atmospheric deposition in Cantabria

The levels of the studied elements in the bulk atmospheric deposition samples are presented in Figure 2. Bulk atmospheric deposition was calculated as the sum of the water soluble and water insoluble fractions. Additionally, the levels of the studied elements in Cantabrian soils, at sites close to the bulk atmospheric sampling points, are presented in Figure 3. These values were calculated from a report on the background levels of heavy metals and trace elements in soils in the Cantabria region (Gobierno de Cantabria, Consejería de Medio Ambiente 2011).

The fluxes of the studied elements in the bulk atmospheric deposition samples from the rural, urban and traffic sites followed a similar order, Zn>Mn>>Cu≈Ti>Pb>V≈Cr>Ni>>As≈Mo>Cd, with the exception of a higher flux of Cr instead of Pb at the urban site (SANT). This order changed for the industrial site, with a much higher deposition flux of Mn, to Mn>>Zn>>Ti>Cu>Pb>Cr>V>Ni>>As≈Mo>Cd.

"This order changed for the industrial site, with a much higher deposition flux of Mn, to Mn>>Zn>>Ti>Cu>Pb>Cr>V>Ni>>As≈Mo>Cd. The element deposition fluxes measured in the present study are compared with those determined in other worldwide regions at urban, industrial, traffic and rural/regional sites (see Table 1). It can be observed that the deposition fluxes of most of the studied elements in Cantabria are within and in some cases below the range found in other regions, with the exception of Mn and Zn. In particular, the Zn deposition flux in Santander is one of the highest found in urban sites; with respect to Mn, its levels in the bulk atmospheric deposition in the urban and mainly in the industrial sites are much higher than those found in other urban and industrial sites. The industrial sampling point was located close to a ferromanganese alloy plant and this dramatically increased the measured manganese deposition flux. Previous studies have shown high Mn levels in particulate matter (Moreno et al. 2011; Arruti et al. 2010, 2011) and atmospheric deposition (Fernández-Olmo et al. 2014) in the south part of the Santander Bay. Titanium, a typical crustal element, showed the highest levels in rural and urban soils; however, at the industrial and traffic sites, it was lower than Mn and Zn. Important differences in the element profiles of the soils were found among the industrial, urban, rural and traffic sites compared with the profiles found in the bulk atmospheric deposition. This is most likely because the "unpolluted" local soil composition strongly contributes to the final soil composition when the metal input by atmospheric deposition is not elevated. This can be observed in the case of Zn at the traffic site; a high average value of Zn in the traffic soil is found (632 mg/kg), but this is due to an abnormal Zn level in one of the soil sampling points (1,830 mg/kg). In the case of the industrial site, the enrichment of Mn in local soils is evident (4,333 mg/kg). The relationship between the manganese enrichment in soils and industrial inputs by atmospheric deposition has been previously identified (Borgese et al. 2013; Herndon et al. 2011; Pavilonis et al. 2014).

Seasonal fluctuations of the monthly average daily fluxes of the studied elements in the water soluble fraction are shown in Figure 4. The rainfall amount was also plotted to detect any possible relationship between metal fluxes and precipitation. As a general rule, higher precipitation amounts registered in the fall and winter lead to higher fluxes of elements in the water soluble fraction of the atmospheric deposition (Figure 4). With the exception of As, Cd and Mo, the lowest element fluxes were observed in the summer, when the lowest rainfall amount was registered. An increase in the rainfall amount may decrease the metal contents in dry deposition samples (Li et al., 2012) but may increase the metal fluxes in wet deposition samples (Morselli et al. 2003; Lynam et al. 2014). At the SANT site, the seasonal fluctuation found in the precipitation amount was consistent with the metal flux variation in the soluble fraction of the atmospheric deposition which was previously shown by Fernández-Olmo et al. (2014). This behavior is more difficult to recognize for the CAB, BAR and MAL sites, most likely due to insufficient data to identify a reliable seasonal trend (13-16 samples instead of 40 at the SANT site).

The contribution of the water soluble fraction to the total bulk deposition was calculated for all studied elements (Figure 5). Important differences in metal solubilities were found among the rural, traffic, urban and industrial sites. The highest metal solubilities were found at the traffic and rural sites (higher than 70 % except for Cr and Ti), the urban site showed intermediate solubilities, and the lowest solubilities were found at the industrial site (all the elements showed solubilities lower than 51 %). The proximity of the MAL site to an industrial facility clearly increased the metal input by atmospheric deposition but with a much higher contribution of insoluble particles, most likely from settled dust. Titanium and Cr were the least soluble elements, whereas Zn and Cd were the most soluble. The low solubility of Ti in the atmospheric deposition samples for all sites can be attributed to its crustal origin, most likely from soil resuspension. These results are consistent with other reports in the literature: the highest metal solubilities found in wet deposition samples from an urban area (Bologna, Italy) were for Zn (74 %) and Cd (68 %), and the lowest was for Cr (39 %) (Morselli et al. 2003).

High solubilities of Zn in wet deposition were also reported by Guieu et al. (1997) and Cizmecioglu and Muezzinoglu (2008).

The correlation coefficients between the studied elements in both the soluble and the insoluble fractions of the atmospheric deposition for the four sites were calculated (see Tables S1 and S2 of the Supplementary Material). The highest correlations between nearly all studied elements were found for the insoluble phase of the atmospheric deposition at the traffic site. This indicates a common origin of the studied elements at this site, most likely due to the resuspension of low solubility road dust. The main difference between the correlation matrices for the soluble and insoluble phases at the traffic site is the lack of correlation between Mn, Pb and Ti with the other elements in the soluble fraction, which might indicate that these elements are not directly emitted from vehicles but are derived from soil resuspension mixed with road dust. A similar result was found at the rural site, where Mn and Ti are not correlated with any element in the soluble phase of the atmospheric deposition. At the rural site, poor correlation coefficients between the studied elements were found in the insoluble phase; the highest correlations were found for As/Cd, As/Ti, Cu/Ti, Cr/Ti, Cr/Ni, Ni/Cr and Ni/Mo, which are assumed to derive from soil resuspension (those associated to Ti) and from long-range transport of particles from a coal-fired power station located 60 km SW (those associated to Ni and Cr). Figure 1 shows that S and SW are the prevailing wind directions in Bárcena Mayor site for the studied period. A previous study carried out in this woodland area showed that the levels of PAHs in PM10 were also influenced by this power plant (Arruti et al. 2012). Higher correlations between almost all elements (with the exception of Mn, Ti and Pb) are found in the soluble phase, which may be associated with the local traffic from an adjacent road and with the aforementioned power station.

At the industrial site, the highest correlations in both the soluble and insoluble fractions were found for As/Cd, As/Ni, Cd/Ni, Pb/Ti, As/Mo and Cd/Mo. In the insoluble phase, Mn is well correlated with Mo, As and Cd. Therefore, taking into account that the origin of Mn in the Maliaño area is closely related to the ferromanganese alloy plant, as it was previously reported in the literature (Moreno et al. 2011; Ruiz et al. 2014), and the low manganese solubility, Mo, As and Cd are assumed to originate partially from this plant, which is located just 1 km S of the MAL site. Although SW and NE are the prevailing wind directions at this site, the contribution of S wind cannot be neglected (see Figure 1). This fact, together with the higher wind speed of S wind observed in Figure 1 and the proximity between the ferromanganese alloy plant and MAL site might explain the good correlation between Mn, Mo As and Cd in the insoluble phase. The later three elements also correlate well with other elements typically derived from combustion (Ni and V), so they may have a mixed origin. A relatively high correlation between Zn and As, Cr, Ni and V is found in both the soluble and the insoluble phases; an important contribution of these elements is assumed to derive from the local metallurgical plants.

Finally, the urban site showed, in general, lower correlations between the studied elements; however, most correlations were statistically significant due to the high number of samples (40). The highest correlations ($r>0.7$, $p<0.01$) in the insoluble phase were found for As/Ni, As/Zn and Cd/Zn, and the highest correlations in the soluble phase were found for As/Ni, Cd/Mo, V/Mo, Cd/Ni, Cr/V and Cr/Mo. Most of these elements are typically found in electric arc furnace dust emitted from steel factories, such as that found 5 km SW of the SANT sampling point.

2. Comparison between urban, rural, industrial and traffic sites

The differences between the element deposition fluxes in the studied sites were assessed initially using the inter-site Pearson correlation coefficient for each trace element (Wilson et al. 2005). This type of analysis allowed the identification of elements from common sources in two sites. The inter-site Pearson correlation coefficients for all studied elements were calculated and can be observed in Table 2. For this calculation, only samples collected simultaneously (from January 2012 to February 2013) were considered. The inter-site correlation coefficients between the BAR and CAB sites were relatively high: As (0.645), Cd (0.631), Cr (0.795), Ti (0.463), Ni (0.688), V (0.741), Mo (0.607), and Zn (0.553), with the exception of Cu, Mn and Pb. Although the BAR site is located in a rural area, a local road may be considered the most important metal source, and this might explain the correlations found between the traffic site and the BAR site.

The inter-site correlation coefficients between the BAR and MAL sites were low and even negative for some elements with the exception of Cd: As (0.401), Cu (-0.251), Cr (-0.046), Ti (-0.132), Mn (0.196), Ni (0.028), Pb (-0.211), V (0.282), Mo (0.396) and Zn (0.489). Therefore, the local industrial activities found at the MAL site clearly decreased the inter-site correlation coefficients of those elements originating from the industrial estates close to the MAL site.

The comparison between the deposition fluxes of the industrial, urban and rural sites was complemented with the use of ternary diagrams. This type of diagram can be used to compare the levels of trace elements from a given environmental matrix for three sampling sites. The traffic site will be discussed later, in terms of its relationship with traffic volume. The relative levels (%) of the studied elements in the bulk atmospheric deposition, in the water soluble fraction of the atmospheric deposition and in local soils from the urban, industrial and rural sites have been plotted in Figure 6.

Because the extent of source impact varies by site, an elevated concentration of a source marker species at a site explains the higher impact of the source, and it appears closer to the corner representing the site in the ternary diagram. Most of the elements in the bulk atmospheric deposition and soil plots (Figures 6a and c) are clustered toward the industrial corner. However, when metals determined in the water soluble phase of the atmospheric deposition are plotted in a ternary diagram (Figure 6b) most elements move to the center of the triangle. So, although the bulk deposition of trace elements may be a good indicator of the total atmospheric input of these elements into the environment, the levels of these elements in the water soluble fraction of the atmospheric deposition should be taken into account in terms of their transfer towards the plant and the ground water. Lead and Cr in the bulk atmospheric deposition are close to the industrial corner (see Figure 6a), and they move to the center of the ternary plot when the water soluble phase is considered (Figure 6b). Manganese is the only element that is always located in the industrial corner, thus indicating industrial dominance. Manganese is a typical tracer of ferroalloy manufacturing plants (Boudissa et al.

2006), and the MAL site is mainly influenced by a ferro-manganese/silico-manganese plant located very close to the sampling station. Although the solubility of the Mn species is much lower at the industrial site, the total flux of Mn in this site is so high that it is still found at the industrial corner of the ternary plot (built from the water soluble data). Finally, a similar location of Zn is found in the ternary plots of the bulk atmospheric deposition and the water soluble fraction, with a slightly larger contribution of the urban than the industrial site. However, the soil plot indicates that the industrial site is enriched in Zn. The degree of soil pollution and its effect on the calculation of the enrichment factors will be discussed in the following section.

3. Enrichment factors

Enrichment factor (EF) analysis was carried out to assess the extent of accumulation of the studied elements in the bulk atmospheric deposition with respect to a reference environmental matrix. The procedure was based on the standardization of the measured element with respect to a reference element. Reference elements are usually characterized by low occurrence variability, and the most commonly used are Al, Ti and Fe. In this study, Ti was selected as a reference for its relative natural abundance, even distribution in the crust and in the Cantabria soils, and a relatively low influence of the anthropogenic activities on its observed levels. Three types of reference environmental matrices have been used in the literature for the calculation of EFs in atmospheric deposition samples: earth's crust (Mijic et al. 2010; Fernández-Olmo et al. 2014), local soil and background soil (Huang et al. 2009; Bermudez et al. 2012).

Accordingly, three procedures were used to calculate EF values:

i) EF = $(X_i/Ti)_{sample}/(X_i/Ti)_{crust}$. Typical elemental crust values were used from Li et al (2009).

ii) EF = $(X_i/Ti)_{sample}/(X_i/Ti)_{Cantabria\ background\ soil}$. Cantabria background soil values were obtained from the Cantabria Environmental Government (Gobierno de Cantabria, Consejería de Medio Ambiente 2011).

iii) EF = $(X_i/Ti)_{sample}/(X_i/Ti)_{local\ soil}$. Local soil values were obtained from the Cantabria Environmental Government (Gobierno de Cantabria, Consejería de Medio Ambiente 2011).

In these calculations, $X_{i,sample}$, $X_{i,crust}$, $X_{i,Cantabria\ soil\ background}$ and $X_{i,local\ soil}$ are the bulk atmospheric deposition, the average concentration in crust and the average concentration in Cantabrian and local soils of a given element, respectively. The EF values, calculated by the three procedures described above for the studied elements in the bulk atmospheric deposition, were averaged for the whole sampling period and are shown in Figure 7. When the earth's crust is used as a reference, the elements can be considered highly enriched (EF>100), intermediately enriched (10<EF<100) and less enriched (EF<10) (Berg et al. 1994). However, when other environmental matrices are used as references, these EF values should be carefully interpreted. This can be clearly observed in the case of As. When the crust composition is considered as reference material, the EF of As is approximately 10 times higher than EFs calculated from the regional background soil composition. This can be explained analyzing the levels of Ti and As in the different reference materials: thus, the As level in crust is much lower than that found in the regional soils of Cantabria (1.5 vs 18.37 mg/kg), while the Ti level is similar (3,000 vs 3,420 mg/kg). Independent of the procedure used, the least enriched elements are V, Ni and Cr for all studied sites, and the most enriched elements are Cd, Zn and Cu. High anthropogenic contributions have also been found for Cu, Ni, Pb and Zn in the atmospheric deposition collected near a metal smelting facility in Ontario, Canada (Jeffries and Snyder 1981); for Zn, Pb, As and Cd in Finland (Kyllönen et al. 2009); and for Zn, Cu, Cd and Pb in Belgrade (Mijic et al. 2010). Manganese is highly enriched at the industrial site of Maliaño but poorly enriched at the rural and traffic sites.

The enrichment factors, based on the local soil, calculated for the industrial site (MAL) are relatively low, due to the contamination in the topsoil layer. This was clearly observed for Mn, Cd, Zn, Pb, Mo, As, Ni and V (Figure 7c). The anthropogenic activities developed in the Santander Bay since the early 1900s, mainly metallurgical and chemical, have enriched the most recent layers of soil. This was clearly demonstrated by Viguri et al (2007), who analyzed the metal profiles (up to 50 cm) in sediment cores collected in the Santander Bay. In a sampling point close to Maliaño, they found a strong profile of Mn, Cu, Pb, Zn and Ni between 0 and 20 cm that corresponded to a geological age range of 2000 to 1900. In the case of Mn, a significant increase in its level above 7 cm corresponded to a geological age of 1960. The authors attributed this to the initiation of two ferromanganese and silicomanganese plants close to Maliaño in 1963. Therefore, the EF values calculated from the levels of elements in a local soil should be carefully interpreted when this local soil has been affected by anthropogenic inputs.

4. Influence of the road traffic intensity on the deposition fluxes of trace elements

The monthly average of the daily traffic volume (DTV) was available for a site close to the roadside sampling point, CAB (kilometer mark 239.3 of A8 motorway), in the same period as the present study. This allowed a comparison between the variability found in the monthly average daily flux of metal deposition and the monthly average DTV. The Pearson correlation coefficients between the monthly deposition fluxes of the studied trace elements and the monthly average DTV were calculated for the insoluble fraction and for the bulk atmospheric deposition. Low correlation coefficients were found for the studied elements in the bulk deposition (lower than 0.35 except for Ti (0.56, $p<0.05$) and Mn (0.58, $p<0.05$)). In contrast, Davis and Birch (2011) found high correlations between the bulk deposition flux of Zn, Cu and Pb and traffic volume; and Gunawardena et al. (2013) found that only Zn was correlated with traffic volume and that Pb, Cd, Ni and Cu were correlated with traffic congestion. Since the bulk atmospheric deposition includes both the water soluble and insoluble fractions and taking into account the high solubility of metals found in the traffic site (between 70 and 90 %, except for Ti) and the positive correlation between the fluxes of most elements in the water soluble fraction and the precipitation amount, the variability of the bulk deposition of these elements is thought to be due to the variability of the precipitation amount, leading to a poor correlation between the bulk deposition and traffic volume found for most elements.

However, the correlations found for all studied elements in the insoluble fraction of the atmospheric deposition was much higher, from 0.53 (Mn) to 0.83 (As). Manganese was the only element that was not statistically significant ($p>0.05$). The typical tracers of traffic emissions exhibited a relatively high correlation coefficient: Cu (0.67, $p<0.01$), Pb (0.78, $p<0.01$), Mo (0.72, $p<0.01$), and Zn (0.69, $p<0.01$). These results suggest that traffic volume affects only the insoluble fraction of the atmospheric deposition, most likely due to the resuspension of particles that originated from vehicle traffic. Other studies have shown that the roadside topsoil concentrations of metals derived from traffic, such as Cu and Sb, are significantly higher with increased traffic intensity (Hjortenkrans et al. 2006; Cal-Prieto et al. 2001). The relationship between trace element deposition flux in the insoluble fraction and traffic volume at the CAB roadside site is clearly shown in Figure 8. The figure has been divided into three parts to take into account the different metals fluxes found in the studied period. The highest fluxes were found for Ti, Zn and Mn (Figure 8a), followed by Cu, Pb, Cr, V and Ni (Figure 8b), and finally Cd, Mo and As (Figure 8c). The maximum element fluxes in the insoluble fraction of the atmospheric deposition were observed in August, in accordance with the maximum traffic intensity, due to the holiday period, as Cantabria is an important tourist destination in northern Spain, and this motorway (A8) also connects the Basque Country with northwestern Spain.

CONCLUSIONS

A comparative study of trace element deposition fluxes in urban, industrial, rural and traffic sites of the Cantabria region (Northern Spain) was conducted. The levels of As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, Zn and V were determined in the water soluble and insoluble fractions of bulk deposition samples. The element deposition fluxes at the rural, urban and traffic sites followed a similar order, Zn>Mn>>Cu≈Ti>Pb>V≈Cr>Ni>>As≈Mo>Cd, with the exception of a higher flux of Cr instead of Pb at the urban site (SANT). The enrichment factor calculations allowed the identification of the most enriched elements at all sites as Cd, Zn and Cu; the least enriched were V, Ni and Cr. At the industrial site (MAL), a much higher deposition of Mn was found. This was also corroborated by the levels of Mn in local soils close to the MAL sampling point, by the location of Mn in ternary plots close to the industrial corner, and by the high enrichment factor values found for Mn at this site, even if the "polluted" local soil is considered to be a reference environmental matrix. A ferro-manganese/silico-manganese production plant located close to the MAL site since 1963 seems to affect to levels of Mn in local soils and bulk atmospheric deposition.

The solubility of the studied elements in the bulk atmospheric deposition was higher at the traffic and rural sites and lower at the urban and industrial sites. The differences found in the solubilities between the sites lead to a different interpretation of the ternary diagrams built from industrial, urban and rural data. Thus, most of the studied elements moved from the industrial/urban corner to the center of the ternary plot when the water soluble fraction was considered. For all studied sites, Zn and Cd were the most soluble elements while Cr and Ti were the least soluble.

The identification of common and local sources from the four sites was studied through the determination of the coefficient of divergence for each element. The BAR and CAB sites were affected by common sources, most likely traffic, because they showed the highest inter-site correlation coefficients for As, Cd, Cr, Ti, Ni, V, Mo and Zn. The MAL and BAR sites showed the lowest inter-site correlation coefficients due to local industrial sources found at the industrial site (MAL).

A good correlation between the daily traffic volume and the element deposition fluxes calculated for the insoluble fraction of the bulk atmospheric deposition was found at the traffic site (CAB). This correlation was not observed in the bulk atmospheric deposition; the highest deposition fluxes found in the soluble fraction when higher rainfall amounts are registered (fall and winter) and the relatively high solubility found for most of the studied elements would explain this lack of correlation.

The different interpretation derived from the inclusion of both the soluble and insoluble fractions of the bulk atmospheric deposition encourages the determination and examination of each fraction separately in future research.

Acknowledgments

The authors are grateful for the financial support from the CTM 2010-16068 (Spanish Ministry of Science and Innovation) and CTM 2013-43904 R (Spanish Ministry of Economy and Competitiveness) projects. The "Consejería de Medio Ambiente" from the Cantabria Government is also acknowledged for sending the report on the background levels of heavy metals and trace elements in soils in the Cantabria region. The authors are also grateful to "Ayuntamiento de Camargo" for helping us with the sampling site of Maliaño.

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Table 1. Trace element levels in bulk atmospheric deposition worldwide ($\mu g \cdot m^{-2} \cdot day^{-1}$) at urban(U), industrial(I), traffic(T) and rural/regional(R) sites

Site	**Country**	**Type**	**Period**	**As**	**Cd**	**Cu**	**Cr**	**Ti**	**Mn**	**Ni**	**Pb**	**V**	**Mo**	**Zn**	**Reference**
Santander	Spain	U	2009-2013	0.30	0.10	11.8	5.2	11.4	153	1.5	4.5	3.2	0.3	183	This work
Notre-Dame de Gravenchon	France	U	2001		0.63	14.3				5.5	13.2			162	Motelay-Massei et al., 2005
Paris	France	U	2001-2002		0.66	16.4				1.7	11.5			82.2	Motelay-Massei et al., 2005
London	UK	U	2004		0.11					1.8	11.5			48.9	Brown et al., 2006
Belgrade	Serbia	U	2002-2006		0.60	94.5	4.5		71.8	31.0	59.5	54.0		113	Mijic et al., 2010
Sibenik	Croacia	U	1999-2004		0.45-0.68						10.2-27.1				Cackovic et al., 2009
Brisbane	Australia	U	2007-2008	0.97	0.32	5.5	1.8		16.0	1.0	5.9	0.90		46.0	Huston et al., 2012
Huelva	Spain	U	2008-2011	1.6	0.27	192	4.4		19.7	3.8	9.3	4.7			Castillo et al., 2013
Sydney	Australia	U	2007-2008			11-20					12-29			118-131	Davis and Birch, 2011
Yangtze River Delta	China	U	2006-2007	4.3	1.1	38.1	36.2			12.6	98.4			245	Huang et al., 2009
Varanasi	India	U	2003-2004		2.5-4.7	13.0-21.3					1.7-3.4			108-165	Sharma et al., 2008
Maliaño	Spain	I	2012-2013	0.60	0.20	28.6	11.6	31.9	2606	3.3	18.1	5.9	0.70	136	This work
Le Havre	France	I	2001-2002		0.99	25.8				11.2	50.4			3211	Motelay-Massei et al., 2005
Huelva	Spain	I	2008-2011	4.7	0.55	1770	4.9		19.5	19.5	27.4	9.0			Castillo et al., 2013
Venice (Murano)	Italy	I	2001-2003	63.0	33.0	57.0	15.7		81.0	43.0	52.0			1005	Rossini et al., 2010
Didouche Mourad	Algeria	I	2002-2003		15.0	395	17.0		202	11.0	384				Ali-Khodja et al., 2008
Cabezón de la Sal	Spain	T	2012-2013	0.40	0.24	9.4	1.8	9.1	37.2	1.6	6.8	2.1	0.28	75.6	This work
Rouen	France	T	2001-2002		0.52	7.7				1.2	8.2			74.0	Motelay-Massei et al., 2005
Sydney	Australia	T	2007-2008			28-246					38-106			238-1354	Davis and Birch, 2011
Bárcena Mayor	Spain	R	2012-2013	0.20	0.09	7.5	1.3	7.3	17.5	1.2	2.5	1.2	0.20	35.3	This work
Versailles	France	R	2001-2002		0.13	10.7				4.1	6.0			42.7	Azimi et al., 2004
Evreux	France	R	2001-2002		0.55	20.5				0.93	4.7			104	Motelay-Massei et al., 2005
Kornaty National Park	Croacia	R	1999-2004		0.44						4.0				Cackovic et al., 2009
Doñana National Park	Spain	R	2008-2011	0.27	0.03	18.9	2.5		19.2	0.82	1.9	3.0			Castillo et al., 2013
Kushiro	Japan	R	2008		0.06	1.6		22.0	13.0	2.0	2.7			11.0	Okubo et al., 2013
Otsuchi	Japan	R	2008		0.14	6.1		58.0	24.0	2.0	9.0			40.0	Okubo et al., 2013
Hedo	Japan	R	2008		0.21	0.96		19.0	9.0	2.2	5.9			15.0	Okubo et al., 2013
Southern Scandinavia	Sweden	R	2002-2005	0.27	0.14	2.7				0.82	2.7	1.4		18.9	Hovman et al., 2008
Virolahti	Finland	R	2007	0.24	0.10	2.7	0.49		6.3	0.38	3.0	0.99		10.4	Kyllonen et al., 2009
Pallas	Finland	R	2007	0.04	0.03	1.6	0.12		1.7	0.15	0.49	0.26		2.5	Kyllonen et al., 2009

Table 2. Inter-site correlation coefficients for the studied elements

As			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.387	0.645	0.572
MALIAÑO		0.401	0.125
BÁRCENA MAYOR			0.680

Cd			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.547	0.631	0.774
MALIAÑO		0.692	0.550
BÁRCENA MAYOR			0.698

Cu			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	-0.034	0.406	0.387
MALIAÑO		-0.251	-0.055
BÁRCENA MAYOR			0.419

Cr			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.290	0.795	0.522
MALIAÑO		-0.046	-0.148
BÁRCENA MAYOR			0.666

Ti			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.592	0.463	-0.224
MALIAÑO		-0.132	0.294
BÁRCENA MAYOR			-0.517

Mn			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	-0.293	-0.179	-0.313
MALIAÑO		0.196	0.477
BÁRCENA MAYOR			-0.208

Ni			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.396	0.688	0.224
MALIAÑO		0.028	-0.134
BÁRCENA MAYOR			0.460

Pb			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	-0.086	-0.220	0.150
MALIAÑO		-0.211	0.184
BÁRCENA MAYOR			0.616

V			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.611	0.741	0.741
MALIAÑO		0.282	0.213
BÁRCENA MAYOR			0.930

Mo			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.132	0.607	0.467
MALIAÑO		0.396	0.475
BÁRCENA MAYOR			0.776

Zn			
	MALIAÑO	BÁRCENA MAYOR	SANTANDER
CABEZÓN DE LA SAL	0.583	0.553	0.650
MALIAÑO		0.489	0.438
BÁRCENA MAYOR			0.823

FIGURE CAPTIONS

Fig. 1 Atmospheric deposition sampling sites and wind roses at sites close to Bárcena Mayor from September 2011 to February 2013 (left) and to Maliaño from January 2012 to February 2013 (right)

Fig. 2 Bulk atmospheric deposition of trace elements ($\mu g \cdot m^{-2} \cdot day^{-1}$) at the studied sites: Cabezón de la Sal (N=13), Bárcena Mayor (N=16), Maliaño (N=13) and Santander (N=40). Bars: minimum and maximum values; boxes: 75th percentile, median and 25th percentile

Fig. 3 Trace metals levels (mg/kg) in soils located near the deposition sampling points: Cabezón de la Sal (N=3), Bárcena Mayor (N=4), Maliaño (N=4) and Santander (N=3). Bars: minimum and maximum values; boxes: 75th percentile, median and 25th percentile

Fig. 4 Seasonal variability of the water soluble fraction of the atmospheric deposition of trace elements ($\mu g/m^2 \cdot day$) and the precipitation amount (l/m^2) at the studied sites

Fig. 5 Water soluble fraction contribution to bulk atmospheric deposition (average and standard deviation, %) at the studied sites

Fig. 6 Comparison between industrial, urban and rural sites using ternary plots of the studied elements for (a) bulk atmospheric deposition; (b) water soluble fraction; (c) soil

Fig. 7 Enrichment factors of elements in bulk atmospheric deposition: (a) Rural site; (b) Traffic site; (c) Industrial site; (d) Urban site

Fig. 8 Relationship between the element bulk deposition fluxes (insoluble fraction) and the daily traffic volume (DTV) in Cabezón de la Sal (traffic site): a) Ti, Zn, Mn; b) Cu, Pb, Cr, V, Ni; c) Cd, Mo, As

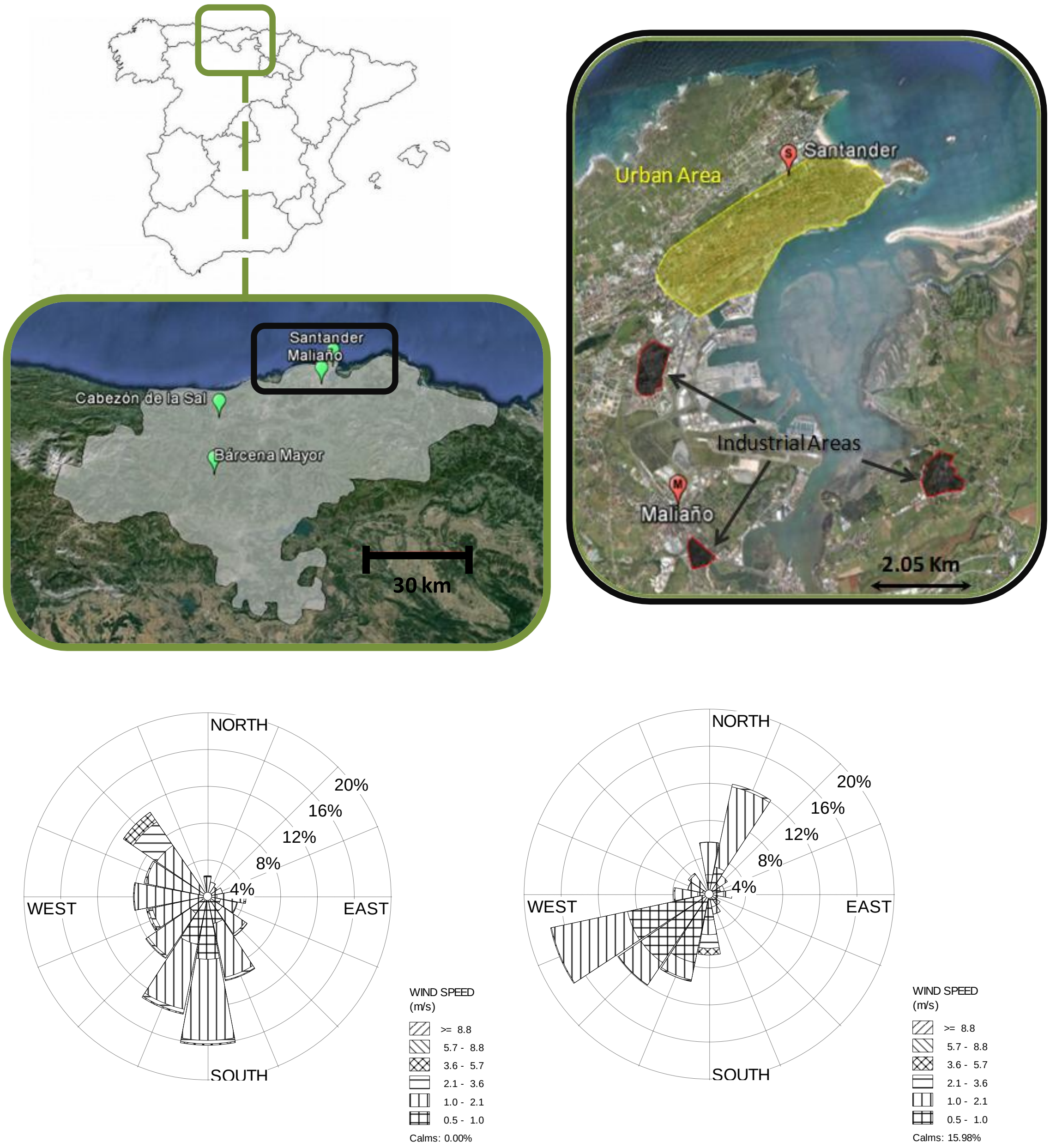


Fig. 1 Atmospheric deposition sampling sites and wind roses at sites close to Bárcena Mayor from September 2011 to February 2013 (left) and to Maliaño from January 2012 to February 2013 (right)

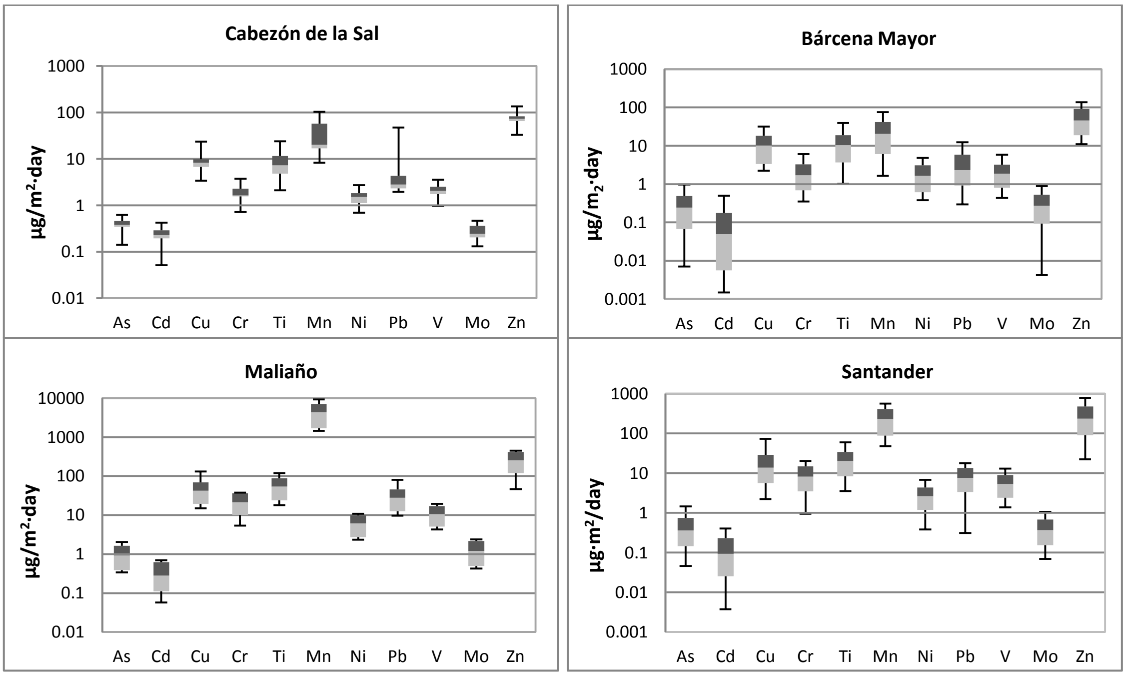


Fig. 2 Bulk atmospheric deposition of trace elements (µg·m^{-2}·day^{-1}) at the studied sites: Cabezón de la Sal (N=13), Bárcena Mayor (N=16), Maliaño (N=13) and Santander (N=40). Bars: minimum and maximum values; boxes: 75th percentile, median and 25th percentile

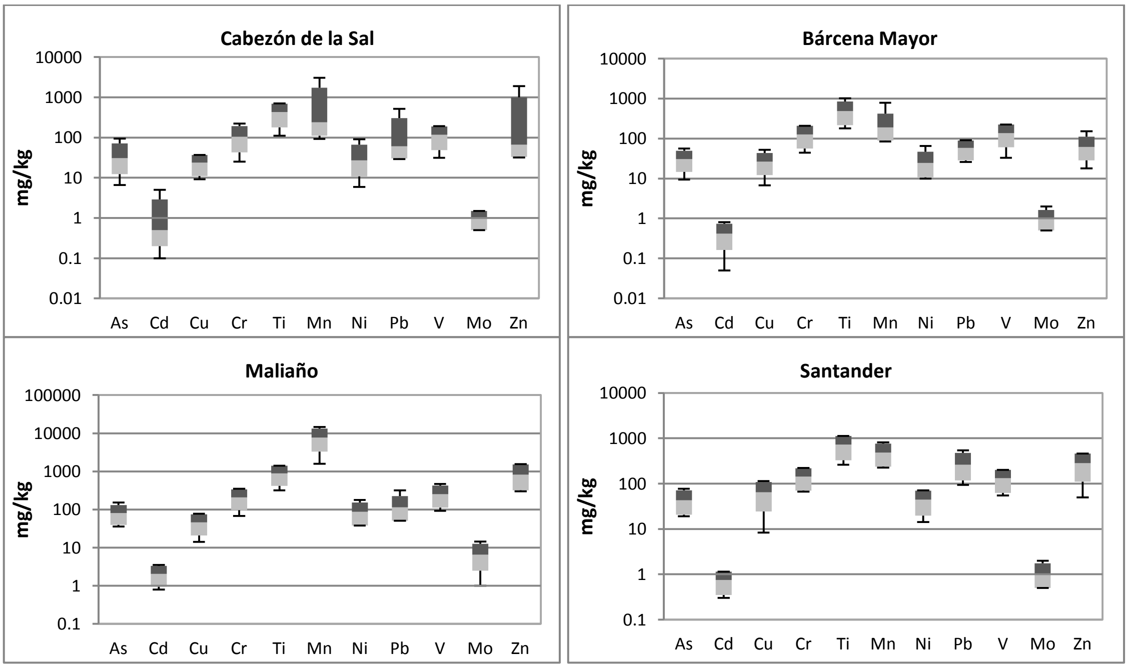


Fig. 3 Trace metals levels (mg/kg) in soils located near the deposition sampling points: Cabezón de la Sal (N=3), Bárcena Mayor (N=4), Maliaño (N=4) and Santander (N=3). Bars: minimum and maximum values; boxes: 75th percentile, median and 25th percentile

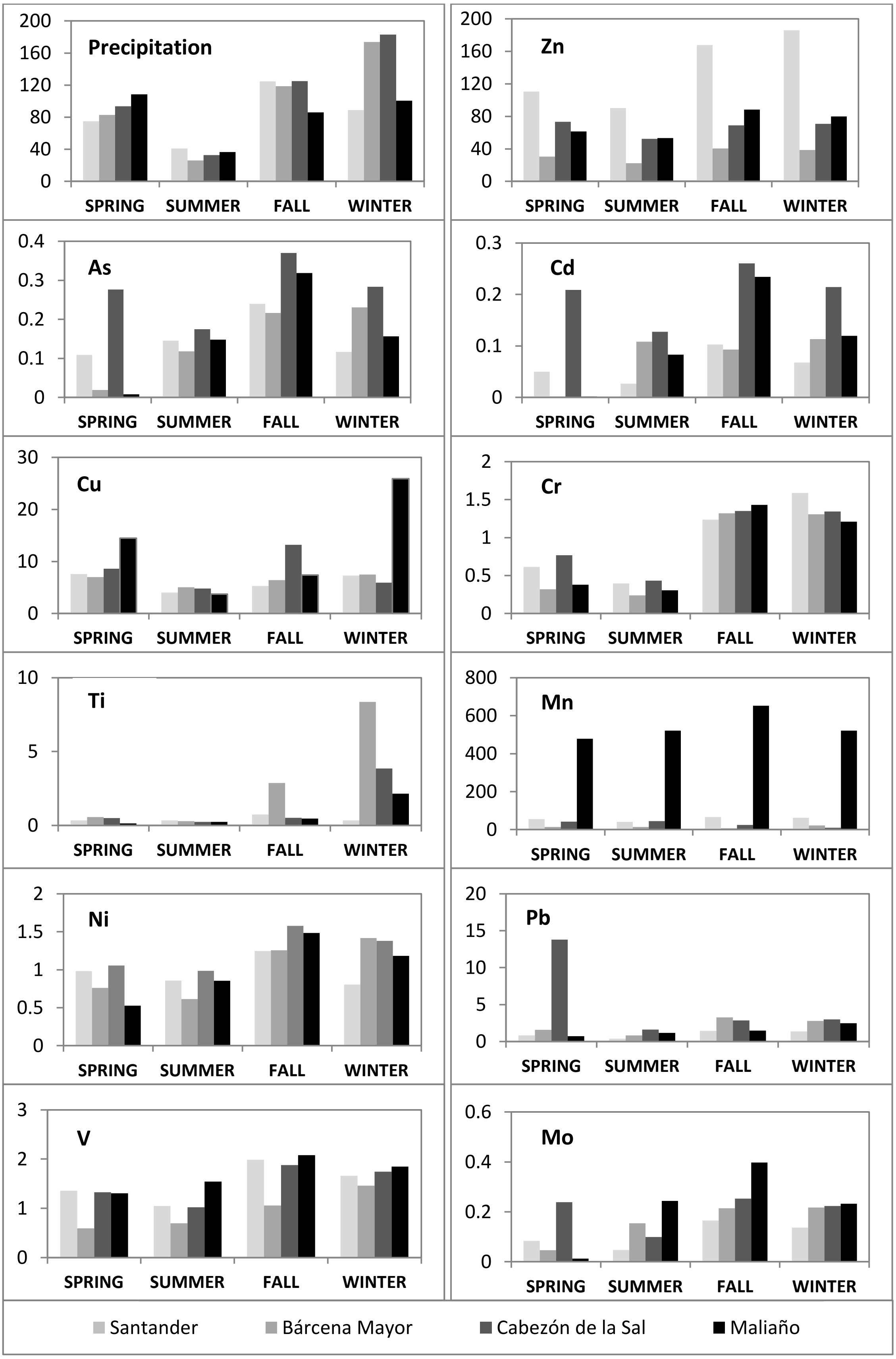


Fig. 4 Seasonal variability of the water soluble fraction of the atmospheric deposition of trace elements ($\mu g/m^2 \cdot day$) and the precipitation amount (l/m^2) at the studied sites

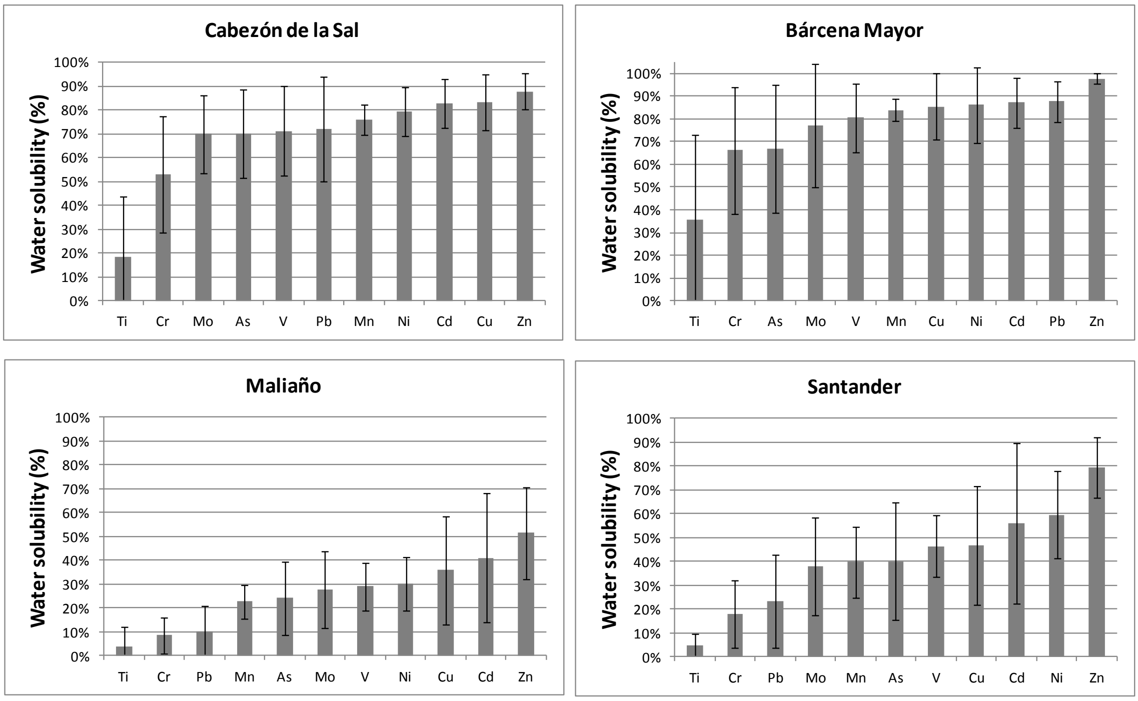
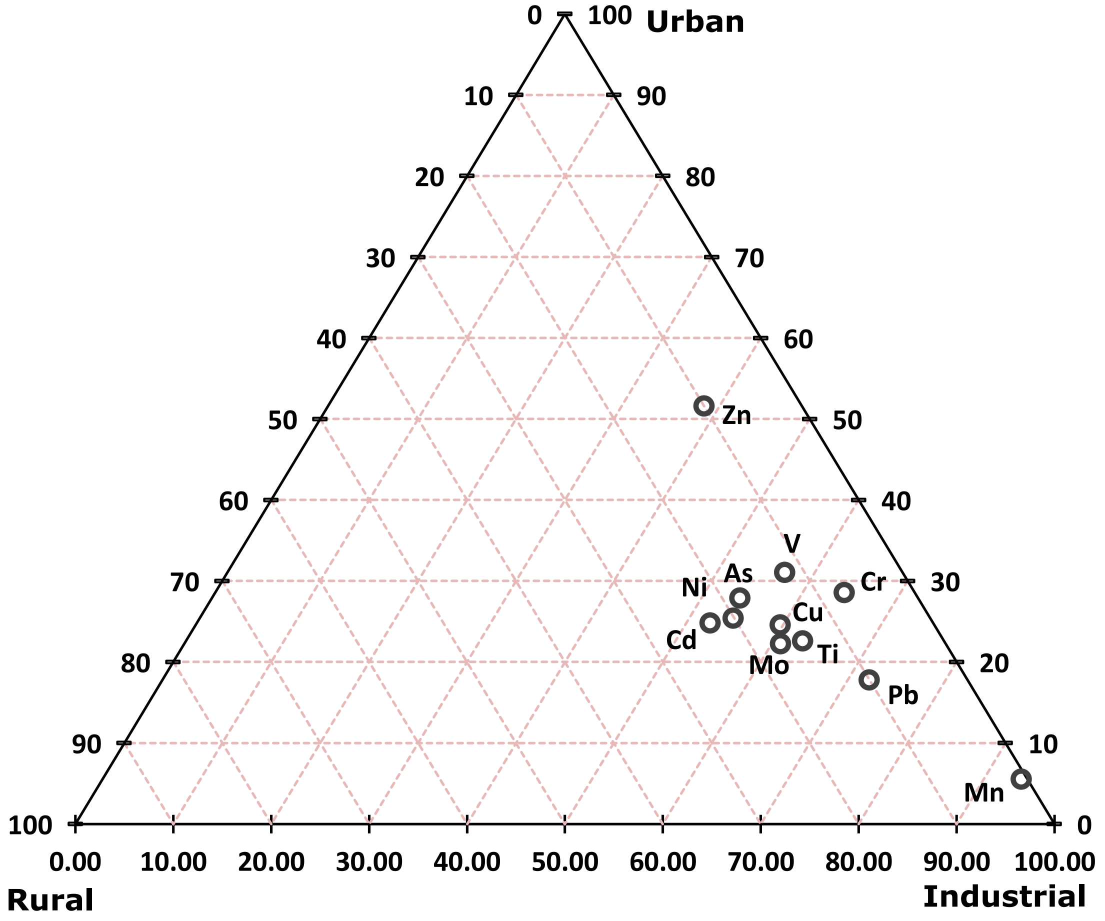
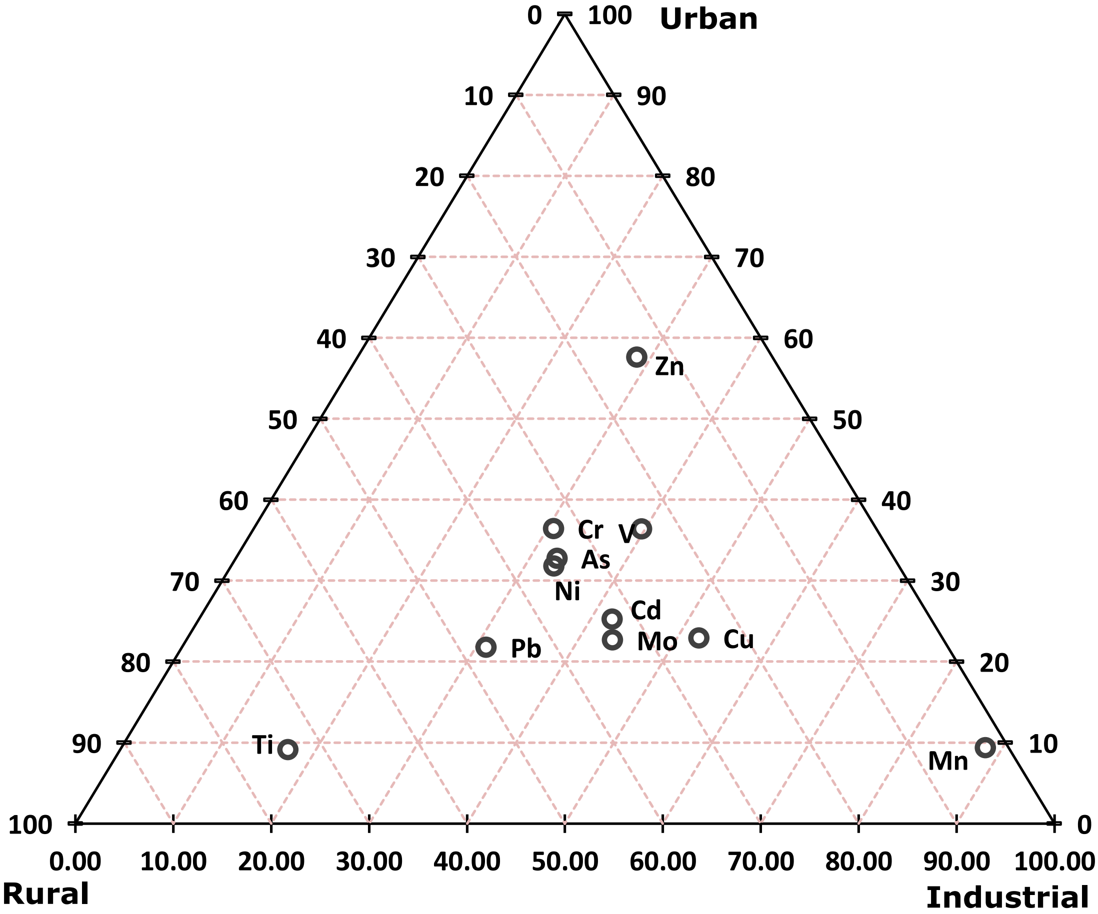


Fig. 5 Water soluble fraction contribution to bulk atmospheric deposition (average and standard deviation, %) at the studied sites

(a)


Urban
Rural
Industrial
0
10
20
30
40
50
60
70
80
90
100
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
Zn
V
As
Ni
Cr
Cu
Cd
Ti
Mo
Pb
Mn

(b)



Urban
Rural
Industrial
0
10
20
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40.00
50.00
60.00
70.00
80.00
90.00
100.00
Zn
Cr
V
As
Ni
Cd
Mo
Cu
Pb
Ti
Mn

(c)

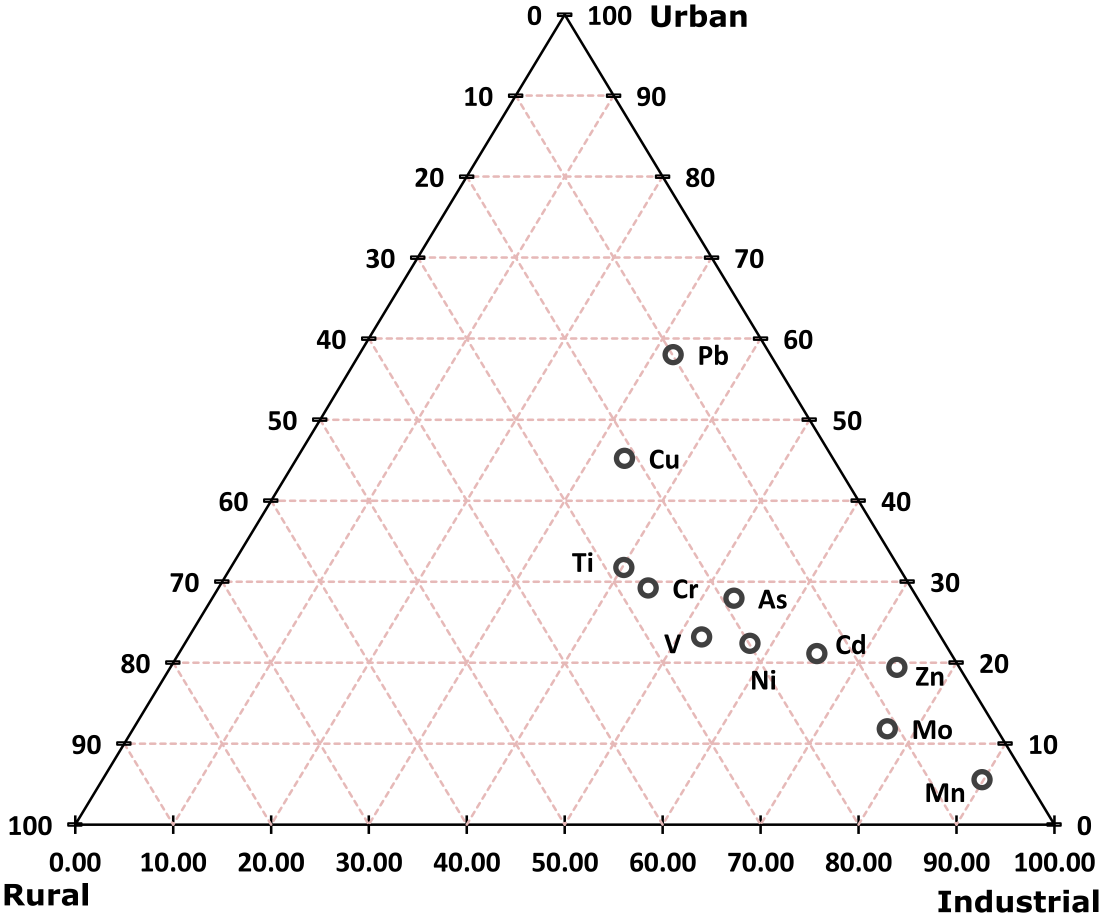
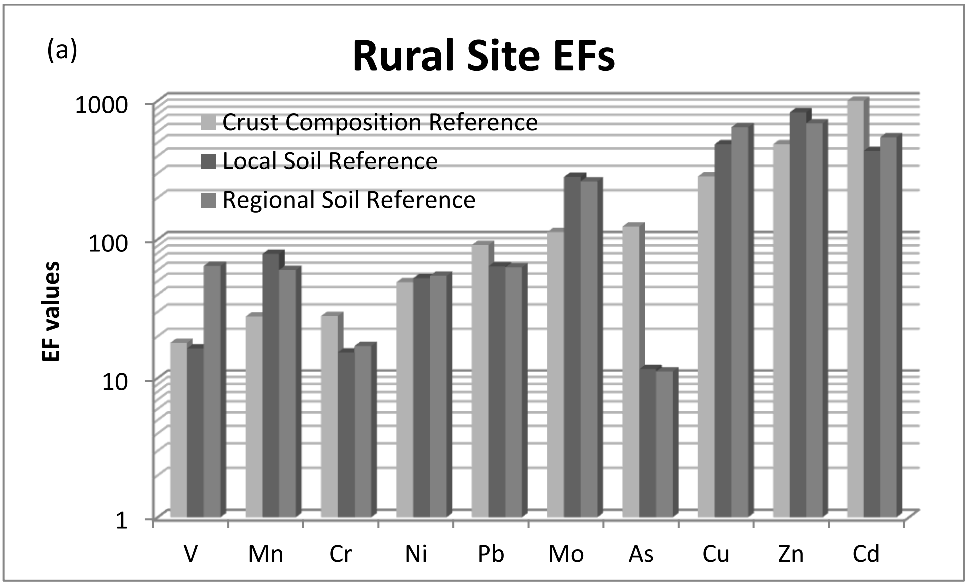
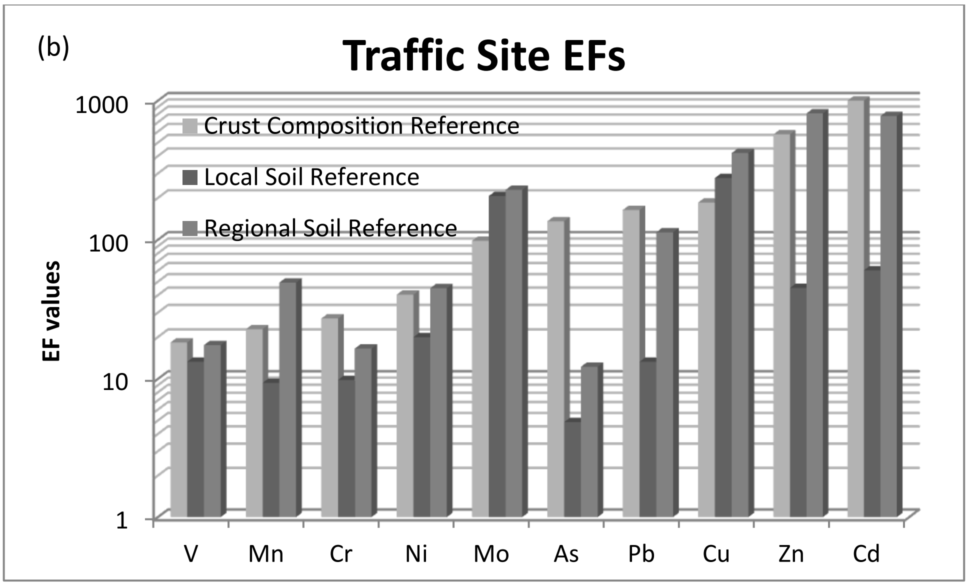


Fig. 6 Comparison between industrial, urban and rural sites using ternary plots of the studied elements for (a) bulk atmospheric deposition; (b) water soluble fraction; (c) soil


(a)
Rural Site EFs
1000
100
10
1
EF values
Crust Composition Reference
Local Soil Reference
Regional Soil Reference
V
Mn
Cr
Ni
Pb
Mo
As
Cu
Zn
Cd


(b)
Traffic Site EFs
1000
100
10
1
EF values
Crust Composition Reference
Local Soil Reference
Regional Soil Reference
V
Mn
Cr
Ni
Mo
As
Pb
Cu
Zn
Cd

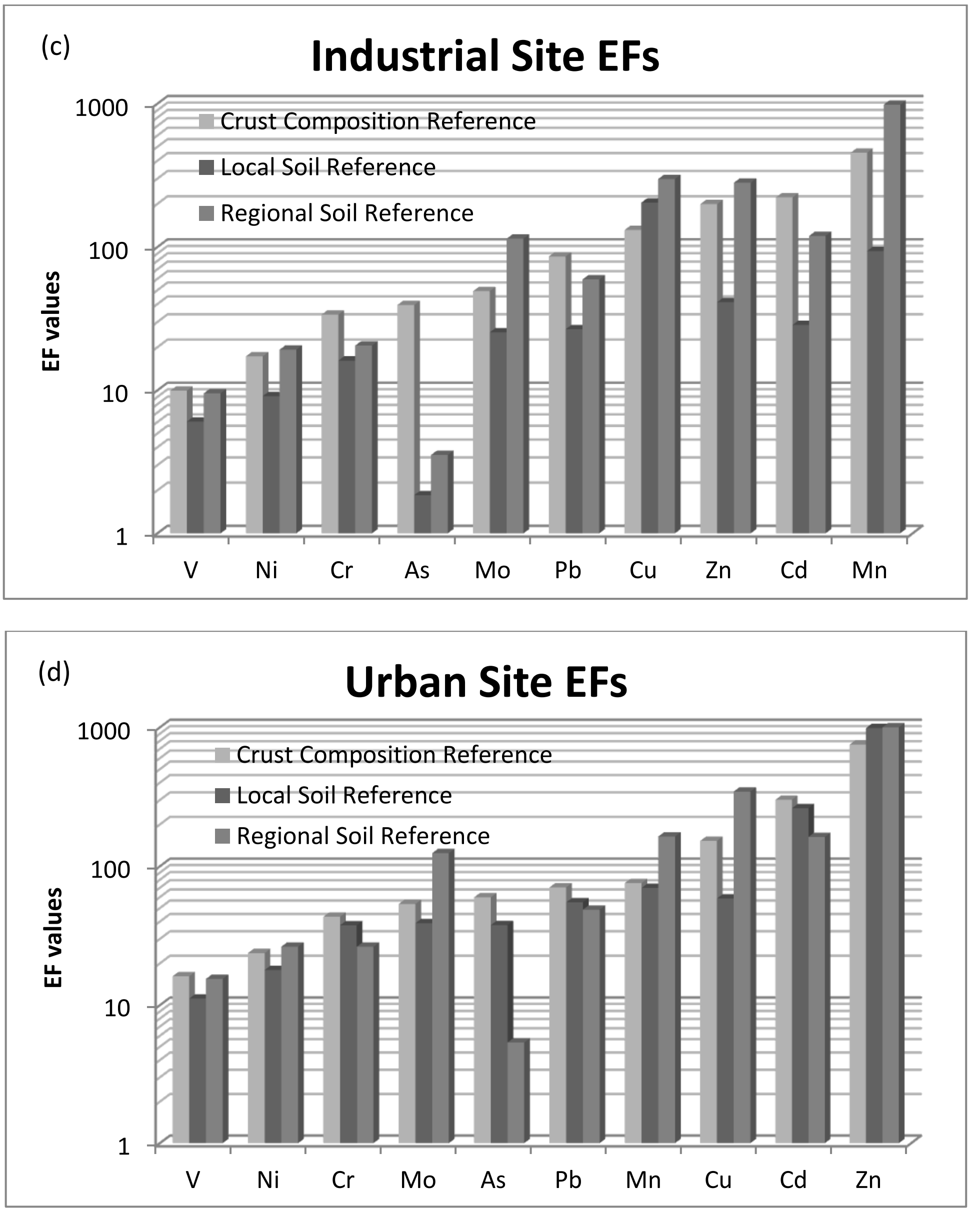
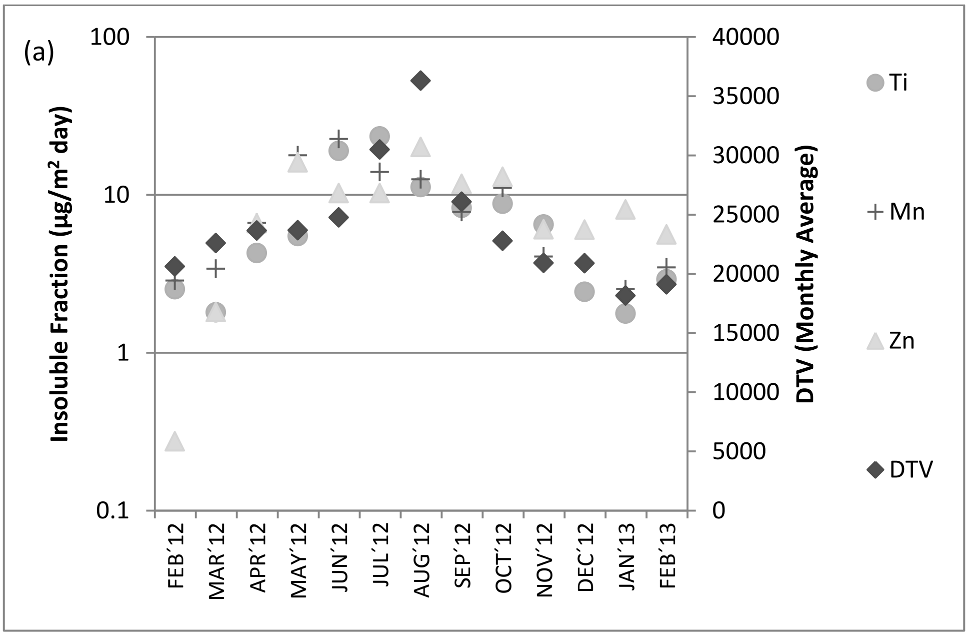
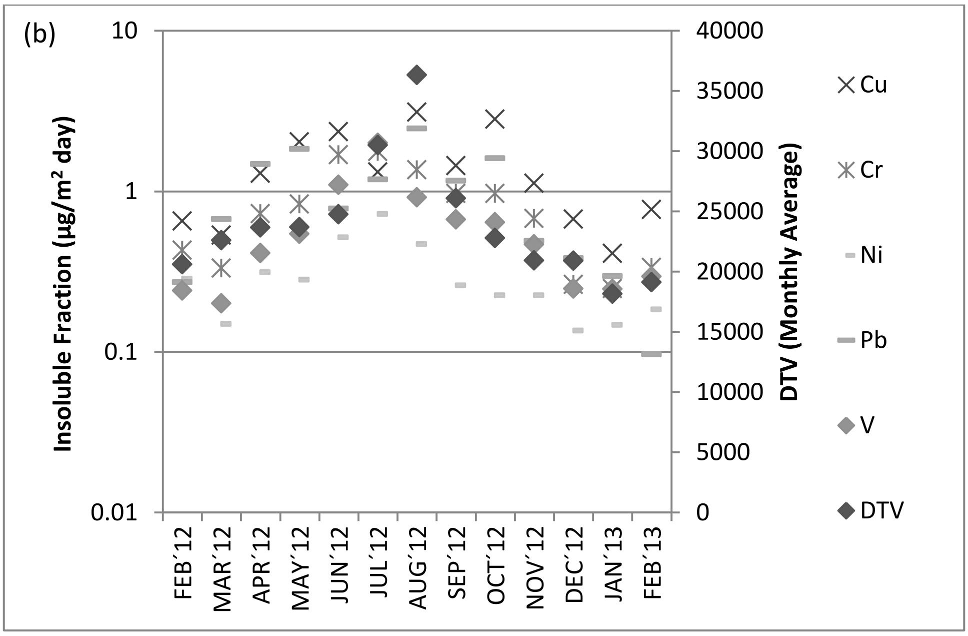


Fig. 7 Enrichment factors of elements in bulk atmospheric deposition: (a) Rural site; (b) Traffic site; (c) Industrial site; (d) Urban site


(a)
Insoluble Fraction (µg/m² day)
100
10
1
0.1
DTV (Monthly Average)
40000
35000
30000
25000
20000
15000
10000
5000
0
FEB´12
MAR´12
APR´12
MAY´12
JUN´12
JUL´12
AUG´12
SEP´12
OCT´12
NOV´12
DEC´12
JAN´13
FEB´13
Ti
Mn
Zn
DTV


(b)
Insoluble Fraction (µg/m² day)
10
1
0.1
0.01
DTV (Monthly Average)
40000
35000
30000
25000
20000
15000
10000
5000
0
FEB´12
MAR´12
APR´12
MAY´12
JUN´12
JUL´12
AUG´12
SEP´12
OCT´12
NOV´12
DEC´12
JAN´13
FEB´13
Cu
Cr
Ni
Pb
V
DTV

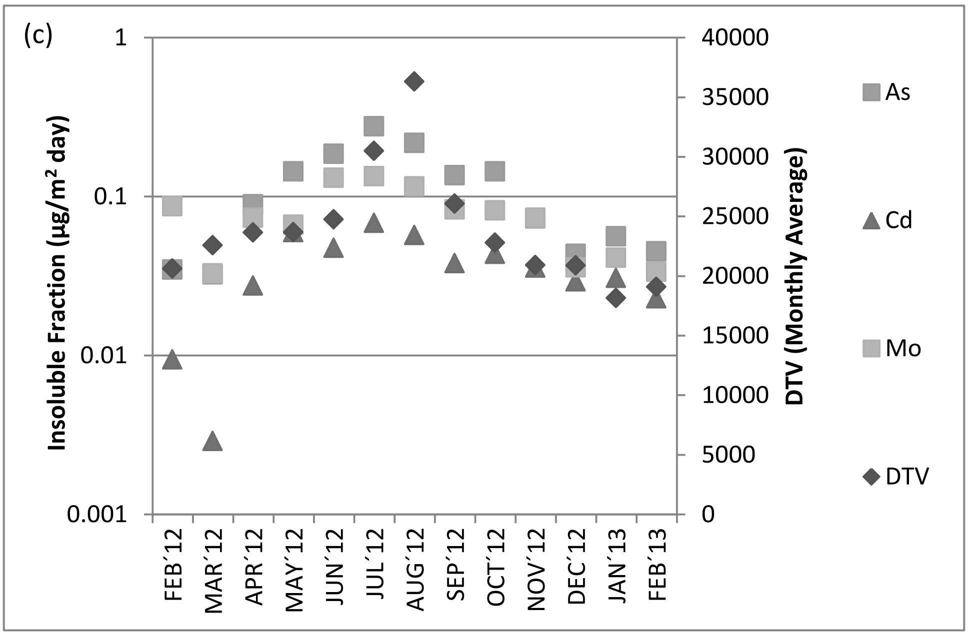


Fig. 8 Relationship between the element bulk deposition fluxes (insoluble fraction) and the daily traffic volume (DTV) in Cabezón de la Sal (traffic site): a) Ti, Zn, Mn; b) Cu, Pb, Cr, V, Ni; c) Cd, Mo, As