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Source contribution to the bulk atmospheric deposition of minor and trace elements in a Northern Spanish coastal urban area

Ignacio Fernández-Olmo*, Mariano Puente, Lucia Montecalvo, Angel Irabien

Universidad de Cantabria, Chemical and Biomolecular Engineering Department, Avda. Los

Castros s/n, 39005 Santander (Cantabria), Spain.

*Corresponding author:

Ignacio Fernández-Olmo: Tel.:+34942206745; Fax: +34942201591, e-mail: fernandi@unican.es

Mariano Puente: Tel.:+34942201579, e-mail: marianopuente@gmail.com

Lucia Montecalvo: Tel.:+34942201579, e-mail: lucia.montecalvo@gmail.com

Angel Irabien: Tel.:+34942201597, e-mail: irabienj@unican.es

ABSTRACT

The bulk atmospheric deposition of the minor and trace elements As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, V and Zn was investigated in Santander, a Northern Spanish coastal city. Bulk deposition samples were collected monthly for three years using a bottle/funnel device. Taking into account that heavy metals are bioavailable only in their soluble forms, water-soluble and water-insoluble fractions were evaluated separately for element concentration. The fluxes of the studied elements in the bulk deposition exhibited the following order: Zn > Mn >> Cu > Cr > Pb > V > Ni >> As > Mo > Cd. The fluxes of Zn and Mn were more than 10 times higher than those of the other elements, with maximum values of 554.5 and 334.1 μg m^{-2} day^{-1}, respectively. Low solubilities (below 22 %) were found for Cr, Ti and Pb, whereas the highest solubility was found for Zn (78 %). With the exception of Cu, all of the studied metals in the water-soluble fraction of the atmospheric deposition showed seasonal dependence, due to the seasonal variability of precipitation. The enrichment factors (EFs) of Cu, Cd and Zn were higher than 100, indicating a clear anthropogenic origin. The EF of Mn (50) was below 100, but an exclusively industrial origin is suggested. Positive Matrix Factorisation (PMF) was used for the source apportionment of the studied minor and trace elements in the soluble fraction. Four factors were identified from PMF, and their chemical profiles were compared with those calculated from known sources that were previously identified in Santander Bay: two industrial sources, the first of which was characterized by Zn and Mn, which contributes 62.5 % of the total deposition flux of the studied elements; a traffic source; and a maritime source. Zinc and Mn are considered to be the most characteristic pollutants of the studied area.

Keywords: Bulk atmospheric deposition, Trace elements, Positive Matrix Factorisation, Seasonal variability.

1. INTRODUCTION

Atmospheric deposition is usually studied in regional and remote areas to investigate the regional and trans-boundary transport of pollutants towards the ecosystems, as opposed to local, urban-influenced inputs (Sweet et al., 1998; Kyllönen et al. 2009; Deboudt et al., 2004; Kim et al., 2012; Okubo et al., 2013). Wet-only samplers are typically used for these measurements, and the deposition data are used to estimate the total deposition load to the studied ecosystems. However, atmospheric deposition can also be determined in industrialised and urban areas to complement studies on point sources of pollution. In these areas, the contribution of dry deposition, mainly coarse particles from local point sources, to total deposition may be of significant importance (Aas et al., 2009). The deposited pollutants may enter terrestrial and aquatic environments and can reach the food chain. Recent studies have evaluated the contribution of the atmospheric deposition of pollutants to storm-water composition (Davis and Birch, 2011; Huston et al., 2012).

Among the pollutants usually studied in atmospheric deposition, heavy metals are of primary concern due to their ability to accumulate. Heavy metals are bioavailable only in their soluble form, so many studies focus their investigations on the soluble fraction of metals from atmospheric deposition (Tate and Bates, 1984, Usero and Gracia, 1986a). Presently, in the EU countries, the Parties to the Convention on Long-range Transboundary Air Pollution (CLTRAP) are obliged to monitor certain trace elements (Pb, Cd, Hg, Pb, Cu, Zn, As, Cr and Ni) in air and precipitation in accordance with the European Monitoring and Evaluation Programme (EMEP) monitoring strategy. Hundreds of papers dealing with the atmospheric deposition of trace elements have been published in recent decades. Most of them have been summarised in review papers (Galloway et al., 1982; Schroeder et al., 1987; Injuk and van Grieken, 1995). Only, a small portion of the published literature addresses to the deposition of elements in urban areas (Azimi et al., 2003, 2004, 2005a,b; Motelay-Massei et al., 2005; Sharma et al., 2008; Tasic et al., 2009; Usero and Gracia, 1986b; Wong et al., 2003) and industrial areas (Jeffries and Snyder, 1981; Tate and Bates, 1984; Rossini et al., 2005, 2010; Soriano et al., 2012). Similarly, few studies have been conducted in Spain's urban areas, and these have been primarily focused on such areas that are highly influenced by nearby industrial activities. Areas that have been studied include the Gibraltar area (Usero and Gracia, 1986a; 1987), Sevilla (Usero and Gracia, 1986b), Cartagena (Moreno-Grau et al., 2002; Vergara et al., 2009), Castellón-Vilareal (Soriano et al., 2012) and Huelva (Castillo et al., 2013).

The identification of the main sources of pollutants in different environmental matrices has been widely carried out using multivariate receptor modelling. Principal Component Analysis (PCA), Chemical Mass Balance (CMB) and Positive Matrix Factorisation (PMF) are the most widely used techniques for source apportionment. These techniques have been applied mainly to airborne particles (Polissar et al., 1998; Chueinta et al., 2000; Pandolfi et al., 2008; Viana et al. 2008) but additionally to rainwater (Kessler et al., 1992; Juntto and Paatero, 1994; Calvo et al., 2010) and bulk deposition samples (Azimi et al., 2005a; Huang et al., 2009; Huston et al., 2012). With respect to precipitation samples, multivariate methods were applied first to identify the sources of the major components (Crawley and Sievering, 1986; Ezcurra et al., 1988; Kessler et al., 1992; Calvo et al., 2010). PCA was also applied to trace metals in rainwater samples (Thomas, 1986) and atmospheric bulk deposition samples (Azimi et al., 2005a; Huang

et al., 2009; Rossini et al., 2005; Cackovic et al., 2009; Castillo et al., 2013; Okubo et al., 2013). PMF was developed by Paatero and Tapper (1994) as an alternative to other factor analysis techniques. The major improvement of this technique is to force all the values in the solution profiles and factor contributions to be non-negative, which is more realistic than their treatment in PCA. PMF was first applied to precipitation data (Juntto and Paatero, 1994) and bulk wet deposition samples (Anttila et al., 1995) with the aim of identifying the most important sources of ions and major elements. Later, PMF was applied extensively to airborne particles for metal and major component apportionment (Reff et al., 2007). However, few studies use PMF to apportion trace metals in bulk deposition (Tasic et al., 2009; Huston et al., 2012).

The present study discusses the fluxes and seasonal variability of the atmospheric deposition of minor and trace elements (As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, V and Zn) in an urban area with a moderate influence of industrial activities (Santander Bay, Northern Spain) for a 3 years sampling period. Special attention is paid to the soluble fraction of elements in the studied samples. The identification of the main sources of elements in the water-soluble fraction of bulk deposition is performed with PMF and compared with sources that were previously identified in Santander Bay (Arruti et al., 2011). To our knowledge, there have been no other studies on this subject conducted in the north of Spain.

2. EXPERIMENTAL METHODS

2.1. Sampling

The atmospheric deposition of pollutants is usually assessed with the surrogate surface approach, using bulk and wet-only deposition samplers. Although errors in assessing atmospheric deposition with this 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), Bergerhoff and wet-only samplers to collect and assess the atmospheric deposition of metals. In 2009, CEN published the "Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition, EN 15841", specifying general requirements for sampling equipment and different sampling strategies depending on sampling sites. Bulk (bottle/funnel) and Bergerhoff samplers are recommended to measure total atmospheric deposition on industrial and urban sites, mainly when total deposition is not just due to precipitation events (Aas et al., 2009). Furthermore, a study that evaluated sampler uncertainties of different collectors (wet only, bulk, Bergerhoff and bulk bottle/funnel) showed that the lowest uncertainty was found for the bulk bottle/funnel sampler (Aas et al., 2009). Therefore, a bulk (bottle/funnel) sampler was selected in the present study.

This study was performed in Santander, a coastal city located in the north of Spain. Santander is a medium-sized city (179,921 inhabitants in 2011) that extends over a wide bay. It is mainly commercial and residential in nature, with a low to middle pollution level. However, an industrial area (with mostly iron, steel and ferroalloy manufacturing plants) is located in the Santander suburbs (5-10 km SW). The sampling site (43º28´26´´N, 3º47´47´´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". Figure 1 shows the location of the sampling site and the major industrial point sources in Santander Bay.

Bulk atmospheric deposition sampling was performed using a collector consisting of a high-density polyethylene bottle (10 L) connected to a funnel with a 779 cm^2 collection area and placed on a steel chassis with a protector ring on top to avoid bird nesting. The device is based on EN-UNE 15841-2009 "Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition." The funnel height was 1.7 m to avoid the collection of re-suspended soil particles. The sampling was carried out monthly from September 2009 to October 2012 (36 samples). At the end of each sampling period, the funnel was rinsed with 200 ml of Milli-Q water, and the entire device was replaced with a clean one.

2.2. Analytical procedures

Bulk atmospheric deposition samples were brought to the laboratory at the end of each sampling period. Precipitation amount was determined by gravimetry. Subsequently, the samples were filtered through 0.45 µm membrane filters (mixed cellulose esters, Millipore, 47 mm i.d.). Water-soluble fractions were acidified to pH=1 with nitric acid and stored at 4 ºC prior to analysis.

The sample treatment for the analysis of trace metals in the insoluble fractions from bulk atmospheric deposition was in accordance with EN-UNE 14902-2005 "Standard method for the measurements of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter." The acid digestion was carried out in a microwave oven (Milestone Ethos 1) using Teflon vessels. Different microwave digestion programs and acid mixtures (8 ml of 65% HNO_3 (Suprapur®, Merck) and 2 ml of 30% H_2O_2 (Suprapur®, Merck)) were tested in order to obtain the best metal recoveries. The digestion program involved a temperature increase to 185 ºC using two ramps within 18 min, followed by a constant temperature step over 40 min. The vessels were then cooled for 60 min and then vented and opened. Finally, the solution was filtered and diluted with Milli-Q water to a final volume of 50 ml. Arsenic, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, Zn and V concentrations were determined by inductively coupled plasma mass-spectrometry (ICP-MS; Agilent 7500 CE).

For quality assurance, Standard Reference Material 1649a "urban dust" and spiked filters were used. SRM 1649a is an atmospheric particulate material collected in an urban area. Element recoveries are shown in Table 1. Low recovery was observed for As (70%) and Ti (68 %), most likely due to incomplete digestion of particulate material. Further details about the procedure for the trace elements analysis are described elsewhere (Arruti et al., 2010).

2.3. Source apportionment

PMF was used as a receptor modelling technique for the water-soluble fraction dataset. Because a thorough discussion on the theoretical basis of PMF is found in the literature (Paatero and Tapper, 1994; Hopke, 2000; Reff et al., 2007), it is only briefly described here. PMF solves the receptor modelling equation (see equation 1), where the input ambient data

matrix (e.g., atmospheric deposition of metals) equals the product of two new matrices, the factor profile (F) and the contribution of each source (G) plus a residual matrix (E). Thus, in matrix form,

$$X = GF + E \qquad (1)$$

which can be also written in index notation as

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}, \quad \text{where} \quad i \in [1, n]; j \in [1, m]; k \in [1, p] \qquad (2)$$

where n is the number of samples and m the number of species. The solution of the equation requires the calculation of the coefficients of the new matrices, F and G, for a given number of factors (p). This is an optimisation problem where the objective function to be minimised is a modified error matrix (Q), which takes into account the uncertainties of each measured pollutant in each sample (σ_{ij}) with the constraints that each of the coefficients of the G and F matrices is to be non-negative (Hopke, 2000).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{\sigma_{ij}} \right]^2 \qquad (3)$$

This offers a more realistic solution than that obtained from PCA. The global minimum of Q calculated from equation (3) is compared with the minimum value of Q ($Q_{theoretical}$) obtained from equation (4):

$$Q_{theoretical} = nm - (n+m)p \qquad (4)$$

Different methods are used in the literature for calculating the uncertainties of observed data, and they were summarised by Reff et al. (2007). In the present work, the uncertainties of the metal fluxes below the method detection limit (MDL) were calculated as 5/6 MDL and as $4\overline{x_{ij}}$ for the identified outliers. For data above the MDL, the uncertainties were calculated according to equation (5):

$$\sigma_{ij} = (MDL_j{}^2 + (d_j x_{ij})^2)^{1/2} \qquad (5)$$

which was first used by Anttila et al. (1995) for bulk deposition samples. Equation (5) is also proposed by the EPA PMF 3.0 software (US EPA, 2008), where d_j is the error fraction calculated from the geometric average of the relative standard deviation (RSD) for each metal, which is the instrumental error associated with the measurements. Any experimental value below the MDS was replaced by half of the MDS, and the geometric mean was used instead of missing data and identified outliers.

A priori outliers were identified when $x_{ij} > 1.5 \times 0.95^{th}$ percentile and when the uncertainty $\sigma_{ij} > \overline{\sigma_{ij}} + SD_{ij}$. Additionally, a model improvement was carried out by detecting *a posteriori* outliers. First, this was done using the Huber function approach (Huber, 1981) included in the

EPA PMF 3.0 program and using a value of the outlier threshold distance (α) of 4, and secondly by readjusting x_{ij} and down-weighting uncertainties when the scaled residuals were higher than ± 6.

Different number of factors was tested in evaluation of the models. Four factors led to the best combination of the Q value and significance test (p-value). A total of 100 random runs were used to ensure that local minima were not obtained. The rotation of factors by assigning different values of F_{peak} did not improve the model performance; therefore, $F_{peak}=0$ was used in the developed models.

The best models were chosen according to the comparison between the predicted and observed data through the time series, the parity plots, the significance test (p-value), the distance between the calculated Q and $Q_{theoretical}$ and the physical meaning of the factor profiles.

3. RESULTS AND DISCUSSION

3.1. Bulk atmospheric deposition fluxes of minor and trace elements

The analysis of elements in the water-soluble and water-insoluble fractions of bulk atmospheric deposition was carried out for the whole measuring period, 2009-2012. Bulk atmospheric deposition of elements was obtained as the sum of both fractions (water-soluble and water-insoluble), and these values are shown in Table 2. The fluxes of the studied elements in bulk deposition followed the order Zn > Mn >> Cu > Cr > Pb > V > Ni >> As > Mo > Cd. The fluxes of Zn and Mn were more than 10 times higher than those of the other elements, with maximum values of 554.5 and 334.1 µg m^{-2} day^{-1} for Zn and Mn, respectively. With the exception of Mn and Pb, this ranking is commonly found in urban environments (Azimi et al., 2004; Motelay-Massei et al., 2005; Mijic et al., 2010). In previous studies, Pb deposition levels in urban areas were usually higher than that found in this work because the emission of such pollutant from traffic has strongly decreased in the last decade (Motelay-Massei et al., 2005). In the case of Mn, higher deposition fluxes were found in this work than in other studies. High Mn levels were also found in PM10 and PM2.5 samples at this site (Arruti et al., 2011).

According to these results, Mn is the main local pollutant found in Santander followed by Zn. Manganese is a typical tracer of steel production (Querol et al., 2007) and ferromanganese manufacturing plants (Borgese et al., 2011), and the Santander agglomeration area is affected by these industries, which are located in the suburbs 5-10 km SW of the sampling site. Pollutant roses confirmed that this local pollutant was mainly related to local industrial sources (Ruiz et al., 2011).

It is important to focus on the water-soluble fraction of the bulk deposition because the metals present in this fraction will be more likely to enter food chains, thus making them a greater hazard to human health than metals from the insoluble fraction (Tate and Bates, 1984). The contribution of the water-soluble fraction to bulk atmospheric deposition is presented in Table 3. Most of elements show an intermediate behaviour; however, Cr, Ti and Pb tend to be present in the insoluble fraction, whereas Zn is largely present in the water-soluble fraction.

High solubilities of Zn (higher than 75%) have also been previously reported in wet deposition samples in the literature (Guieu et al., 1997; Cizmecioglu and Muezzinoglu, 2008).

Correlation coefficients between the studied elements in the soluble and insoluble fractions of the atmospheric deposition were calculated. The correlation matrices are shown in Tables 4 and 5 for the soluble and insoluble fraction of the atmospheric deposition, respectively. The strongest correlations ($r>0.6$, $p<0.01$) were found for Cd-Ni, As-Ni, Cd-Mo, Ti-Ni, Cd-Ti, Ti-Mo, As-Ti, As-Cd, V-Mo and Cd-Pb in the soluble fraction and for As-Zn, As-Ni, Cd-Zn, Ni-V, As-Cd, Cr-Mo, Cd-Mn and Ni-Zn in the insoluble fraction. When both correlation matrices are compared an important difference is observed: no correlation between the most abundant metals (i.e., Zn and Mn) and the other elements was found in the water soluble fraction, whereas both metals show significant correlations with the other elements in the insoluble fraction. Therefore, Zn is well correlated with As, Cd and Ni and Mn is well correlated with Cd ($r>0.6$, $p<0.01$) in the insoluble fraction. Weaker but significant correlations between Zn and Ti, Mn, Pb and V and between Mn and Ni, Pb, Zn, As and Cr ($0.4<r<0.6$, $p<0.01$) were also found in the insoluble fraction. The differences in metal solubilities and distances from point sources may explain the differences found between both correlation matrices. For example, electric arc furnace dust, which is emitted from a steel plant located 5 km SW, typically contains Zn, Pb, Mn, Ni, As, Cd and V among other trace metals; however, their solubilities in water are quite different. This observation would explain the lack of correlation between Zn and the other elements in the soluble fraction. Cupper was not correlated with any element in either the soluble or insoluble fractions.

3.2. Seasonal variability

In some deposition studies, wet deposition fluxes of trace metals are well correlated with the precipitation amounts (Tate and Bates, 1984; Sakata et al., 2006; Okubo et al., 2013). Taking into account the seasonal variability of precipitation, the seasonal fluctuation of element deposition in the soluble fraction was studied. In Figure 2, the average deposition of elements in the water-soluble fraction for each season was plotted against the average monthly precipitation amount. A similar trend was observed for most of the studied elements, consistent with the average precipitation: the maximum values were found in fall, followed by spring, winter and summer.

Similar results (i.e., maximum deposition fluxes of minor and trace elements associated with the periodic fluctuations in rainfall periods) were observed in Castellon, Spain (Soriano et al., 2012), Pearl River Delta in China (Wong et al., 2003), the "Campo de Gibraltar" region in Spain (Usero and Gracia, 1986a), and Ontario (Canada) in a site not directly affected by point sources (Jeffries and Snyder, 1981). However, other seasonal patterns not directly related to precipitation events are also found in the literature. Two examples are higher fluxes of V and Ni in winter due to combustion of fossil fuels (Mijic et al., 2010) or seasonal variability of heavy metals due to fluctuation of wind direction and emissions from a local point source (Jeffries and Snyder, 1981). In contrast, other works on atmospheric deposition have shown that deposition fluxes of trace elements were only weakly dependent on seasons, at least when the main sources are relatively constant throughout the year (Azimi et al., 2004; 2005b; Motelay-Massei et al., 2005).

The relation between the seasonal trend of precipitation and element deposition in the soluble phase in Santander was confirmed by Pearson's correlation coefficients analysis. Cadmium, Cr, Mn, V and Mo average seasonal depositions were strongly correlated with seasonal average precipitation (Pearson's correlation higher than 0.9), As, Ti, Ni, Pb and Zn were reasonably correlated (Pearson's correlation between 0.6 and 0.9), but Cu was not correlated. Thus, element deposition fluctuations in the water soluble fraction follow the same pattern than precipitation, probably due to the washing effect of rain events. However, Cu was the only element that did not follow this trend. Since metal deposition fluctuations may be due to the variability in metal emissions and in precipitation along the seasons, it is assumed that Cu deposition trend is mostly affected by fluctuations in metal emissions from its sources. These results indicate that the variability in the deposition of the studied elements, with the exception of Cu, in the soluble phase was associated with the seasonal variability in precipitation. When Pearson's correlation coefficients analysis was repeated with the insoluble phase of the atmospheric deposition, only Mn showed a good correlation (higher than 0.9). Arsenic, Cu, Ti, Ni and V were not correlated, whereas Cd, Cr, Pb, Mo and Zn showed intermediate correlations between 0.6 and 0.9. The lack of correlation of As, Ti, Ni and V in the insoluble phase with precipitation is probably due to an important contribution of dry periods to the deposition of these elements.

3.3 Enrichment factors

Enrichment factor (EF) analysis was carried out to assess the relative contribution of anthropogenic sources compared to those of natural origin. The procedure was based on the standardisation of the measured element with respect to a reference element. Reference elements are usually characterised by low occurrence variability, and the most commonly used are Al, Ti and Fe. In this case, Ti was selected as a reference. The EF was calculated according to equation (6):

$$EF_i = (X_i/Ti)_{deposition}/(X_i/Ti)_{crust} \tag{6}$$

where X_i is a given element concentration/deposition. Elemental crust values were obtained from Li et al. (2009). Titanium deposition values were corrected using a recovery value of 68 % (see Table 1).

EF values for the studied elements in bulk atmospheric deposition are shown in Figure 3. Averages for the whole sampling period were calculated. In general, according to the enrichment degree, the elements can be considered as highly enriched (EF>100), intermediately enriched (10<EF<100) and less enriched (EF<10) (Berg et al., 1994). High EF values (>100) were found for Cu, Cd and Zn, pointing to significant anthropogenic sources, mainly from traffic and industrial activities (Sharma et al., 2008; Hou et al., 2005). High anthropogenic contributions were also found for Cu, Ni, Pb and Zn in the atmospheric deposition collected near a metal smelting industry in Ontario, Canada (Jeffries and Snyder, 1981); for Zn, Pb, As and Cd in Finland (Kyllönen et al., 2009) and Korea (Kim et al., 2012); and for Zn, Cu, Cd and Pb in Belgrade (Mijic et al., 2010).

The rest of the elements have EF values between 10 and 100, indicating that these elements are likely emitted by natural and anthropogenic sources. In this group, it is important to focus on Mn. The EF value of Mn is 50, which could indicate a coupled contribution of anthropogenic and natural sources; however, similar values were obtained for this metal on a different matrix (PM10). EF values of 54 and 62 were obtained at the same sampling site (urban background) and at an industrial site by Arruti et al. (2010) and Cozzi et al. (2008), respectively. In both cases, the anthropogenic (industrial) origin of Mn was clearly demonstrated.

3.4. Source apportionment

PMF analysis was performed only on the water-soluble fraction of the atmospheric deposition because this fraction may directly affect the living organisms in soils, continental water and oceans. Four factors were chosen to solve the PMF models. The performance of the developed models can be seen in Figure 4, where the time series of the observed and calculated deposition fluxes of some studied elements are shown.

The source profiles obtained from the PMF analysis are shown in Figure 5. The percentages for each species among the factors are shown with square symbols (right y-axis), and the contribution of each species to the deposition flux for each factor is given in bar charts (left y-axis). The factors were sorted according to the amount of flux explained by the model. The first factor (F1) explains 62.5 % of the total deposition flux, while the values for the others are 10.6 % (F2), 6.6 % (F3) and 2.6 % (F4). Globally, 82.26 % of the deposition flux is modelled. These percentages show how much each source contributes to urban pollution.

The first source is mainly composed of Zn and Mn, with lower contributions by Cr and V. The second factor is mainly composed of Cu and Pb; however, while Zn and Mn are mostly associated with factor 1, the estimated flux of both metals in factor 2 is still noticeable. The third factor is mainly composed of As, Cd, Ni, V, and Mo, and the last factor is composed of Cu, Ni, Ti and Mo. No time patterns are recognised for the first and the fourth factor; however, the second profile exhibits a pattern in the winter periods, and the third profile exhibits peaks in the cold months (see Figure 6).

A preliminary analysis was performed to associate the factors derived from PMF with known metal sources in Santander Bay, based on the factor profiles shown in Figure 5 and the profiles of these sources calculated from emission and literature data. Thus, the element deposition fluxes in each factor shown in Figure 5 were expressed in percentages in Figure 7 and compared with the contribution (%) of each element to the total emission rate of each identified source. The emission profiles of factor 1 and 2 for most elements were calculated from annual emission rates from local point sources obtained from the Pollutant Release and Transfer Register (PRTR). Due to the fact that the emission rates of Mn from these point sources were not reported in the PRTR, they were calculated from emission factors (US EPA, 1984) applied to the main industrial activities in Santander Bay: ferromanganese and silicomanganese production, steel production with electric arc furnaces, and iron foundry and casting. The emission profiles of factors 3 and 4 that were associated to urban traffic and navigation were built from emission factors derived from the literature.

The first factor explains the largest part of the metal atmospheric pollution. It represents the pollution caused by the industrial area located in the SW of the bay, and Mn and Zn are the footprints leading to this association. A ferromanganese and silicomanganese plant, a non-integrated steel plant, and an iron foundry are located in this area approximately 5-10 km SW of the receptor site. Their emissions are resumed and are classified in a unique homogeneous category called Industrial 1. Figure 7a shows the relative contribution of each studied element of factor 1 and that obtained from the sum of the emissions of the three identified point sources.

Arsenic and Cd emissions from the industrial area are lower than those from other sources; therefore, the model does not attribute any concentration in the first factor. Chromium, Mn, Ni and Zn are similar in both profiles. Looking at the whole factor 1 profile (Figure 5), a notable amount of Ti and V could also be ascribed to the Industrial 1 factor, but no emission rates of these elements were given in PRTR.

Figure 7b also shows a good match between the relative contribution of the studied elements of factor 2 and that obtained from the emissions of a local iron foundry located 7 km W of the sampling point. For the sake of simplicity, this factor is called Industrial 2. Pb is the main tracer of this activity, together with Zn and Mn, as is observed in Figure 5. Arsenic, Cd and Ni are not observed in factor 2, most likely due to their low emission rates reported by this plant in PRTR.

For the interpretation of factor 3, a profile was constructed based on the emissions of fuel, lube oil and engine wear of cars, trucks and motorcycles in the Santander urban area. These calculations were based on EMEP/EEA guidelines (EMEP/EEA, 2009) using the emission factors of As, Cd, Cr, Cu, Ni, Pb and Zn, the number of the different categories of vehicles in Santander and a typical mileage of 12 km/day. The calculated profile was compared with factor 3 and is shown in Figure 7c. Both are characterised by a high percentage of Cd, Cr, Ni and Zn. Vanadium and Mo were clearly observed in factor 3, but unfortunately, the emission factors of V and Mo were not included in the EMEP/EEA guide. Vanadium is typically considered as a tracer of diesel combustion together with Ni (Fabretti et al., 2009), and Mo is usually found in engine lubricants as MoS_2 (Spada et al., 2012). Furthermore, a high correlation between Mo and total carbon (TC) was found in PM10 in Santander in a previous study, indicating that Mo and TC were tracers of traffic (Arruti et al., 2011). Although Cu is typically found in factor profiles related to traffic, it was not observed in factor 3. It should be considered that most of the Cu associated with traffic usually derives from brake line abrasion (Fabretti et al., 2009), and the profile shown in Figure 5 matches better with fuel combustion, lube oil and engine wear of vehicles.

The last factor, which represents less than 3% of the studied elements atmospheric pollution in the water-soluble fraction of the deposition, was compared with ship emissions. Santander is an important harbour in the North of Spain, with maritime traffic of 1250 ships in 2009 (approximately 4.5 million tons). The emission factors of metals from ship emissions strongly depend on the type of fuel. Fuel oil contains important amounts of Ni and V, and the characteristic chemical profile is different than that of factor 4, while marine diesel oil (MDO) and marine gas oil (MGO) profiles match better to factor 4, as is observed in Figure 7d. This finding is reasonable because the maritime traffic inside Santander Bay must be fuelled by low-

sulphur marine distillates (MDO/MGO). The ship emissions profile for marine distillates was calculated from Cooper and Gustafsson (2004) because the EMEP/EEA guide for ship emissions does not include the emission factor of vanadium. A clear analogy between the estimated and modelled factors can be observed in Figure 7d: As, Cu, Cr, Ni and V match reasonably well, but Pb, Zn and Cd are not found in factor 4. Further analysis is needed to explain the lack of Pb, Zn and Cd in the last factor.

CONCLUSIONS

This study addressed the bulk atmospheric deposition fluxes and sources of the minor and trace elements As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, V and Zn in Santander, a Northern Spanish coastal urban area. The fluxes of the studied elements in bulk deposition are similar or lower than those found in some other studies, with the exception of Zn and Mn, which show deposition fluxes more than 10 times higher than those of the other elements. A wide range in element solubilities was found, from 4 % (Ti) to 78 % (Zn). The higher solubility of Zn as compared with the other elements could explain the lack of correlation of Zn with those elements in the soluble fraction and the good correlation in the insoluble phase. All of the elements studied in the water-soluble fraction of the atmospheric deposition showed seasonal dependence, with the exception of Cu, due to the seasonal variability in precipitation. The different behaviour of Cu may be explained because its deposition trend is probably affected by fluctuations in Cu emissions from its sources. In the insoluble fraction, only Mn showed a strong seasonal variability.

Positive Matrix Factorisation (PMF) was used for the source apportionment of the analysed elements in the soluble fraction of the atmospheric deposition. Four factors were identified from PMF. According to the factor profile obtained and the potential characteristics of the sources, the best matches were achieved between the first factor and the sum of three industrial plants located to the SW: a ferromanganese and silicomanganese plant, a non-integrated steel plant and an iron foundry and casting facility. The second factor matched with an iron foundry and casting facility located 7 km W of the sampling point, while the third factor matched with an urban factor that included fuel, lube oil and engine wear emission. The fourth factor and a navigation emission profile were well matched. Because the first factor contributes 62.5 % of the total deposition flux of the studied elements and because it shows high loadings of Zn and Mn, both elements are considered as the most characteristic anthropogenic tracers of the studied area, even though the enrichment factor of Mn is below 100.

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TABLES

Table 1. Element recoveries and standard deviations (%) of SRM 1649a (n=8) and spiked filters (n=6) by ICP-MS after microwave-assisted acid digestion.

Element	SRM 1649a	S.D.	Spiked filters	S.D.
As	70	6	84	7
Cd	125	20	88	7
Cu	91	14	102	5
Cr	80	12	127	7
Ti	68*	22	128	13
Mn	138	23	111	2
Ni	107	23	116	3
Pb	90	9	126	18
V	103	14	107	4
Mo	119	17	112	3
Zn	117	22	**	**

* Ti is not determined in SRM 1649a; the recovery was calculated from the literature (Piñeiro-Iglesias et al., 2003)

** Zn is not quantified due to high blank filter values

Table 2. Bulk atmospheric deposition of minor and trace elements (μg m^{-2} day^{-1}) in Santander (September 2009-October 2012).

Element	As	Cd	Cu	Cr	Ti	Mn	Ni	Pb	V	Mo	Zn
N	36	36	36	36	36	36	36	36	36	36	36
Average	0.3	0.1	11.2	4.7	11.4	146.6	1.5	4.4	3.0	0.2	173.1
S.D.	0.2	0.1	11.1	2.1	6.1	67.0	0.7	2.2	1.0	0.1	125.8
Max	1.1	0.3	60.1	10.2	39.7	334.1	4.2	10.4	5.2	0.7	554.5
Min	0.05	<d.l.	2.2	0.9	3.5	48.3	<d.l.	0.3	1.4	<d.l.	22.5

N-number of samples; S.D.-Standard deviation; d.l.-Detection limit

Table 3. Water-soluble fraction contribution (%) to bulk atmospheric deposition.

Element	As	Cd	Cu	Cr	Ti	Mn	Ni	Pb	V	Mo	Zn
Average	37	52	43	15	4	39	58	22	45	36	78
Max	90	99	82	42	27	83	91	69	66	75	98
S.D.	25	34	24	10	5	15	19	19	12	20	13

S.D.-Standard deviation

Table 4. Pearson correlation matrix for the deposition of minor and trace elements (soluble fraction).

	Cd	Cu	Cr	Ti	Mn	Ni	Pb	V	Mo	Zn
As	**0.660**	0.352	0.236	**0.666**	0.208	**0.793**	**0.475**	0.395	0.409	-0.064
Cd		0.309	**0.459**	**0.692**	0.339	**0.802**	**0.601**	**0.521**	**0.745**	-0.026
Cu			-0.092	0.175	0.068	0.378	0.340	0.283	0.294	-0.170
Cr				0.218	0.038	0.298	0.095	**0.470**	0.422	0.266
Ti					0.365	**0.731**	**0.583**	**0.571**	**0.678**	-0.035
Mn						0.145	0.365	0.225	0.369	0.173
Ni							**0.594**	0.353	**0.476**	-0.037
Pb								0.364	0.399	0.164
V									**0.637**	-0.074
Mo										-0.102

In **bold** character: correlation is significant at the 0.01 level

Table 5. Pearson correlation matrix for the deposition of minor and trace elements (insoluble fraction).

	Cd	Cu	Cr	Ti	Mn	Ni	Pb	V	Mo	Zn
As	**0.630**	-0.077	0.154	**0.427**	**0.459**	**0.730**	**0.499**	**0.590**	0.068	**0.743**
Cd		0.015	0.265	0.109	**0.623**	**0.559**	**0.549**	0.233	0.361	**0.711**
Cu			0.120	-0.043	0.127	-0.007	0.419	0.020	0.102	-0.001
Cr				0.010	**0.576**	0.357	**0.457**	0.418	**0.629**	0.061
Ti					0.158	0.419	-0.002	**0.519**	-0.080	**0.562**
Mn						**0.436**	**0.536**	0.272	0.218	**0.555**
Ni							**0.542**	**0.663**	**0.451**	**0.601**
Pb								**0.438**	0.206	**0.478**
V									0.155	**0.433**
Mo										-0.092

In **bold** character: correlation is significant at the 0.01 level

FIGURE CAPTIONS

Figure 1. The sampling site and main industrial point sources in Santander Bay.

Figure 2. Seasonal trend of the studied elements in the water-soluble fraction of the atmospheric deposition. The average monthly precipitation is also shown in the figure: (a) Cr, Ti, Ni, Pb, V; (b) As, Cd, Mo and (c) Mn, Zn, Cu.
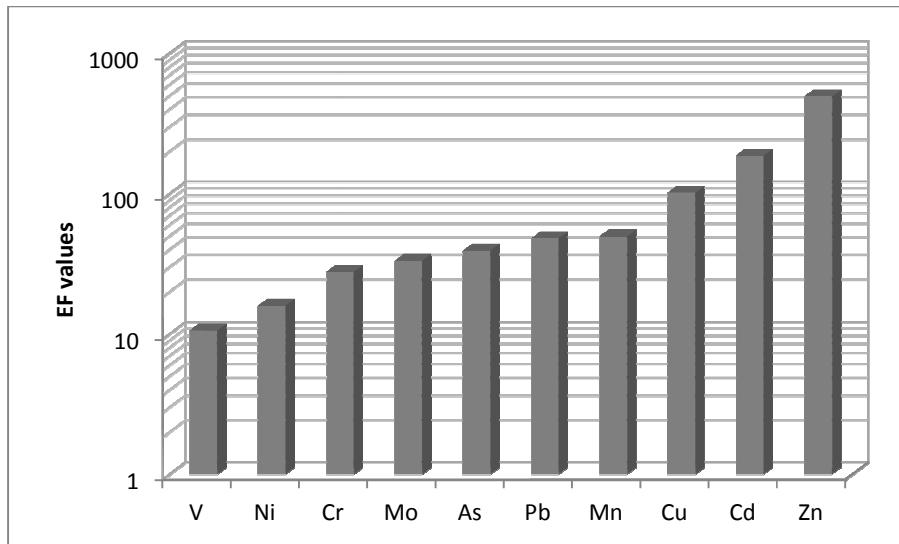
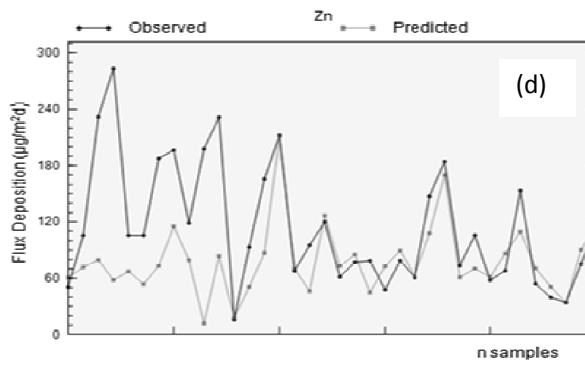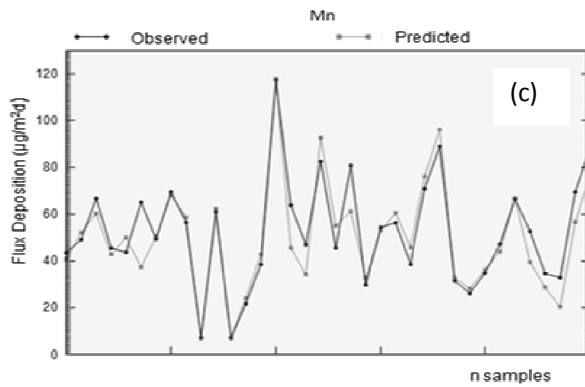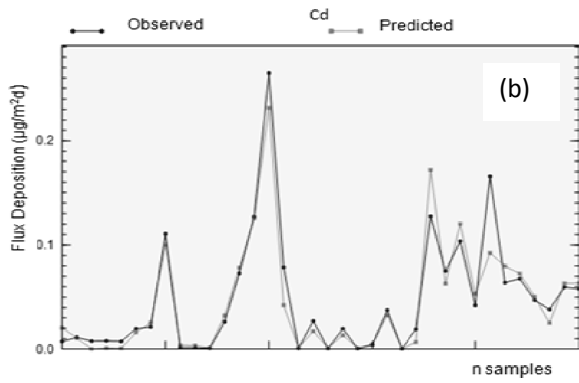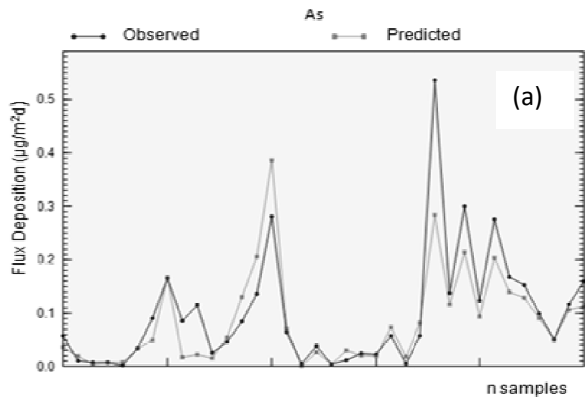Figure 3. Enrichment factors of elements in bulk atmospheric deposition.

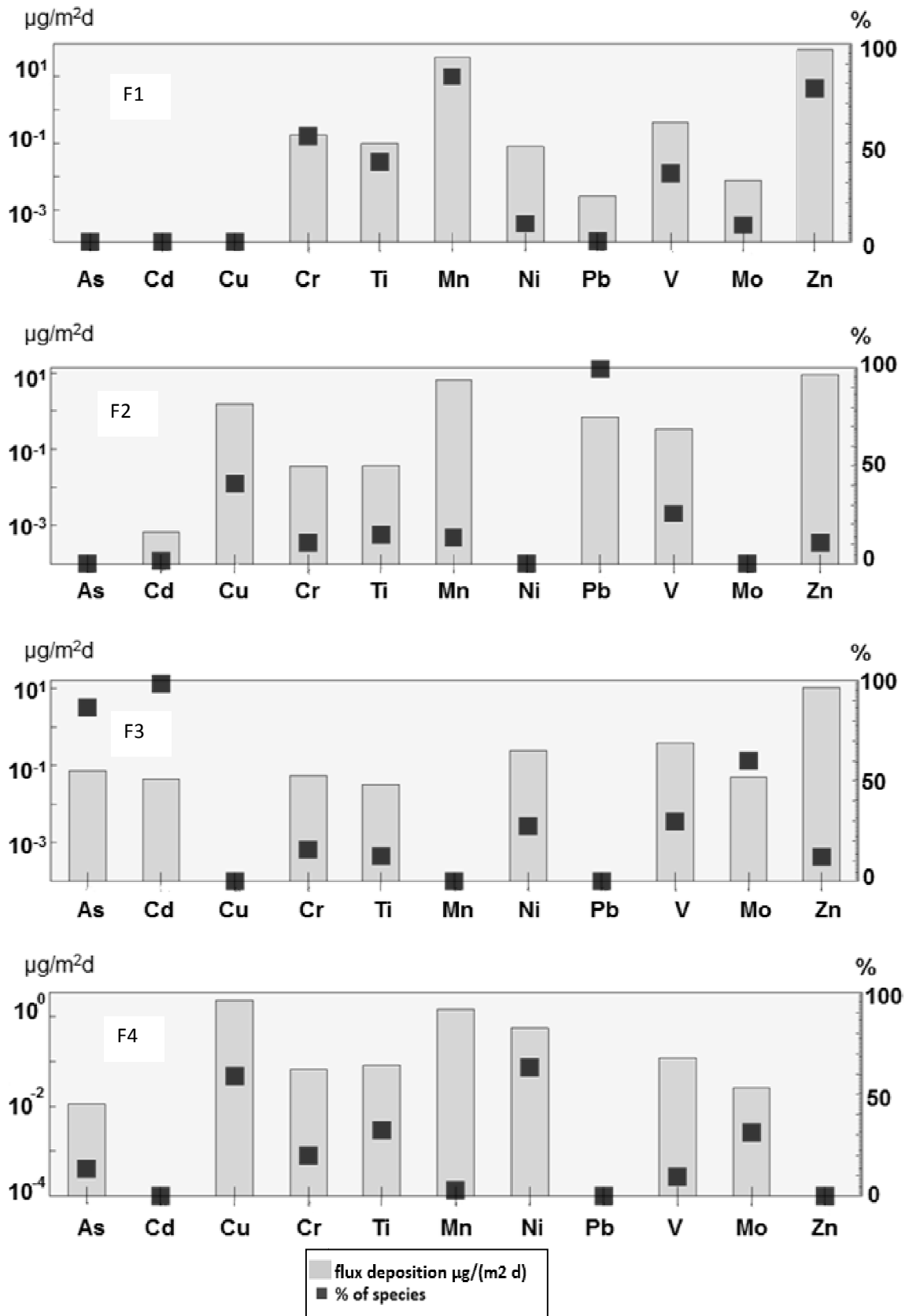Figure 4. Time series of predicted and observed fluxes: (a) As, (b) Cd, (c) Mn and (d) Zn.

Figure 5. Factor profiles from PMF at Santander.

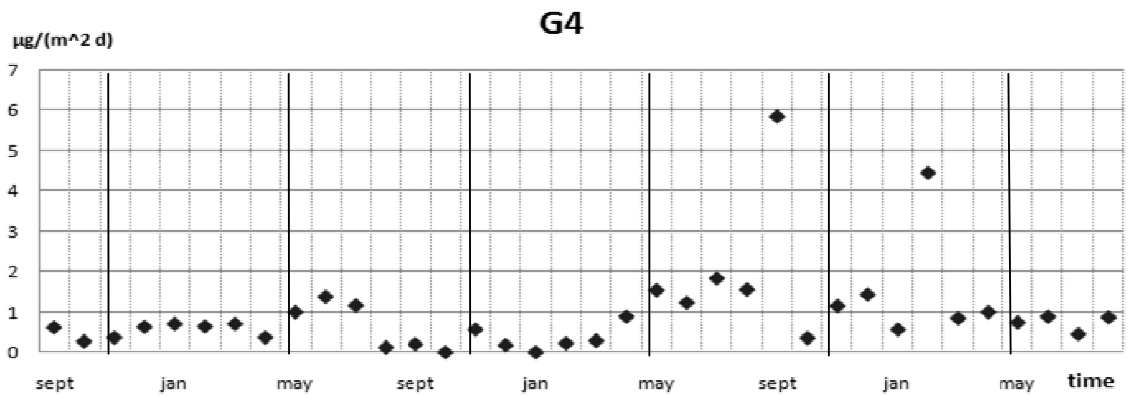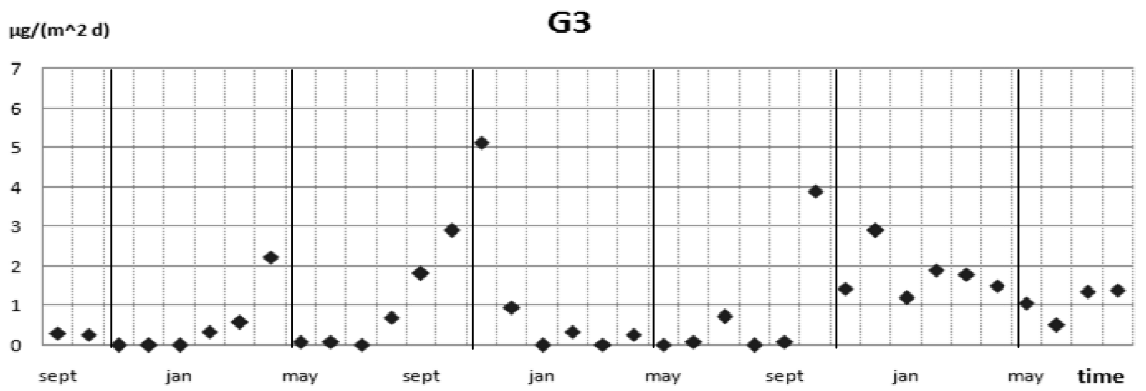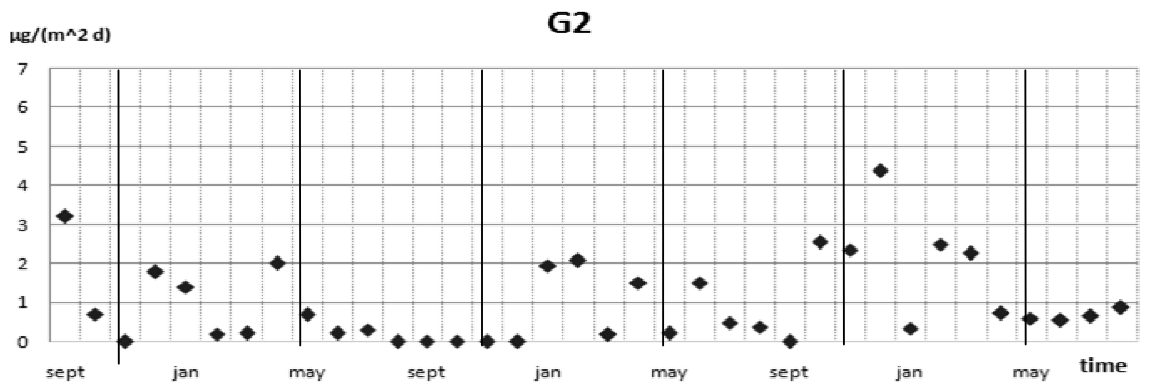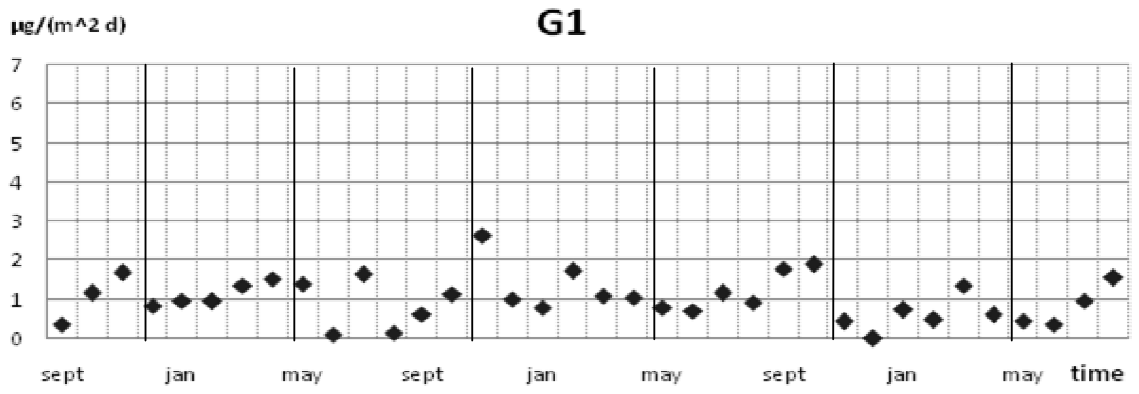Figure 6. Time series of factor contributions obtained from PMF at Santander.
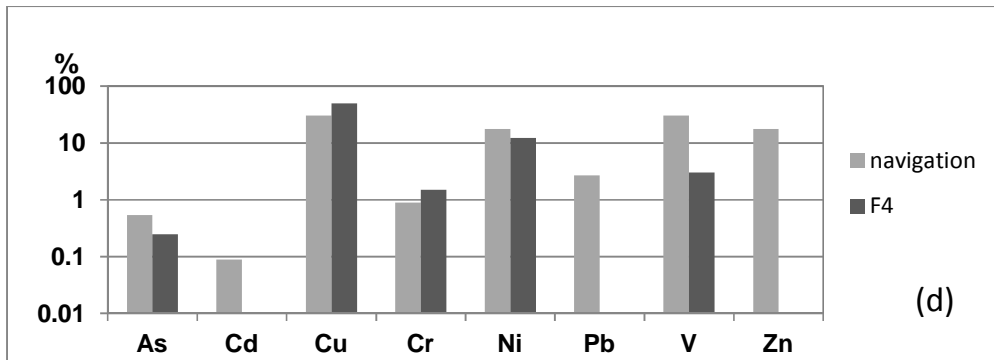
Figure 7. Comparison between the factor profiles obtained from PMF at Santander and the calculated source profiles from identified sources: (a) Factor 1 vs. Industrial 1 source, (b) Factor 2 vs. Industrial 2 source, (c) Factor 3 vs. fuel, lube oil and engine wear emissions and (d) Factor 4 vs. ship emissions (marine distillates).

FIGURES

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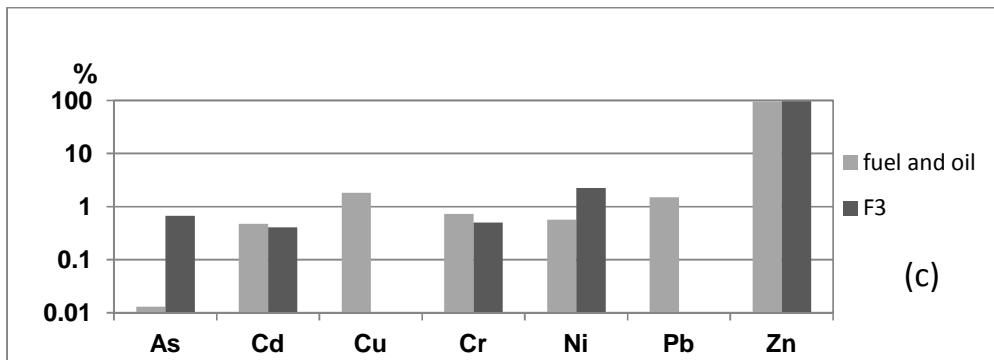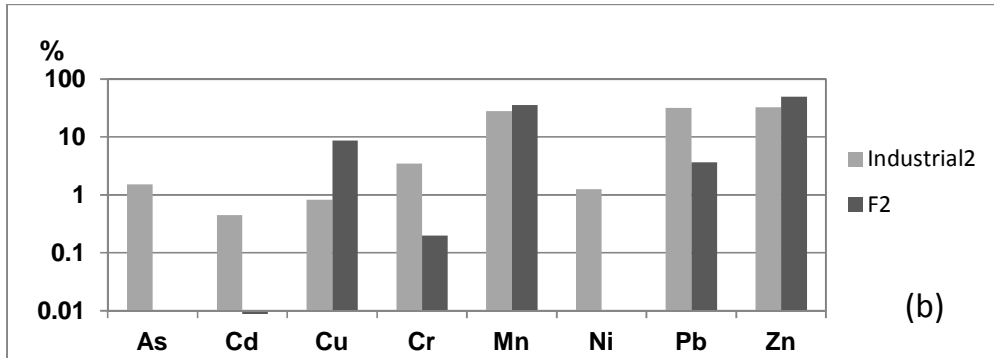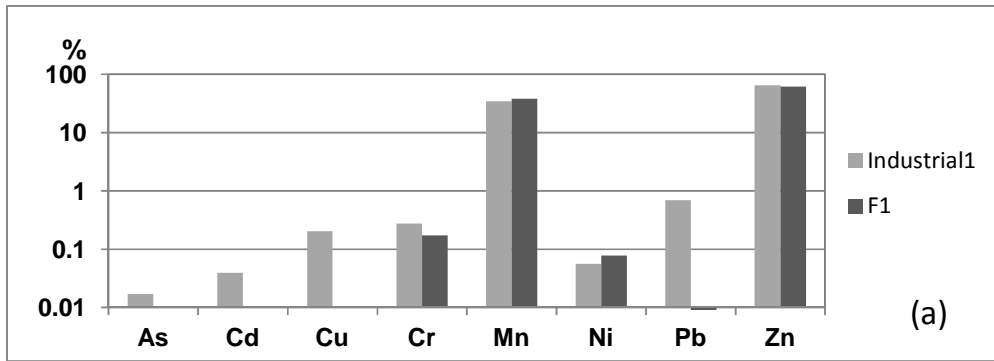Figure 6. Time series of factor contributions obtained from PMF at Santander.

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