Variability in metal deposition among industrial, rural and urban areas in the Cantabria Region (Northern Spain)

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Abstract

Cantabria is a small region located in Northern Spain that combines different land uses; thus, urban, industrial and rural areas are present in a relatively small area (5300 km^2); however, the anthropogenic influence is evident by studying the deposition of metals towards these areas. Three sampling sites (industrial, urban and rural) were selected to assess the variability in metal deposition. Sampling was carried out monthly (from January 2012 to July 2012) using a bulk (funnel-bottle) sampler. As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Ti, Zn and V were determined in the water-soluble and in the insoluble fractions of deposition samples. The impact of the human activities in the industrial area can be seen on several metals such as Pb, Zn, Cu and Mn. The most obvious influence was found for Mn, high fluxes were measured in the industrial site with a mean value of 2260 µg/m^2·day; in contrast to urban (99.6 µg/m^2·day) and rural (15.3 µg/m^2·day) areas. The lowest flux values were found in the rural area for all the elements. Enrichment Factor (EF) analysis were also studied for the three sites. The high EFs values found for Pb, Mn, Cu, and Zn (>100) in the industrial site point to significant anthropogenic sources, mainly originated from industrial activities (steel and ferro-manganese alloy manufacturing plants) and road traffic.
Keywords: atmospheric deposition, trace metals, deposition variability.

1   Introduction

Trace metals are toxic substances that can be emitted into the air from both natural and anthropogenic sources. The effects of some trace metals on human health via the food chain or the environment as a whole, occur through

concentrations in ambient air and via deposition; atmospheric deposition is the major pathway into the surface environment. Therefore, the accumulation of such metals in soils and the protection of ground water should be taken into account. Major anthropogenic sources of trace metals include vehicular emissions (Cr, Mn, Fe, Cu, Zn, Ba, Pb), stationary fossil fuel combustion (V, Cr, Ni) and non-ferrous metal production (Mn, Cu, Zn, Cd) [1, 2]. The concentration of some metals in ambient air has been limited by the European legislation under the Fourth Air Quality Daughter Directive. In addition the European Commission shall consider regulating the deposition of As, Cd, Ni and Hg [3]. Accurate and comparable ambient air measurements of these compounds are therefore needed, and standard measurement techniques for metals in atmospheric deposition were published in 2009 by the European Committee for Standardization (CEN) [4].

The aim of the present work is to determine the trace metals atmospheric deposition in three different sites in order to assess the spatial heterogeneity of atmospheric deposition of metals in a region influenced in different ways by anthropogenic activities.

2 Methodology

2.1 Study site

This study was performed in the Cantabria Region (593,121 inhabitants, 2011) located in the Northern Spain. Different land uses are combined, thus, urban, industrial and rural areas are present in a relatively small area (5300 km^2).

In this context, three different sampling sites were evaluated, situated at urban (Santander (SANT)), rural (Los Tojos (TOJ)) and industrial (Maliaño (MAL)) areas (fig. 1).
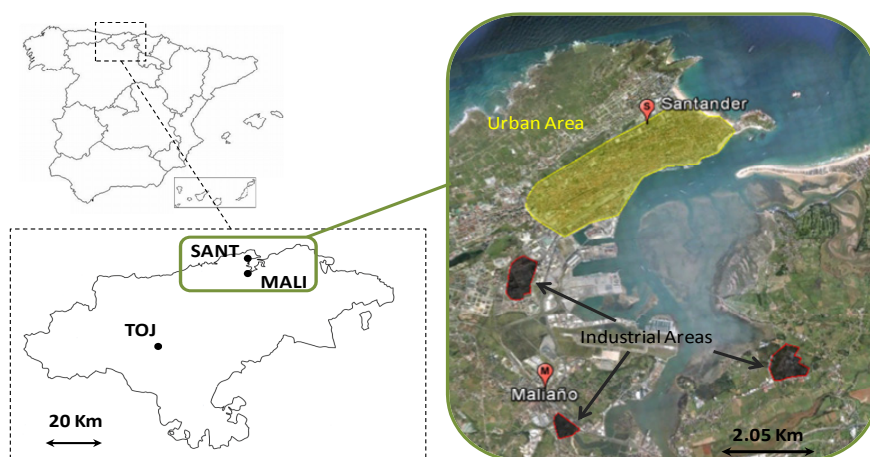

Figure 1:   Selected sampling sites in the Cantabria Region.

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

Maliaño (MAL) (9,609 inhabitants, 2011) is a small town highly influenced by close industrial areas, mainly by a ferro-manganese plant located 0.66 Km SE from the monitoring station. MALI sampling site (43°25'12.35"N, 3°50'30.13"W, 5 m a.s.l.) is situated on the rooftop of a municipal building ("Casa El Botiquín").

Los Tojos (TOJ) (434 inhabitants, 2011) is a small village at the heart of Cantabria located in the Nature Reserve of Saja-Besaya. TOJ sampling site (43°09′25.86″ N, 4°14′21.44″ W, 431 m a.s.l.) is situated in a plot surrounded by woodland area and close to a cottage and a low traffic road, 50 km SW from Santander.

2.2 Sampling methodology

Bulk atmospheric deposition sampling was performed using 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 steel chassis with a protector ring on top to avoid bird nesting. The device is based on EN 15841:2009 Standard [4] and recommended to measure total atmospheric deposition at industrial and urban sites, mainly when total deposition is not only due to precipitation events [5]. The funnel was 1.7 m above the ground to avoid the collection of re-suspended soil particles. The sampling was carried out monthly from January to July 2012. At the end of each sampling period the funnel was rinsed with 250 ml of Milli-Q water and all this equipment was replaced by a clean one.

2.3 Sample treatment and chemical analysis

Bulk atmospheric deposition samples were brought to the laboratory at the end of each sampling period. Precipitation amount was determined by gravimetry. Subsequently, 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 and stored at 4ºC prior to analysis.

The sample treatment for the analysis of trace metals in the insoluble fraction from bulk atmospheric deposition is in accordance with EN 14902:2005 [6]. A microwave-assisted acid digestion of filters was performed during 1 h; the temperature increased slowly to the higher temperature of 185ºC. The acid mixture was 8 ml of 65% HNO_3 (Suprapur®, Merck) and 2 ml of 30% H_2O_2 (Suprapur®, Merck). Further details about the procedure for the trace metals analysis are described elsewhere (Arruti *et al.* [7]). As, Cd, Cr, Cu, Mn, Mo, Ni,

Pb, Ti, Zn and V were determined by inductively coupled plasma mass-spectrometry (ICP-MS; Agilent 7500 CE).

3   Results and discussion

3.1 Metal atmospheric deposition levels

Trace metals levels in atmospheric deposition are presented in table 1. These fluxes are similar or even lower than those widely reported in the literature [8–10], except for Mn and Zn. The highest fluxes were found for these metals in the industrial site (maximum values of 4279 and 170 μg/m^2·day, respectively).

Table 1:   Bulk atmospheric deposition of metals (μg/m^2·day) in the studied sites.

	Industrial Site (MALIAÑO)			Urban Site (SANTANDER)			Rural Site (LOS TOJOS)		
	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
As	0.64	0.34	0.42	0.54	0.21	0.34	0.28	0.01	0.10
Cd	0.12	0.06	0.09	0.19	0.06	0.10	0.01	0.00	0.01
Cu	89.1	15.6	36.3	37.8	5.3	17.1	15.2	2.2	5.5
Cr	16.0	9.2	12.1	6.8	0.95	4.0	2.5	0.4	1.3
Ti	66.0	20.4	32.5	14.1	3.5	7.6	28.8	4.0	10.8
Mn	4280	1437	2260	167.5	63.1	99.6	54.9	1.63	15.3
Ni	3.9	2.3	2.8	3.4	1.1	1.8	3.2	0.4	1.2
Pb	52.6	15.1	22.7	7.2	1.6	4.9	10.1	0.3	3.1
V	8.1	4.4	5.6	4.6	2.4	3.4	1.6	0.43	0.90
Mo	0.59	0.43	0.50	0.40	0.12	0.26	0.33	0.00	0.13
Zn	170.0	46.8	118.1	169.6	56.2	93.9	45.9	11.1	26.6

In terms of spatial variation, a notable pattern was found for Mn, Zn, Pb, Cu and Cr: industrial > urban > rural. Ratios for these metals in bulk atmospheric deposition and in the water-soluble fraction of the bulk deposition are shown in table 2. The most evident variation was found for Mn between industrial and rural sites. Furthermore, a high urban/rural ratio was found for this metal, pointing that Santander is highly influenced by industrial areas located in the suburbs. However, these metal ratios decrease when they are calculated from the water-soluble fraction data, mainly for Cr and Pb, as shown in table 2.

It is important to focus on the water soluble fraction of the atmospheric deposition because metals presented in this fraction will be more likely to enter

food chains and therefore to be of a greater hazard to human health than metals from the insoluble fraction. The contribution of the water-soluble fraction to bulk atmospheric deposition is presented in table 3.

Table 2:   Metal ratios calculated at the studied sampling points.

	Bulk atmospheric deposition			Water soluble fraction		
	Ind/Urb	Ind/Rur	Urb/Rur	Ind/Urb	Ind/Rur	Urb/Rur
Mn	23	148	6.5	12	40	3.4
Zn	1.3	4.4	3.5	0.7	2.1	3.0
Cu	2.1	6.6	2.6	1.7	5.1	2.9
Cr	3	9.3	3.1	0.6	0.4	0.7
Pb	4.6	7.3	1.6	1.4	0.6	0.4

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

	As	Cd	Cu	Cr	Ti	Mn	Ni	Pb	V	Mo	Zn
Industrial											
Max	37	56	92	6	30	38	53	40	46	40	85
Min	1	2	15	1	1	15	14	1	13	1	24
Mean	13	18	41	3	7	25	27	9	27	16	46
Urban											
Max	71	99	82	22	9	83	81	41	52	75	96
Min	32	70	37	5	1	30	52	6	31	36	69
Mean	54	82	70	14	6	44	65	24	46	53	83
Rural											
Max	92	96	95	92	96	89	97	99	95	94	99
Min	5	61	43	12	4	78	29	67	42	3	94
Mean	51	81	80	62	57	84	83	88	81	65	98

The solubility of the studied elements strongly depends on the sampling site. In this way, metals from bulk atmospheric deposition collected in the industrial site are mainly in the insoluble phase, probably due to insoluble metal species contained in the deposition of sedimenting particles emitted from point sources, which are located very close to the industrial sampling point.

Nevertheless, the main fraction in the rural site is the water soluble fraction; metals are mostly present dissolved in the rainwater. Since no point sources are located in the vicinities of the studied rural area, the origin of metals determined in this sampling point can be associated to medium to long-range transport from different sources. Thus, the residence time of these metals bound to particles in the atmosphere is much higher; originating that rainwater dissolves these metals.

Finally, an intermediate behavior between industrial and rural is found for the urban site, where the influence of some industrial point sources has been previously reported by Arruti *et al.* [11]. Therefore, in terms of water soluble fraction fluxes the difference between the three sites is not so evident.

3.2 Ternary plots

Bulk atmospheric deposition and water soluble fraction fluxes of metals from the three sampling sites can be compared in a ternary diagram, which is commonly used for a variety of applications in Earth Sciences, such as rock classification and phase transition, to represent the relative contents of three components [12]. Ternary diagrams of bulk atmospheric deposition and the water soluble fraction of the deposition calculated for the industrial (MAL), urban (SANT) and rural (TOJ) sites are shown in figure 2.

Since the extent of source impact varies by site, elevated concentrations of a source marker species at a site explains higher impact by the source, and therefore it appears closer to the corner representing the site in the ternary diagram. Most of the elements in the bulk atmospheric deposition plot (fig. 2A) are clustered towards the industrial corner. However, when metals determined in the water-soluble phase of the atmospheric deposition are plotted in a ternary diagram (fig.2B), a completely different distribution of metal data is observed. Thus, Pb and Cr were close to the industrial corner in fig.2A move to the center of the ternary plot when the water soluble phase is considered. The rest of metals except Mn and Ti move towards the urban corner.
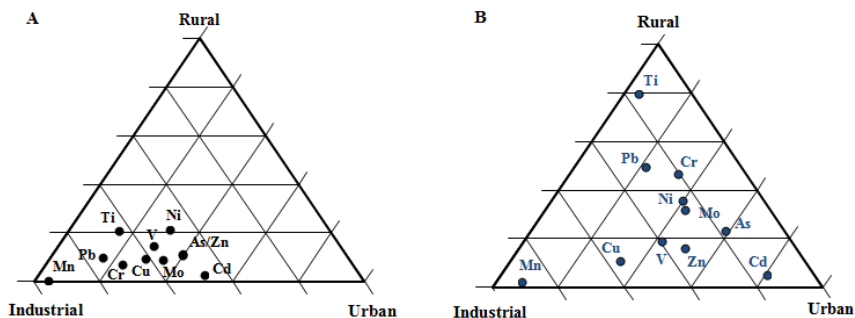

Figure 2:   Ternary plots of the studied metals for: (A) bulk atmospheric deposition, (B) water soluble fraction.

However, both diagrams show a similar behavior for Mn. It is oriented towards the industrial corner indicating an industrial large dominance. Mn is a typical tracer of ferroalloy manufacturing plants [13] and MAL site is mainly influenced by a ferro-manganese plant located very close from the sampling station. Although the solubility of the Mn species is much lower in the industrial site, the total flux of Mn in this site is so high that it is still found in the industrial corner of the ternary plot built from water soluble data.

3.3 Enrichment factors

Enrichment factor (EF) analysis was carried out to assess the relative contribution of anthropogenic sources respect to those of natural origin. The

procedure was based on standardization of the measured element respect to a reference element. Reference elements have natural origin are often characterized by low occurrence variability; the most commonly used are Al, Ti and Fe. In this case, Ti was selected as reference. Two procedures to calculate EF were assessed:

i) $EF = (X_i/Ti)_{sample}/(X_i/Ti)_{crust}$. Typical elemental crust values were used by Li *et al.* [14].

ii) $EF = (X_i/Ti)_{sample}/(X_i/Ti)_{Cantabria\ soil\ background}$. Cantabria soil background values were obtained from Cantabria Environmental Government [15].

where $X_{i,\ sample}$, $X_{i,\ crust}$, and $X_{i,\ Cantabria\ soil\ background}$ are the bulk atmospheric deposition, the average concentration in crust and the average concentration in Cantabrian soils of a given element.

Averages for the whole sampling period were calculated for the three different sampling points. 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). EF values obtained with procedure i) are shown in fig. 2A. In this case the lowest EF values (EF<100) were found for Cr, Ni, Mo and V for the three sites. Cu and Pb show a similar behavior, EF>100 in the industrial and urban sites and EF<100 in the rural site, indicating that both metals are highly influenced by anthropogenic activities such as industrial and road traffic. Finally, the high EF values (>100) found for Zn and Mn pointed to significant anthropogenic sources, probably originated from industrial activities (steel and ferroalloy manufacturing plants) located around the Santander bay. Fig. 2B shows EFs obtained with the procedure ii). It takes into account the Cantabria soil background composition, the reference soil in the region, without influence from anthropogenic sources. Results are similar to those obtained by the former procedure: high values for Mn and Zn (EF>100), similar behaviour for Cu and Pb and low values for the rest of the elements.

4   Conclusions

The most important conclusions of the present study may be summarized as follows.

Trace metals levels in bulk atmospheric deposition collected in three different sites (industrial, urban and rural) were similar or lower than those widely reported in the literature, except for Mn and Zn. High levels of Mn were found in the industrial and urban sites (mean value: 2260 and 99.6 μg/m^2·day, respectively). Moreover, high deposition fluxes of Zn were found in these two sites (industrial mean value: 118.1 μg/m2·day; urban mean value: 93.9 μg/m^2·day).

The spatial variation was also assessed. A common pattern was found for Mn, Zn, Pb, Cu and Cr: industrial > urban > rural. In this way, ratios for metals in the different sites were evaluated. The ratios for Mn between industrial and rural
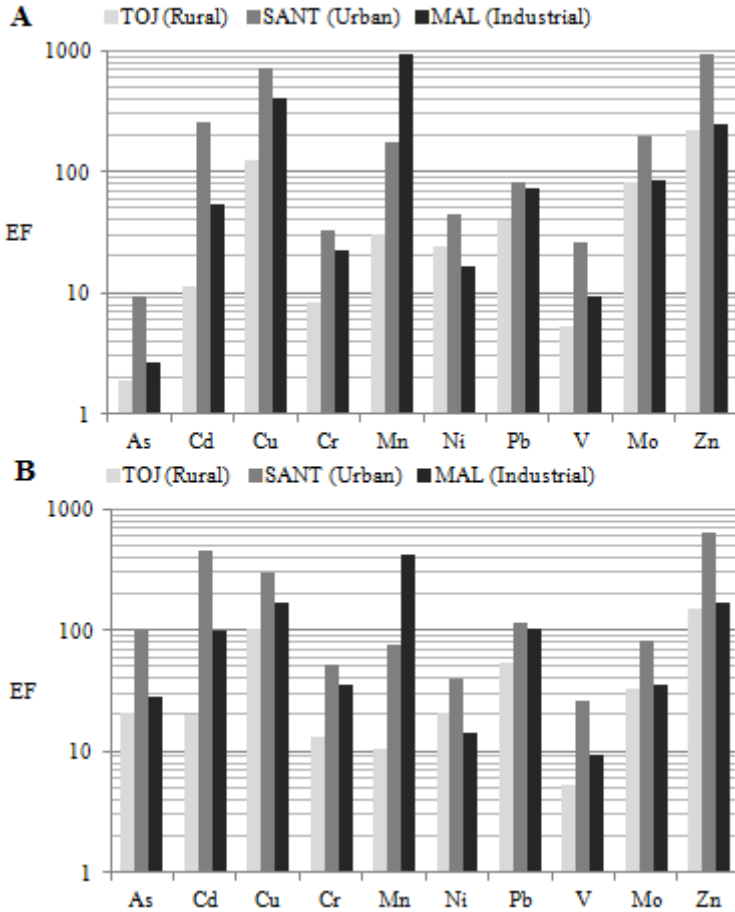
Figure 3:   Enrichment factors of elements in bulk atmospheric deposition: (a) procedure i); (b) procedure ii).

sites and between urban and rural sites were 148 and 23, respectively. These values indicate that Santander and Maliaño are highly influenced by industrial areas located in the Santander suburbs.

The water soluble fraction from the atmospheric deposition was studied. Different behaviors were found depending on the sampling site: metals from the industrial site are mainly in the insoluble phase, probably due to metals are bound to sedimenting particles emitted from point sources, which are located very close to the sampling point. On the other hand, metals from the rural site tend to be present dissolved in the rainwater. No point sources are located in the vicinities of the studied rural area. The origin can be associated to medium to long-range transport from different sources. For this site, the residence time of metals bound to particles is much higher; originating that rainwater tends to

dissolve metals. Finally, an intermediate behavior between these sites was found for the urban site.

   Since no point sources are located in the vicinities of the studied rural area, the origin of metals determined in this sampling point can be associated to medium to long-range transport from different sources. Thus, the residence time of these metals bound to particles in the atmosphere is much higher; originating that rainwater dissolves these metals.

   Finally, enrichment factor (EF) analysis was carried out to assess the relative contribution of anthropogenic sources respect to those of natural origin. Low values were found for Cr, Ni, Mo and V (EF<100 for the three sites). Cu and Pb showed a similar trend, EF>100 in the industrial and urban sites and EF<100 in the rural site, indicating a large influence by anthropogenic activities (industrial and road traffic). The high EF values (>100) found for Zn and Mn pointed to significant anthropogenic sources, probably originated from industrial activities (steel and ferroalloy manufacturing plants) located around the Santander bay.

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