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

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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 characterised 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.

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

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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 the deposition of elements in urban areas (Azimi et al., 2003, 2004, 2005a, 2005b; 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 year 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 (Dammgen 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 (43° 28′ 26″ N, 3° 47′ 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". Fig. 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