Chemosphere 92 (2013) 882–891

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Determination of soluble ultra-trace metals and metalloids in rainwater and atmospheric deposition fluxes: A 2-year survey and assessment

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HIGHLIGHTS

- Today, also coarse particles cause harmful effects through ground depositions.
- Industrial (Cr) and traffic (Pb) pollutants were deposited in soils along the time.
- Toxic metals (Cd, Ni, Mo, Cu) and metalloids (As) were best removed by rain.
- Heavy rainfalls remove better B ≫ Tl, Th, U > Be, Ti, Cr, Mn > Co, As, Fe, Ni.
- Light rainfalls remove better Zn, Pb > Sb, Ba > Mo, Cu.

ARTICLE INFO

Article history:
Received 29 August 2012
Received in revised form 9 February 2013
Accepted 16 February 2013
Available online 4 April 2013

Keywords:
Trace elements
Rainwater
Dry deposition fluxes
Sequential PCA

ABSTRACT

The present work investigates the relationships between composition of rainwater and dry deposition fluxes by trace metals and metalloids. A modification in automatic "wet-only" and "dry-only" samplers was applied, which allowed the collection and conservation of samples separately. ICP-MS technique was used for the determination of analytes in samples. Concentrations of soluble elements in rainwater were measured directly in filtered samples. A sequential acid treatment with nitric, hydrofluoric and finally perchloric acids was used to measure the total contents of metals and metalloids in coarse particles. Variation between periods of heavy and light rains was assessed. Almost all of the metals and metalloids – B, Tl, Th, U, Al, Cs, Be, Ti and others – studied in dry deposition showed important decreases in concentrations (40–92%) during periods of heavy rainfall. Most of these metals and metalloids – As, Cr, Co, Ni – presented their highest levels (53–90%) in heavy rainfall periods in rainwater samples. Sources were identified in both types of samples collected using a new chemometric tool (SPCA). Urban traffic, surrounding contaminated soils and local anthropogenic sources were identified for rainwater samples. Natural and contaminated soils and general anthropogenic emissions were the sources identified for dry deposition fluxes.

1. Introduction

The chemical composition of atmospheric precipitation is closely related with the degree of air pollution in urban, industrial and rural ecosystems. It is well known that due to the dynamic nature of the atmosphere, metals in particle form can be deposited in areas far away from their original sources (Andreae and Rosenfeld, 2008). Trace metals in precipitation can also accumulate in surface water and soil, where they can cause harmful effects on aquatic life, forest ecosystems and plants (Barrie et al., 1987; Fernández Espinosa and Rossini Oliva, 2006).

The composition of the ambient air depends on contributions from hydrocarbon combustion, industrial processes, combustion in vehicles, etc., which provide organic and inorganic (metals and metalloids) pollutants. Rainwater composition provides crucial information on sources of air pollution (Vázquez et al., 2003; Montoya-Mayor et al., 2011). Composition on atmospheric deposition fluxes shows also information on atmospheric sources (Usero et al., 1983; Melgarejo et al., 1986). Sources of metals and metalloids in Seville have been previously studied from 30 years ago employing multivariate statistical analysis (Usero et al., 1988). The origin of air pollution in this city come from the vehicular traffic, metal foundries, waste combustions, agriculture works and resuspension of earth crustal particles (Fernández et al., 1999, 2000, 2004a).

The elimination of particles in the atmosphere can occur by: (1) aerosols can fall to the earth surface when particles are coarse, as dry deposition; (2) wet precipitation as rain or snow can remove coarse and fine particles, as wet deposition.

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.02.044

Dry deposition is effective for particles larger than 2 μm in size where gravitational attraction is more effective. Dry deposition of atmospheric particles can occur by inertial impaction, Brownian diffusion or gravitational sedimentation (Grantz et al., 2003). Also, dry deposition is resulting from winds delivering the smog particles directly into the biosphere without rain precipitation. Before dry deposition can occur, sulphates and nitrates, along with other pollutants, contribute to a uniform haze that obscures scenic views in most cities. At most low elevation locations in the eastern United States, the annual amount of wet and dry deposition is similar (USDA, 2007).

In terms of wet deposition, it is accepted that there are two major wet scavenging processes: in-cloud scavenging and below-cloud scavenging (Slinn 1974; Charlson et al., 1983; Colin et al., 1987). Scavenging processes are determined by such particulate properties as particle size, gas solubility and the characteristics of precipitation. Other factors such as particle availability in the lower atmosphere (Zobler, 1986) and vertical distribution could determine the relative significance of different removal processes during a single event (Lim et al., 1991; Alastuey et al., 2001). Besides, the potential capacity of rainwater to dissolve toxic metals from atmospheric particulate matter was also studied employing speciation schemes (Fernández et al., 2000; Fernández and Ternero, 2004b). Similar studies demonstrate the importance of the soluble and mobile fraction regarding the total metal content (Davis et al., 2001; Joshi and Balasubramanian, 2010).

The importance of a correct and simultaneous collection of atmospheric rainwater and deposition fluxes constitutes a necessary requirement for the current kind of study. The most single way of sampling is to use a volumetric rain gauge device to collect and measure wet precipitation for a daily or weekly basis (Trigo et al., 2005). For dry deposition it is common to employ a bulk collector that collects coarse particles during 1 month (Usero et al., 1983). However, the first device has the disadvantage that rainwater collected also contain coarse particles from dry deposition and the second could collect rainwater during the monthly period of sampling (Chantara and Chunsuk, 2008). A complete sampler allows the collection and preservation of the two types of samples separately. For this, "wet-only" and "dry-only" samplers are crucial. The solution is automated samplers for collecting both types of samples, which would collect simultaneously only-coarse particles and only-rainwater samples during any kind of weather conditions without mixing.

Furthermore, as the current commercial samplers have no sample preservation devices, it is necessary to modify the collectors and design additional modules for conservation of collected samples. This constitutes one of the particular objectives of the present study, the optimization of sampling conditions, mainly for aqueous samples.

Recently, a lot of information about the composition of precipitations has been gathered in America, Central and Northern Europe (Arsene et al., 2007; Celle-Jeanton et al., 2009) and other parts of the world, as China (Wei et al., 2005), Japan (Hou et al., 2005), India (Momin et al., 2005), etc. In Spain, several authors have studied the chemistry of atmospheric precipitation (Alastuey et al., 1999, 2001; Encinas et al., 2004). Furthermore, the papers pertaining to rainwater and dry deposition composition are scarce when compared to those referring to Total Suspended Particles (TSPs) (Fernández et al., 2004a).

Therefore, the aim and novelty of this work is to study the relationship between atmospheric pollutants in wet deposition and in dry deposition samples in an urban location, covering a long period of more than 2 years; additionally other objective is to investigate the relationship between pollutants in periods of heavy rainfall and periods of light rainfall. Finally, concentrations measured will allow identifying sources of atmospheric pollutants using a recent novel chemometric tool –SPCA– on both types of samples.

2. Experimental

2.1. Measurement site and sampling

In this paper, the results corresponding to over 2 years of sampling and analysis of rainwater and atmospheric deposition loads are presented. Samples were simultaneously collected in an urban-trafficked site close to the navigable Guadalquivir River (Andalusia, Spain). This study was undertaken in the city of Sevilla (38°12′–36°51′N, 4°39′–6°32′W, 141.3 km^2), a city 60 km from the sea and only 8 m above sea level, the capital of Andalusia, in South West Spain. The collector was installed at 4 m over the floor into the University Campus of Reina Mercedes.

Sevilla is characterized by high temperatures and low wind speeds and prevalent air currents come from the southwest–northeast direction for the 1961–2000 period (Montoya-Mayor et al., 2011). The majority of rain episodes and Saharan inputs enter into the region of Andalusia through this valley from a westerly direction, mainly from the southwest. Important episodes of 'heat wave' occur frequently in summer coming from Sahara and Sahel deserts.

Rainwater samples (wet deposition) and bulk depositions fluxes (dry deposition) were collected with a TISCH ENVIRONMENTAL 78 100 APS (Tisch Environmental Inc., South Miami Ave., Cleves, Ohio, USA) automatic wet-only and dry-only sampler. This type of sampler is designed to collect atmospheric depositions in two separate buckets of 15 L (Fig. 1): one of these, the rainfall bucket ("Wet" bucket), opens only during episodes of rain, detected by an electronic sensor, and the other, the dust fall bucket ("Dry" bucket) is always open during dry periods. This allows the collection of both wet deposition (rainwater) and dry deposition (dust depositions) separately. All samples were collected during a period of over 2 years, from September 2006 to January 2009.

Samples of rainwater were collected dairy during each rain episode and accumulated later for a period of a week according to the recommendations of the OSPAR (EC, 1998; OSPAR, 2007) and Barcelona Conventions (EC, 1977; MAGRAMA, 2012) for the coastal zones protection. Samples of dust depositions were collected every 28 d, once per month, according to the Federal methods of the USA (USEPA, 2008) and regional laws of Spain (BOJA, 2006). This resulted in a total of 67 dairy samples collected and 39 weekly values accumulated for rainwater and a total of 22 samples collected of bulk samples, which are presented in this study. Also, for relationships with 22 monthly samples of dry deposition fluxes, 20 monthly values were accumulated for rainwater samples.

According to these conventions (BOJA, 2006; USEPA, 2008), dry deposition fluxes were expressed as mg m^{-2} d^{-1} (dividing total monthly depositions by 28 d) and cited in the present work as MDD, monthly dry deposition. Additionally to the weekly period – expressed as L m^{-2} $week^{-1}$ – rainwater samples were also averaged over monthly periods to give an objective relationship with dry depositions, expressing it as L m^{-2} d^{-1}, not by month, and cited as MWP, Monthly Wet Precipitation. For metal and metalloid, concentrations in dry deposition fluxes and in rainwater were expressed as μg m^{-2} d^{-1}. Additionally concentrations of analytes in rainwater samples were also expressed as μg L^{-1} $week^{-1}$ referring to a concentration in an aqueous basis for comparison with other world results.

2.2. Design of the modifications on the sampling engine

To ensure the optimal preservation of samples during dairy rain events, some modifications were carried out to the automatic collector (Fig. 1):

Firstly, a small-fridge was protected from the sun under the sampler. The rainwater was collected in bottles made of low