Talanta 125 (2014) 125–130

Contents lists available at ScienceDirect

Talanta

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

Fractionation of trace elements in total atmospheric deposition by filtrating-bulk passive sampling

F. Rueda-Holgado [a,*], M.R. Palomo-Marín [a], L. Calvo-Blázquez [a],
F. Cereceda-Balic [b], E. Pinilla-Gil [a]

[a] *Departamento de Química Analítica, Universidad de Extremadura, Av. de Elvas, s/n 06006, Badajoz, Spain*
[b] *Centro de Tecnologías Ambientales, Universidad Técnica Federico Santa María, Av. de España, Valparaíso, Chile*

ARTICLE INFO

Article history:
Received 14 October 2013
Received in revised form
31 January 2014
Accepted 7 February 2014
Available online 22 February 2014

Keywords:
Elemental fractionation
Atmospheric deposition
Inductively coupled plasma–mass spectrometry
Atmospheric sampling
Atmospheric pollution assessment

ABSTRACT

We have developed and validated a new simple and effective methodology for fractionation of soluble and insoluble forms of trace elements in total atmospheric deposition. The proposed methodology is based on the modification of a standard total deposition passive sampler by integrating a quartz fiber filter that retains the insoluble material, allowing the soluble fraction to pass through and flow to a receiving bottle. The quartz filter containing the insoluble fraction and the liquid containing the soluble fraction are then separately assayed by standardized ICP–MS protocols. The proposed atmospheric elemental fractionation sampler (AEFS) was validated by analyzing a Coal Fly Ash reference material with proper recoveries, and tested for field fractionation of a set of 10 key trace elements in total atmospheric deposition at the industrial area of Puchuncaví–Ventanas, Chile. The AEFS was proven useful for pollution assessment and also to identify variability of the soluble and insoluble fractions of the selected elements within the study area, improving the analytical information attainable by standard passive samplers for total deposition without the need of using sophisticated and high cost wet-only/dry only collectors.

1. Introduction

Elemental profile is a key fingerprint for the chemical characterization of atmospheric deposition providing interesting data for the evaluation of its impact on human health and the environment, including the identification of specific emission sources [1]. Trace element analysis of atmospheric deposition is highly demanded for assessing air quality, health and environmental risks, and therefore a great deal of research has been focused on the metal composition of atmospheric suspended particulate matter. Most of the studies dealing with determination of trace metals in atmospheric deposition are focused on the determination of total metal concentration without distinguishing the various species that are present, but for risk assessment of metal toxicity, it is important to determine bio-accessible concentrations instead of total metal contents [2,3]. Furthermore, it is widely recognized that the study of elemental solubility provides useful information about the biological and environmental availability of specific elements contained in particulate matter. As a result, growing research interest is focused on novel, optimized procedures for extracting airborne elements, and for acquiring and interpreting data on their solubility. A range of single and multiple steps fractionation schemes have been developed to characterize different degrees of elemental solubility in atmospheric particulate matter, by utilizing water, solvents of varying acid strengths, and physiological media [3]. The fractionation schemes reported in the literature have been used to characterize pollution sources, to evaluate metal mobility and bioavailability, and to identify binding sites of metals in order to assess metal accumulation, pollution and transport mechanisms. Weak (aqueous) extraction procedure simulating particle dissolution close to neutral pH, such as in the human lung, can be used for toxicological purposes [4]. Water extraction is also representative for particle weathering after deposition, informing about bio-accessibility for soil organism and plants [5].

Several authors have explored extractability of airborne elemental species in water as an indication of bio-accesibility, as recently reviewed by Mukhtar and Limbeck [3]. The most common approach is active sampling of aerosols (PM10 and PM2.5) at the sampling site by aspiration of air through a filtering media. The sample is then transferred to the lab and treated with water by mechanical shaking [6,7], ultrasound energy [8], or microwave assisted heating [9]. Active air sampling is an expensive and sophisticated technique requiring a power source, a vacuum pump and a caudal meter, appropriate fitting and casing for outdoor use, making it inappropriate for unattended operation during

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[*] Corresponding author. Tel.: +34661007299.
E-mail address: fernandorh@unex.es (F. Rueda-Holgado).

http://dx.doi.org/10.1016/j.talanta.2014.02.019
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experimental campaigns, especially at remote places. On the other hand, passive sampling has emerged as a tool for obtaining reliable analytical information in environmental quality monitoring [10]. Collection of atmospheric deposition by passive sampling can be performed by different experimental approaches, including a set of automatic dry-only, wet-only and water surface collectors, but the simplest mode is based on the so called atmospheric total deposition collectors (sometimes referred as bulk deposition collectors), offering distinct advantages through equipment simplification and ease of operation. The technique has been standardized by inclusion in the European norm EN 15841:2010 [11] for the determination of arsenic, cadmium, lead and nickel in atmospheric deposition as standard, and it is routinely incorporated in monitoring campaigns for atmospheric trace elements [12–14].

Trace element fractionation in atmospheric deposition collected by passive samplers has been attempted by some researchers. Morselli et al. [15] estimated soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions by a DDAS (dry deposition on aquatic surface) sampler. A similar approach was used by Muezzinoglu et al. [16] for the measurement of suspended and dissolved forms of selected heavy metals.

In the present study, we propose the new concept of fractionation of elements in atmospheric deposition by a passive atmospheric total deposition collector modified with a quartz fiber filter. This concept, designed as filtrating-bulk sampler, has been explored by some researchers for pH and major ions monitoring in the frame of acid rain investigations [17–19] but no reference has been found about its use for elemental fractionation. We propose this system and a simple and convenient analytical tool to obtain enriched chemical information from atmospheric deposition, allowing potential toxicity estimation with significant cost savings in atmospheric monitoring protocols.

2. Experimental

2.1. Reagents

All chemicals used for the preparation of stock and standard solutions were of analytical grade. Y(III) 1000 mg L^{-1} solution was supplied by Panreac (Barcelona, Spain). 1000 mg L^{-1} elemental standard solutions were supplied by Scharlau (Barcelona, Spain). Working solutions were prepared by dilution with ultrapure water obtained from a Wasserlab Ultramatic (Navarra de Tratamiento del Agua S.L., Pamplona, Spain) system. Reference materials and real samples were adjusted to pH 2 with sub-boiled HNO_3 obtained from a quartz sub-boiling system (Kürner, Rosenheim, Germany). 70% $HClO_4$ suprapur (Merck, Darmstadt, Germany) and 48% HF Hiperpur (Panreac, Barcelona, Spain) were used for sample treatments.

2.1.1. Reference materials and real samples

Certified Reference Material 1633c Coal Fly Ash (NIST, USA) was used for accuracy testing.

Weekly, atmospheric deposition samples were collected from several air quality monitoring stations in the vicinity of a copper smelter located at Puchuncaví, Chile. The Puchuncaví valley, a Mediterranean climate region placed in the coastal area of central Chile (71°24′S, 32°40′N), is characterized by marked pollution due to the discharge of gaseous pollutants and atmospheric particulates, and deposition of metal-rich particles from diverse industrial facilities including coal-fired power plants, a copper refinery and smelter, natural gas terminals and cement companies. A total of 14 samples were collected at the locations of La Greda (LG), Los Maitenes (LM), Puchuncaví (Pu) and Valle Alegre (VA) as shown in Fig. 1.

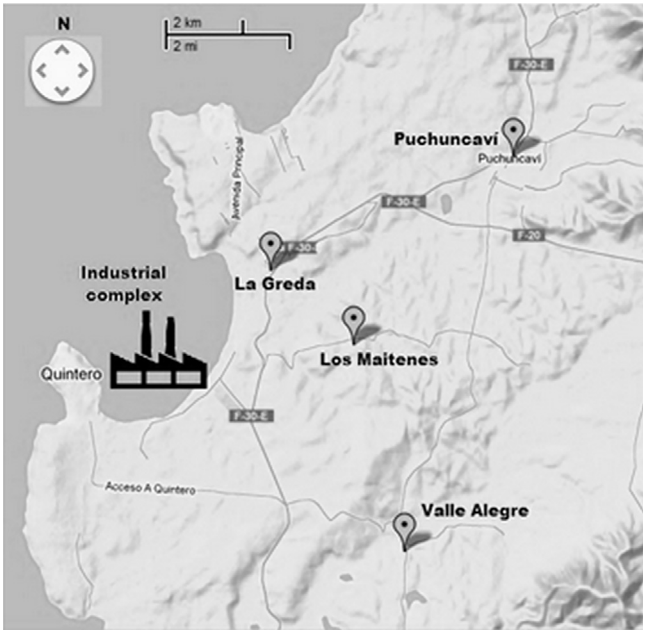

Fig. 1. Sampling locations of atmospheric deposition around the industrial complex of Puchuncaví–Ventanas, V Region, Chile.

2.2. Instrumentation

The AEFS devices we propose here for soluble and insoluble trace element fractionation in atmospheric deposition are derived from standard total atmospheric deposition polyethylene collectors (as described, e.g. in [11]). As depicted in Fig. 2, the proposed AEFS consists of: 1) an upper polyethylene bottle with a funnel end; 2) a polyethylene connection ring; 3) a perforated disk aimed to retain extraneous matter (insects, leaves, straws and the like); 4) a polypropylene connector body; 5) a quartz filter Teflon® support; 6) a quartz filter (0.3 μm pore diameter) to retain the insoluble fraction of total atmospheric deposition; 7) an O-ring to fix the quartz filter onto the support; 8) a filter polypropylene container; and 9) a 1 L receiving polyethylene bottle for the soluble fraction of atmospheric deposition.

A standard ICP–MS protocol for Cu(II), Mn(II), As(III), Cd(II), Pb(II), Sb(III), V(III), Sr(II), Co(II) and Rb(II) determination was applied on a PerkinElmer ELAN9000 equipment (Waltham, MA, USA). The instrument conditions and measurement parameters used in the analytical determination were 1000 W RF power, a carrier gas flow rate of 1 L min^{-1}, lens voltage of 7.25 V, a wash time of 35 s and three replicates for each sample. Quantification of elements was performed by an internal standard protocol with Y(III).

2.3. Experimental procedure for elemental fractionation in atmospheric deposition by the AEFS

A strict protocol for preparation and washing of the AEFSs was followed before field deployment for sampling. All parts were first washed in 2% aqueous solution of phosphate free Extran detergent (Merck, Darmstadt, Germany) for 24 h. Then the pieces were rinsed with water and placed in 9:1 HCl:ethanol bath for 24 h. Finally, the pieces were rinsed with suprapure water, dried under an extraction hood and stored in sealed bags until use.

47 mm diameter grade QMA quartz filters Whatman (0.3 μm pore diameter) (Maidstone, Kent, United Kingdom) were weighed and placed in AEFSs just before sampling. The AEFSs were then anchored to the top of a 2 m height pole and exposed to atmospheric deposition for one week. After the sampling period, the AEFSs were sealed in plastic bags and transferred to the lab.