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Temporal and spatial variation of trace elements in atmospheric deposition around the industrial area of Puchuncaví-Ventanas (Chile) and its influence on exceedances of lead and cadmium critical loads in soils

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HIGHLIGHTS

- Atmospheric elemental fractionation sampler for long-term monitoring of deposition.
- Major and trace elements in atmospheric deposition at Puchuncaví industrial area.
- Significant impact of pollutants depending of sampling locations and periods.
- PCA and cluster analysis identified industrial, traffic and mineral-crustal sources.
- Significant critical loads exceedances of Pb due to atmospheric deposition.

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ABSTRACT

Fractionation of elemental contents in atmospheric samples is useful to evaluate pollution levels for risk assessment and pollution sources assignment. We present here the main results of long-term characterization of atmospheric deposition by using a recently developed atmospheric elemental fractionation sampler (AEFS) for major and trace elements monitoring around an important industrial complex located in Puchuncaví region (Chile). Atmospheric deposition samples were collected during two sampling campaigns (2010 and 2011) at four sampling locations: La Greda (LG), Los Maitenes (LM), Puchuncaví (PU) and Valle Alegre (VA). Sample digestion and ICP-MS gave elements deposition values (Al, As, Ba, Cd, Co, Cu, Fe, K, Mn, Pb, Sb, Ti, V and Zn) in the insoluble fraction of the total atmospheric deposition. Results showed that LG location, the closest location to the industrial complex, was the more polluted sampling site having the highest values for the analyzed elements. PU and LM were the next more polluted and, finally, the lowest elements concentrations were registered at VA. The application of Principal Component Analysis and Cluster Analysis identified industrial, traffic and mineral-crustal factors. We found critical loads exceedances for Pb at all sampling locations in the area affected by the industrial emissions, more significant in LG close to the industrial complex, with a trend to decrease in 2011, whereas no exceedances due to atmospheric deposition were detected for Cd.

1. Introduction

The measurement of elemental composition is an important part of the chemical characterization of atmospheric deposition that provides relevant data for the assessment of its impact on human health and the environment, including the assignment and apportionment of specific emission sources (Viana et al., 2008). Toxic element quantification in atmospheric deposition is also valuable to identify and tackle possible emergencies in the environment resulting from poor air quality, and for the designing and monitoring of air quality improvement action plans.

Total concentration of elements in atmospheric deposition is a valuable but incomplete environmental information.

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Complementary data are desirable to estimate environmental impact and dynamics of the elements in the receptor ecosystems, especially regarding chemical speciation or at least fractionation of the most significant components. A number of research groups have explored different single and multiple steps fractionation schemes for a range of elements in atmospheric deposition, based on water and solvents of varying acid strengths, including physiological media (Smichowski et al., 2005; Mukhtar and Limbeck, 2013). Most fractionation methodologies include lab based extraction treatments after active or passive sampling of atmospheric deposition, but the concept of on line fractionation of elements during the sampling step has been also exploited to benefit from unattended semiautomatic operation of passive atmospheric total deposition samples. An atmospheric elemental fractionation sampler (AEFS), consisting in a passive atmospheric total deposition sampler modified with quartz fiber filter (filtering-bulk concept) has been described and validated (Rueda-Holgado et al., 2014) for pollution assessment in industrial areas. This device can be categorized as a modified funnel-bottle atmospheric collector (Amodio et al., 2014), and allows the determination of soluble (SF) and insoluble (IF) fractions of elements in atmospheric deposition during the sampling step, the separated fractions being collected and later assayed in the lab for elemental composition.

In this study we demonstrate the applicability of the AEFS as a simple but reliable tool for environmental impact assessment of atmospheric deposition during long-term operation, focusing on the insoluble fraction as the most persistent pollutant factor. With this aim, we have conducted systematic monitoring campaigns of elemental composition in atmospheric deposition collected at four selected locations around the industrial area of Puchuncaví-Ventanas (Chile), during the years 2010 and 2011. The study area is characterized by very high pollution due to the historical 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, cement companies, among other type of industries (Bernalte et al., 2015).

Published studies about environmental impact of industrial activities elemental atmospheric deposition levels in the Puchuncaví-Ventanas area are scarce and mainly focused on the soil impacted by the atmospheric deposition of emitted pollutants. Ginocchio (2000) investigated the effect of copper smelter on grassland in terms of physicochemical soil characteristics, abundance and plant species diversity, founding a significant impact on plant species regeneration capabilities. De Gregori et al. (2002) carried out the redox speciation of selenium present at ultratrace levels in rainwater collected al the area. The same group (De Gregori et al., 2003) conducted a work aimed to the monitoring of copper, arsenic and antimony levels in agricultural soils impacted and non-impacted by mining activities, from three regions in Chile including the Puchuncaví-Ventanas industrial area. The high concentrations measured in impacted soils from Puchuncaví-Ventanas (300 mg kg^{-1} Cu, 34.5 mg kg^{-1} As and 5.3 mg kg^{-1} Sb) clearly shows the impact produced in this zone by the industrial and mining activities developed in their proximities. Ginocchio et al. (2004) reported Cu, Zn, Pb and Cd concentrations (among other parameters) in different soil layers around the area. The levels found in the 0–5 cm layer were 361.6 mg kg^{-1} for Cu, 157.8 mg kg^{-1} for Zn, 79.9 mg kg^{-1} for Pb and 0.8 mg kg^{-1} for Cd. Copper mobility in soil around the copper smelter was investigated by Neaman et al. (2009). The same author reported results about the effectiveness of lime and compost for in-situ immobilization of trace elements in soil by using earthworms as bioindicators of toxicity (Neaman et al., 2012). A more detailed evaluation of trace elements in soils, focused on the study of their distribution in particle size fractions has been published by Parra et al. (2014). The composition and risk assessment of total atmospheric deposition has not been described, so we attempt here to obtain this information and connect the results with those previously described. Based on our measurements, we have characterized the elemental pollution status of the study area taking into account both the spatial and temporal variations in concentration levels. Moreover, we have used the information to identify pollution sources in the area by applying statistical techniques as Hierarchical cluster (HCA) and principal components (PCA) analysis.

We have also used the elemental deposition results to estimate the contribution of atmospheric deposition to exceedances of critical loads (de Vries and Groenenberg, 2009) of Cd and Pb in the soils at surrounding areas. The concept of critical loads has emerged in the frame of the convention on Long-Range Transboundary Air Pollution (LRTAP) of the United Nations Economic Commission for Europe (UNECE), specifically for Cd, Pb and Hg as the most relevant toxic elements contained in atmospheric deposition. The general definition of a critical load is “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” (Nilsson and Grennfelt, 1988). This definition applies to different receptors such as terrestrial ecosystems, groundwater, aquatic ecosystems, and/or human health. The estimation of critical loads is based on the balance of all relevant metal fluxes in and out of a considered ecosystem in a steady state situation. So the critical load of a metal can be calculated from the sum of tolerable outputs from the considered system in terms of net metal uptake and metal leaching. Among terrestrial ecosystems, critical loads of Cd and Pb can be calculated from the viewpoint of ecotoxicology for areas covered by non-agricultural land (forests, semi-natural vegetation) or agricultural land (arable land and grassland) (Meili et al., 2003).

2. Materials and methods

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. 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), 48% HF Hiperpur (Panreac, Barcelona, Spain) were used for simple treatments.

2.2. Instrumentation

The insoluble fraction of the total atmospheric deposition was sampled using a validated atmospheric elemental fractionation sampler (AEFS) (Rueda-Holgado et al., 2014). Briefly, 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 fraction (IF), allowing the soluble fraction (SF) to pass through and flow to a receiving bottle. Both fractions are subsequently assayed by the appropriate methodologies.

A standard ICP-MS protocol for As, Al, Ba, Cd, Co, Cu, Fe, K, Mn, Pb, Sb, Ti, V and Zn determination was applied on a Perkin Elmer ELAN 9000 equipment (Waltham, MA, USA). The instrument conditions and measurements parameters used in the analytical determination were 1000 W RF power, a carrier gas flow rate of