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Chemical profile of size-fractionated soils collected in a semiarid industrial area of Argentina

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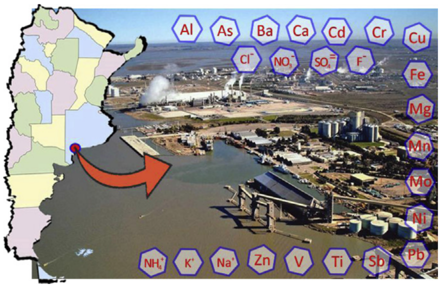
HIGHLIGHTS

- The chemical profile of size-fractionated semiarid soils was assessed.
- Cadmium is a marker of traffic, industries and agricultural activities.
- $Cl^- > Ca > Na^+ > Mo > SO_4^{2-}$ are key chemical markers for future assessment of APM.
- X_i/Ca differentiates chemical profiles by site for the top soils and finer fraction.

GRAPHICAL ABSTRACT



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ABSTRACT

A study was undertaken to assess the chemical profile of soil collected in Bahía Blanca (Argentina). In this industrial city, semiarid soils are affected by different industrial and agricultural activities, the presence of a saltpeter extraction facility, traffic and increasing urbanization. Sixteen soil samples (superficial and sub-superficial) were collected. Samples were sieved in two fractions ($A < 37$ μm, and $37 < B < 50$ μm) before elemental analysis. Major, minor and trace elements namely, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Ti, V and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP OES). Anions (Cl^-, F^-, SO_4^{2-}) and cations (K^+, Na^+ and NH_4^+) were determined by high performance liquid chromatography (HPLC) after an aqueous extraction. As expected, crustal elements namely, Al, Ca, Fe, Mg and Ti exhibited the highest concentrations. Mean elemental concentration ranged from <0.3 $\mu g\ g^{-1}$ (Sb) to 14.6 ± 0.6% (Ca). Ions concentrations in the soluble fraction measured at $mg\ g^{-1}$ levels were in the order $Cl^- > Na^+ \cong SO_4^{2-} > K^+ > NO_3^-$. Three indicators, namely, (*i*) coefficient of variation, (*ii*) coefficient of divergence and (*iii*) ratio of elemental concentration with respect to Ca were used to assess chemical, spatial and inter-profile variability. Chloride > Ca > Na^+ > Mo > SO_4^{2-}, dominated the variability indicating that these are key chemical markers for future assessment of crustal contribution to airborne particles in the area. The ratios X_i/Ca allowed discriminating the soil of the semi-arid region surrounding Bahía Blanca. The chemical profiles obtained in this study, particularly those of

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topsoil, will be a key input to characterize soil resuspension and its contribution to airborne particulate matter in a forthcoming receptor model analysis.

1. Introduction

With the development of more and more industries and intensive land use, soil contamination became a serious problem in many countries. Metals and metalloids are ubiquitous in rural and urban areas as a result of a wide range of human activities and natural geochemical processes. In urban soils, metal content has a tendency to increase as a consequence of vehicular emission, atmospheric deposition of dust and aerosols and industrial sources. In agricultural areas, the intake of metals via the soil-crop system has been considered as the main pathway of human exposure to environmental heavy metals (Liu et al., 2007).

For developing policies on pollution control and environmental management as well as to make decisions on soil remediation procedures it is of prime importance to have an accurate assessment of the contributions and impacts of potential anthropogenic sources. From the health standpoint of view it is important to gain information on the presence of different soil contaminants. Among them, heavy metals are well documented (Ogunsola et al., 1994; Fergusson and Kim, 1991) for their long-term toxicity effects (Gülten Yaylalı-Abanuz, 2011; Melaku et al., 2005) the possibility to be introduced into the food chain by plants and animals feeding. Therefore, guidelines and legislations have been issued concerning maximum allowance for total trace elements concentrations (Sastre et al., 2002; Gidhagen et al., 2002).

Assessing metal content in soils is also valuable information in studies devoted to the chemical characterization of atmospheric particulate matter (PM) since metal content reflects the extent of the potential emissions of these elements from natural and anthropogenic sources. The characterization of different categories of soil for assessing source apportionment of atmospheric aerosol is a permanent topic of research with the aim of interpreting the metal content of atmospheric particles (Manoli et al., 2002; Doređević et al., 2005; Cesari et al., 2012). Viana and coworkers reported evidence that a crustal contribution to atmospheric PM_{10} has been observed in almost all sites in Europe, with significant spatial variability ranging from 5% up to 37% on long-term averages (Viana et al., 2008). Wind-driven suspension of surface soils and desert dusts gives rise to airborne particles whose composition has much in common with road dusts, the main difference being a different trace element profile (Moreno et al., 2009). The crustal source represents an important contribution that can be originated from long-range transport, from eolian re-suspension of local soils and also from an anthropogenic contribution due to industrial and agricultural activity as well as re-suspension of road dust.

When topsoil is not covered by vegetation, its finer fractions can be easily released to the atmosphere and may contribute to PM. Recently, Pietrodangelo et al. (2013) characterized the contribution of local topsoil to airborne particulate matter in the area of Rome (Italy). Other authors reported the evaluation of chemical profiles of different categories of soil for application to source apportionment of atmospheric aerosol (Manoli et al., 2002; Doređević et al., 2005; Viana et al., 2008).

Bahía Blanca is one of the most important port city of Argentina and presents a large and intense industrial activity that includes: chemical and petrochemical plants, a refinery and natural gas separation plant, urea and ammonia production, PVC production from chlor-alkali process, and an important natural gas-fueled power plant. The soils destined to agricultural exploitation and granaries are concentrated in the surroundings of the city and this area is characterized by the use of fertilizers. Vehicular traffic is an increasing source of the so-called traffic related elements (TREs) in urban areas (Smichowski et al., 2008). As a consequence, atmospheric pollution may convert in a potential source of heavy metal contamination in soil and roadside dust in urban areas. Materials used in construction/demolition activities and urban works are additional sources of crustal elements. Among the potential natural sources of PM, in fact, dust from semi-desertic areas and sea salt aerosol are significant contributors to aerosols particles.

In the Bahía Blanca area, three essential factors for the occurrence of dust transport are present: (*i*) intense surface wind speed, (*ii*) low soil water content, and (*iii*) sparse vegetation cover. A recent study reported a dust flux ranging from 0.4 to 7.4 g m^{-2} $month^{-1}$, with a yearly mean of 26 g m^{-2}. The authors concluded that these aeolian dust materials reaching the Bahía Blanca zone have transition metals compositions similar to that found in regional topsoils (Gaiero et al., 2003).

The scenario depicted above shows that Bahía Blanca is a peculiar and complex area that deserves to be deeply studied. This research is part of a wider project directed at assessing the influence of the different sources including natural events such as dust storms influencing on the concentration and chemical composition of particulate matter in the city of Bahía Blanca. In this regard, this first insight focuses to report the chemical and physical characterization of soils of the city of Bahía Blanca as a potential source of airborne particles to be used for chemical mass balance models. These studies of sources will contribute to create an essential quantitative data set of soil source profiles, based on a well-documented methodology.

2. Experimental

2.1. Instrumentation and reagents

A PerkinElmer (Norwalk, CT, USA) ICP Optima 3100 XL, 40 MHz (axial view) simultaneous inductively coupled Ar plasma optical emission spectrometer provided with a Model AS 90 autosampler was used for elemental determination. An ultrasonic nebulizer (USN) was also used (U5000 AT, CETAC Technologies, Omaha, NE, USA) for determining elements found at very low levels. Main instrumental details and operating conditions are: Ar gas flow rates (in L min^{-1}): coolant, 15; auxiliary, 0.6; sample, 0.8. Nebulizer: cross-flow with Scott type expansion chamber. Detector: segmented-array charge coupled device.

Different techniques were used and compared for ions determination. A Konik (Barcelona, Spain) KNK-500A liquid chromatograph equipped with a Rheodyne (Cotati, CA, USA) Model 7125 injector, a 100 μl sample loop and analytical columns was used for anions and cations determination. Conductimetric detection was used in all cases. Data were transferred to a personal computer via an A/D interface and processed by means of integration software, Konikrom Chromatography Data System V.5 (Barcelona, Spain).

For the conductimetric analysis of chlorides a Thermo Electron Orion® (Waltham, Massachusetts, USA) instrument, model 115A