



Plasma-based techniques applied to the determination of 17 elements in partitioned top soils



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ABSTRACT

An investigation was carried out to characterize top soils collected in a prototypical urban area impacted by industrial and agricultural activities. Soils of the studied zone receive also the contribution of traffic from the urban area, marine aerosols from the Atlantic Ocean and dust from the Patagonian steppe. Top soil samples were sampled and then sieved in two fractions ($F1 < 37 \mu\text{m}$, and $37 < F2 < 50 \mu\text{m}$) for subsequent digestion using an acid mixture containing HCl, HNO₃ and HF (6:2:1). Elemental determination of Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Ti, V and Zn was carried out by inductively coupled plasma optical emission spectrometry (ICP OES) and/or inductively coupled plasma-mass spectrometry (ICP-MS). Accuracy tests for the entire analytical procedure were performed by means of the certified reference material NIST SRM 2711 Montana soil. Limit of detection reached varied from $0.08 \mu\text{g g}^{-1}$ (Cd) to $2.4 \mu\text{g g}^{-1}$ (Ba). Elemental concentrations ranged from $0.10 \pm 0.01 \mu\text{g g}^{-1}$ (Mo) to $14.6 \pm 0.6\%$ (Ca). Aluminum, Ca, Fe, Mg and Ti (geological elements) were found at concentrations in the percentage order. The ratios of elemental concentrations Mo/Ca, Ni/Ca and Ti/Ca were identified as chemical markers suitable for distinguishing the different soil samples by exposing the relative differences in the 4-element chemical profile. The concentrations of metals and metalloids in size-fractionated top soils reported in this study will be an important tool for future studies aimed to characterize soil resuspension and its contribution to airborne particulate matter.

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1. Introduction

It is of prime importance to develop analytical methods that can provide reliable concentrations of metals and metalloids in environmental samples. Among the most important matrices, sediments and soils constitute environmental compartments that have a profound impact on the contamination, both natural and anthropogenic, of the biosphere. 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 the case of urban and residential areas, soils also receive the contribution of metals from vehicular emission, atmospheric deposition of dust and aerosols. When agricultural areas are considered, the contribution of metals is mainly attributed to the soil-crop representing a significant exposure for inhabitants located in the area or in the surroundings. In

addition, cities located in the vicinity of a port receive emissions originated from the harbor and ship traffic.

The first step to gain information on metal contribution and to have an accurate assessment of the inputs and impacts of potential natural and anthropogenic sources is to characterize the soil by the determination of key elements. Heavy metals are well known [1,2] for their long-term toxicity effects [3,4] and the possibility to be introduced into the food chain by plants and animals feeding.

Soil characterization research is also a valuable tool for researchers involved in studies devoted to the chemical characterization of airborne particulate matter (APM) since metal content reflects the extent of the potential emissions of these elements from natural and anthropogenic sources [5]. When topsoil is not covered by vegetation, its finer fractions can be easily released to the atmosphere and may contribute to the particulate matter as reflected by different studies [5–8].

Soils constitute a complex matrix with different amounts of mineral phases, co-precipitated and sorbed species associated with soil minerals or organic matter, and dissolved species that may be complexed by a variety of organic and/or inorganic ligands [9]. When plasma-based techniques are used for the analysis it is necessary a previous digestion of

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the sample and numerous applications aimed at developing reliable methods for soil sample digestion have been reported [10,11]. The most convenient sample digestion method will depend on the analytes under study and the chemical nature of the soil [9].

Airborne particulate matter from industrial activities and natural resources represent a significant contribution to soil contamination. These particles are deposited by gravity on the ground through dry or wet deposition causing contamination when different pollutants, including heavy metals, are components of these particles. In this context, to assess the concentration of metals and metalloids in soils where settleable particulate matter was deposited is valuable to study the influence of air pollution on soil composition. On the other hand, in arid and semiarid zones, soils are a source of metals in atmospheric aerosols.

This study is part of a project focused to study the role of the different sources, including natural events such as dust storms, influencing the concentration and chemical composition of the particulate matter in the studied area. In this first step, our interest is related to assess the methodologies for sample digestion and multi element determination of major, minor and trace elements in soils that receive natural and anthropogenic inputs.

2. Experimental

2.1. Instrumentation and reagents

A PerkinElmer (Norwalk, CT, USA) ICP Optima 5100 DV, 40 MHz (axial view) simultaneous inductively coupled Ar plasma optical emission spectrometer (ICP OES) provided with a Model AS 90 autosampler and a PerkinElmer inductively coupled Ar plasma quadrupole mass spectrometer (Q-ICP-MS) model NexIon 300X provided with a CETAC AXS-520 autosampler were used for elemental determinations. Instrumental details and operating conditions for both instruments are summarized in Tables 1 and 2.

Welding and 99.998% (minimum purity) Ar from Indura (Buenos Aires, Argentina) were used for ICP OES and ICP-MS determinations, respectively. Deionized distilled water (DDW) was produced by a commercial mixed-bed ion-exchange system Barnstead (Dubuque, IA, USA) fed with distilled water. All reagents were of analytical grade. Hydrochloric, hydrofluoric and nitric acids (Merck, Darmstadt, Germany) were used for sample treatment and preparation of the standards. Commercially available 1000 mg L⁻¹ standard solutions (Merck) of the elements analyzed were used. Diluted working solutions were prepared daily by serial dilutions of those stock solutions.

All glassware and plastic bottles used were cleaned by rinsing with DDW, soaking with a 10% (v/v) nitric acid solution for 24 h and then rinsing several times with DDW. All samples and standards were stored in polyethylene bottles (50 mL) or Falcon® tubes (Becton Dickison, Lincoln Park, NJ, USA). A cascade sieve (Zonytest EJR, Buenos Aires, Argentina) was used for the size fractionation of the samples.

Table 1

Instrumental characteristics and settings for ICP OES.

Instrument	Perkin Elmer Optima 3100 XL
Frequency of rf generator	40 MHz (axial view)
Coolant gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	0.6 L min ⁻¹
Sample gas flow rate	0.8 L min ⁻¹
Solution delivery	1.0 mL min ⁻¹
Automatic sampler	PerkinElmer AS90
Nebulizer	Cross-flow with Scott type expansion chamber
Polychromator	Echelle grating. Cross-dispersed wavelength range (nm): 165–403
Detector	Segmented-array charge coupled device
Measurement mode	Continuous nebulization

Table 2

Instrumental characteristics and settings for quadrupole ICP-MS.

Instrument	PerkinElmer NexIon 300X
RF generator	1250 W
Nebulizer	MEINHARD® Concentric Nebulizer
Interface	Sampler and skimmer cones in Ni; hyper skimmer in Al
Argon flows	Nebulizer, 0.95: Plasma, 16; auxiliary, 1.2 (all in L min ⁻¹)
Solution delivery	0.85 mL min ⁻¹
Automatic sampler	CETAC ASX-520
Detector voltages	– 1875 V (analog); 1050 V (pulse)
Scanning conditions	Sweeps per reading, 20; readings per replicate, 1; number of replicates, 3
Scanning mode	Peak-hopping
Vacuum	Analytical zone, <2.2 10 ⁻⁶ Torr

2.2. Location, sampling collection and fractionation

Soil samples were collected in an area centered at the metropolitan and agricultural areas of the city of Bahía Blanca located in the southwestern part of the province of Buenos Aires (Argentina) on the Atlantic Ocean. The sampling campaign considered the collection of samples in different land use categories of soils from highly populated to surrounding areas. Among the most important industries that are a potential source of metals we can mention: (i) chemical and petrochemical plants, (ii) a refinery and natural gas separation plant, (iii) PVC production from chlor-alkali process, (iv) ammonia and urea production, and (v) a natural gas-fueled power plant. The soils destined to agricultural exploitation and granaries are characterized by the use of fertilizers. It is well-documented that vehicular traffic is an increasing source of the so-called traffic related elements (TRES) in urban areas [12]. As a consequence, atmospheric pollution may convert in a potential source of heavy metal contamination in soil and roadside dust in urban areas. An additional source of crustal elements is: construction/demolition activities and urban works performed in the last years in the city and its surroundings.

Specific sites selection was based on the variety of sources that are potential emitters of fugitive dust from soil. Several types of sources were identified according to industrial activities, land use and predominant direction of winds [5]. The sampled area was divided into five sectors and three samples were collected in each sector (total of 15 samples). The material collected at each site was composited to form a simple sample resulting in a total of five composited samples (namely, S1–S5).

Once collected, samples were placed in polyethylene bags and transported to the laboratory where they were firstly dried at 100 °C for 24 h and then sieved at two grain sizes (A < 37 μm and 37 < B < 50 μm). Ten samples (five of each fraction) were obtained and named; S1A, S1B, S2A, S2B, S3A, S3B, S4A, S4B, S5A and S5B for subsequent analysis by plasma-based techniques.

2.3. Dissolution procedure

Soil samples were prepared for multielement analysis by plasma-based techniques. Chemical analysis of metals in soils requires matrix destruction particularly of siliceous material and consequently, an acid mixture with HF was adopted. In addition, it is important to select a digestion procedure that represents the best compromise for the 17 elements under study in terms of the wide range of elemental concentrations and results reliability.

Aliquots of 0.5 g of each sample were weighed into a PTFE beaker and 9 mL of an acid mixture containing HCl, HNO₃ and HF (6:2:1) was added. The mixture was left overnight at room temperature and then heated on a hot plate set at ~85 °C for 2 h. The digest was slowly evaporated to near dryness and then dissolved in 5 mL of DDW. No visible residual solid particles were detected. The evaporation step was necessary to reduce acid concentration and in this way reduce potential damage in

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