



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, HNO_3 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

the plasma systems. The solution was filtered through a 0.45 μm PTFE filter, transferred into a 50 mL volumetric flask and diluted to the mark. Two portions were weighted for each sample. For checking accuracy aliquots of the certified reference material NIST SRM 2711, Montana soil (NIST, Gaithersburg, MD, USA) were subjected to the same procedure as the samples and included in the over-all analytical process.

2.4. Sample analysis

Plasma-based techniques namely, ICP OES and ICP-MS were employed for the determination of metals and metalloids in soil samples. These techniques can be applied to different matrices and analytes, after a suitable dissolution procedure, and are characterized by extended dynamic concentration ranges (several orders of magnitude), are multielemental in nature and possess high sensitivity and appropriate detection power to reach the levels of metal and metalloids present in studied soil samples. In particular, Al, Ba, Ca, Cu, Mg, Mn, Fe, Ti, V and Zn were determined by ICP OES while As, Cd, Cr, Ni, Pb, Mo and Sb were measured by ICP-MS.

In both cases, five sets of multi-elemental calibrants were prepared by dilution of commercially available 1000 $\mu\text{g L}^{-1}$ standard solutions of the individual elements. Working solutions were prepared daily in polyethylene tubes (Falcon®). Screening experiments showed that in spite of the complexity of the matrix analyzed no standard addition was necessary for calibration. All measurements were performed by triplicate and the reported results are averaged values.

3. Results and discussion

3.1. ICP-MS measurements

Without any doubts, ICP-MS is a well established and powerful analytical technique for the determination of trace and ultra-trace elements in a variety of matrices. However, the formation of spectral interferences originating from atomic and molecular ions produced in the plasma from Ar and matrix components present in the analytical solutions may sometimes seriously affect the reliable determination of elements. For this reason, the determination of elements potentially affected for spectral interferences was attempted by both techniques. The levels of Sb were very low and its quantification was only attempted by ICP-MS. In the particular case of As, the contribution of the $^{40}\text{Ar}^{35}\text{Cl}$ interfering species to the signal at mass 75 was not significant. This assumption is further supported by the concentrations of As measured in the reference material due to a satisfactory agreement between the concentrations determined and the certified values. Other example is ^{52}Cr , the potential contribution of $^{40}\text{Ar}^{12}\text{C}$ was checked and it seemed not to be significant. Although the certification report gives noncertified values for Cr, our results are in satisfactory agreement between the determined concentration and the noncertified value.

3.2. Metal and metalloid concentration in soils

Fig. 1 depicts the profile corresponding to the 17 elements measured in size-fractionated soils collected in Bahía Blanca. Soil composition of the investigated area is complex, as a consequence of the geodynamic context where Bahía Blanca is located. According to the levels observed metals can be classified as major, minor and trace elements.

As expected, geological elements (Al, Ca, Fe, Mg and Ti) are predominant and exhibited the highest concentrations. The analysis of the data obtained for major elements shows that Al, Ca and Mg concentrations resulted generally slightly higher in the fine fraction while for Fe and Ti the contrary situation was observed. Calcium is the element with higher concentrations in both fractions, likely to the high levels of CaCO_3 in the soils of the sampled area or to a possible redistribution of this element through pedogenic processes [13]. The analysis of data for trace elements showed that $\text{As} > \text{Ni} > \text{Mo} > \text{Cd} > \text{Sb}$ exhibited the

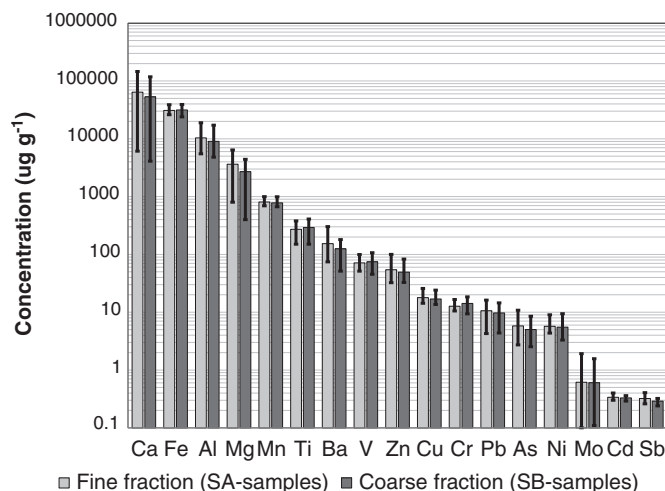


Fig. 1. Average (bars), minimum and maximum concentrations (whiskers) of determined elements in the five soil samples and two size fractions ($A < 37 \mu\text{m}$ and $37 < B < 50 \mu\text{m}$).

lowest levels varying from 1.85 $\mu\text{g g}^{-1}$ (mean concentration) for As to 0.32 $\mu\text{g g}^{-1}$ (mean concentration) for Sb.

Calcium concentrations exhibited a large variability (0.39–15.1 $\mu\text{g g}^{-1}$) in both fractions. The lowest levels were detected in the dry sandy soil of the deserted area while the highest ones were measured at zones where typical Ca-rich materials are customarily used. In samples S5A and S5B, Ca levels were considerably higher. This could be attributed to the fact that Ca is an element present in asphalt and these samples were collected in soils where debris from construction materials is deposited.

Other major elements namely, Fe and Ti showed a more homogeneous pattern in both fractions (A and B). The highest levels of major elements were detected in Fraction A (finer fraction). This can be attributed to the presence of minerals (quartz, pyroxene and feldspar) that are primary constituents of the mineralogical composition of the parent material of the modern cultivated soils of the Southern Pampas [13]. Magnesium is an element abundant in cement and also abundant in asphalt [14] and consequently high levels were measured in samples collected in urban areas. Manganese $>$ Ti $>$ Ba $>$ V $>$ Zn $>$ Cu $>$ Cr $>$ Pb can be considered minor elements with similar concentrations in the fine and coarse fraction.

Trace elements generally exhibited minor variations among the ten composite soils analyzed which reflect their domain-related geochemical differences. Arsenic $>$ Mo $>$ Mo $>$ Cd $>$ Sb were mostly detected in the smaller fraction. This is can be explained by considering that the presence of trace metals is controlled by small-sized mineral phases in each rock type [12].

Several of the elements determined are selective markers of vehicular traffic.

Antimony is a well known tracer of traffic associated with brake wear. In this study, Sb was the element detected at the lowest and similar concentrations (0.24–0.32 $\mu\text{g g}^{-1}$) even in samples collected close to high traffic density areas. Other trace elements are traffic and industry related elements such as Ba (BaSO_4 : used as filler in brake linings), Cu and Mo (components of brake dust), Pb and V (diesel oil and gasoline), Cr (industries), and Ni and V (typical tracers for diesel and oil combustion). Manganese concentrations varied from 666 to 1000 $\mu\text{g g}^{-1}$. This metal is also a TRE associated with mechanical wear of automotive parts and the use of methylcyclopentadienyl Mn tricarbonyl (MMT) as fuel additive.

For As, our results are in good agreement with values reported in the literature for the sand fraction (50–2000 μm) of disturbed soils collected in the same area of study [15]. According to the study of Blanco and co-workers As is removed from the sand fraction due to the occurrence of mineral weathering reactions controlled by local geochemical factors.

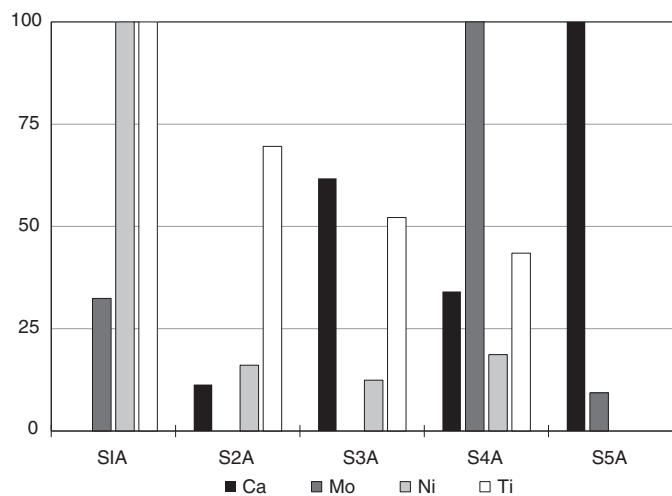


Fig. 3. Icon column plots of the four-element profiles (Ca, Mo, Ni, Ti) for the five A-samples. Minimum concentration of each element has been assigned a zero value and maximum concentration a value of 100. Relative concentration values for each A-sample are represented by the height of consecutive columns.

confirms that the three concentration ratios Mo/Ca, Ni/Ca and Ti/Ca have been effective to differentiate the five samples under consideration although samples S3A and S5A appear to be lying closely in the scatter plot of Fig. 2.

3.3. Reliability criteria and quality parameters

Using optimized conditions, analytical figures of merit including detection limit and precision of replicate measurements were established. Detection limits were calculated following the IUPAC rules on the basis of 3 σ -criterion for ten replicate measurements of the blank signal. Limit of detection reached varied from 0.08 $\mu\text{g g}^{-1}$ (Cd) to 2.4 $\mu\text{g g}^{-1}$ (Ba). Relative standard deviations (RSDs) resulted in a more than satisfactory interval (4.3.5–10.3%), especially if one considers the complexity of the matrix under study.

Table 4 denotes the concentrations of the analytes in the Standard Reference Material NIST 2711 (Montana Soil) as determined by ICP OES and/or ICP-MS. The overall picture can be considered satisfactory in terms of the recovery and the repeatability especially if one considers that in certain instances (e.g., major elements) digestion solutions were diluted to reduce the analytical signal to acceptable levels. The good

Table 4
Accuracy check analysis of the standard reference material NIST 2709 (Montana Soil) by ICP OES.

Element	Certified	Found ^a
Al	6.53 \pm 0.09%	6.58 \pm 0.32%
As	105 \pm 0.8 $\mu\text{g g}^{-1}$	106 \pm 7 $\mu\text{g g}^{-1}$
Ba	726 \pm 38 $\mu\text{g g}^{-1}$	738 \pm 40 $\mu\text{g g}^{-1}$
Ca	2.88 \pm 0.08%	2.99 \pm 0.13%
Cd	41.70 \pm 0.25 $\mu\text{g g}^{-1}$	39.6 \pm 1.8 $\mu\text{g g}^{-1}$
Cr	(47 $\mu\text{g g}^{-1}$)	50 \pm 2 $\mu\text{g g}^{-1}$
Cu	114 \pm 2 $\mu\text{g g}^{-1}$	98 \pm 8 $\mu\text{g g}^{-1}$
Fe	2.89 \pm 0.06%	3.00 \pm 0.19%
Mg	1.05 \pm 0.03%	1.08 \pm 0.08%
Mn	638 \pm 28 $\mu\text{g g}^{-1}$	629 \pm 28 $\mu\text{g g}^{-1}$
Mo	(1.6 $\mu\text{g g}^{-1}$)	1.71 \pm 0.11 $\mu\text{g g}^{-1}$
Ni	20.6 \pm 1.1 $\mu\text{g g}^{-1}$	21.3 \pm 2.2 $\mu\text{g g}^{-1}$
Pb	1162 \pm 31 $\mu\text{g g}^{-1}$	1089 \pm 49 $\mu\text{g g}^{-1}$
Sb	19.4 \pm 1.8 $\mu\text{g g}^{-1}$	20.9 \pm 1.8 $\mu\text{g g}^{-1}$
Ti	0.306 \pm 0.023%	0.295 \pm 0.019%
V	81.6 \pm 2.9 $\mu\text{g g}^{-1}$	77.4 \pm 5.2 $\mu\text{g g}^{-1}$
Zn	350.4 \pm 4.8 $\mu\text{g g}^{-1}$	424 \pm 28 $\mu\text{g g}^{-1}$

Data enclosed in brackets are noncertified values.

^a Two set of replicates, each set consisting of ten measurements.

recovery observed for many elements such as Al (6.53 \pm 0.09 vs 6.58 \pm 0.32%) demonstrates that the selected digestion procedure was adequate since Al was not underestimated by the formation of complexes between HF and Al. The recovery of Zn (350.4 \pm 4.8 vs 424 \pm 28 $\mu\text{g g}^{-1}$) was high when it was quantified by ICP OES, as judged on the basis of the recovery value calculated (121%). It could be attributed to an unexpected contamination of the samples took place. Unfortunately for Cr and Mo only noncertified values are reported. The found values depicted in Table 4 show slightly high values. Consequently in other test, the SRM was spiked with both analytes to obtain recovery data. The experiments gave a final recovery of 101% for Cr and 96% for Mo.

4. Conclusions

ICP OES is a fully able technique to determine major, minor and trace elements in soils. However, for the quantification of As, Cd, Cr, Ni, Pb, Mo and Sb a more sensitive technique (ICP-MS) was employed to reach the levels at which these elements were expected in the sampled soils.

The concentration of the 17 elements determined in soils resulted in general below crustal values. Only three elements, As, Ca and Cd exhibited higher levels in the analyzed soils when compared with their levels in the Earth's crust. In the particular case of As, measured concentrations resulted similar to those determined in the sand fraction in the same Pampean region. For this reason, it is plausible to ascribe for this element a natural origin. Taking into account the possibility of identifying chemical markers able to discriminate the different soil samples, the ratios Mo/Ca, Ni/Ca and Ti/Ca proved to be effective for this task.

Our study leads to confirm the importance to assess metal and metalloid content in top soils as part of a wider scientific project aimed to characterize areas in Argentina impacted by different particle sources (natural and/or anthropogenic) as a first step to identify sources of airborne particulate matter.

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References

- [1] O.J. Ogunsola, A.F. Oluwole, O.I. Asubiojo, M.A. Durosinmi, A.O. Fatusi, W. Ruck, Environmental impact of vehicular traffic in Nigeria: health aspects, *Sci. Total Environ.* 146–147 (1994) 111–116.
- [2] J.E. Fergusson, N.D. Kim, Trace elements in street and house dusts: sources and speciation, *Sci. Total Environ.* 100 (1991) 125–150.
- [3] Yaylalı-Abanuz Gülten, Heavy metal contamination of surface soil around Gebze industrial area, Turkey, *Microchem. J.* 99 (2011) 82–92.
- [4] S. Melaku, R. Dams, L. Moens, Determination of trace elements in agricultural soil samples by inductively coupled plasma-mass spectrometry: microwave acid digestion versus aqua regia extraction, *Anal. Chim. Acta* 543 (2005) 117–123.
- [5] A. Morales Del Mastro, M. Pereyra, A. Londonio, V. Pereyra, R. Jimenez Rebagliati, L. Dawidowski, D. Gomez, P. Smichowski, Chemical profile of size-fractionated soils collected in a semiarid industrial area of Argentina, *Atmos. Environ.* 98 (2014) 299–307.
- [6] A. Pietrodangelo, R. Salzano, E. Rantica, C. Perrino, Characterisation of the local topsoil contribution to airborne particulate matter in the area of Rome (Italy). Source profiles, *Atmos. Environ.* 69 (2013) 1–14.
- [7] Đ. Doređević, A. Mihajliđi-Zelić, D. Relić, Differentiation of the contribution of local resuspension from that of regional and remote sources on trace elements content in the atmospheric aerosol in the Mediterranean area, *Atmos. Environ.* 39 (2005) 6271–6281.
- [8] M. Viana, T.A.J. Kuhlbusch, X. Querol, A. Alastuey, R.M. Harrison, P.K. Hopke, W. Winiwarter, M. Vallius, S. Szidat, A.S.H. Prevot, C. Hueglin, H. Bloemen, P. Wahlin, R. Vecchi, A.I. Miranda, A. Kasper-Giebl, W. Maenhaut, R. Hitzanberger, Source apportionment of particulate matter in Europe: a review of methods and results, *J. Aerosol Sci.* 39 (2008) 827–849.
- [9] E. Engström, A. Stenberg, D.C. Baxter, D. Malinovsky, I. Mäkinen, S. Pönni, I. Rodushkin, Effects of sample preparation and calibration strategy on accuracy and precision in the multi-elemental analysis of soil by sector-field ICP-MS, *J. Anal. At. Spectrom.* 19 (2004) 858–866.
- [10] M. Bettinelli, G.M. Beone, S. Spezia, C. Baffi, Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis, *Anal. Chim. Acta* 424 (2000) 289–296.

- [11] A. Soriano, S. Pallarés, F. Pardo, A.B. Vicente, T. Sanfeliu, J. Bech, Deposition of heavy metals from particulate settleable matter in soils of an industrialised area, *J. Geochem. Explor.* 113 (2012) 36–44.
- [12] P. Smichowski, D. Gómez, C. Frazzoli, S. Caroli, Traffic-related elements in airborne particulate matter, *Appl. Spectrosc. Rev.* 43 (2008) 22–48.
- [13] M.A. Zárata, Loess of Southern South America, *Quat. Sci. Rev.* 22 (2003) 1987–2006.
- [14] N. Galindo, E. Yubero, J.F. Nicolás, J. Crespo, C. Pastor, A. Carratalá, M. Santacatalina, Water-soluble ions measured in fine particulate matter next to cement works, *Atmos. Environ.* 45 (2011) 2043–2049.
- [15] M.C. Blanco, J.D. Paoloni, H. Morrás, C. Fiorentino, M.E. Sequeira, N.N. Amiotti, O. Bravo, S. Diaz, M. Esposito, Partition of arsenic in soils sediments and the origin of naturally elevated concentrations in groundwater of the southern pampa region (Argentina), *Environ. Earth Sci.* 66 (2012) 2075–2084.
- [16] H. Bourennane, F. Douay, T. Sterckeman, E. Villanneau, H. Ciesielski, D. King, D. Baize, Mapping of anthropogenic trace elements inputs in agricultural topsoil from Northern France using enrichment factors, *Geoderma* 157 (2010) 165–174.