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
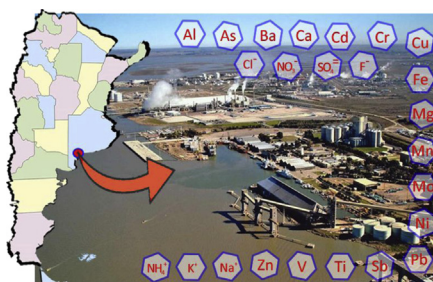
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ABSTRACT

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 μg g^{-1} (Sb) to $14.6 \pm 0.6\%$ (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; Dorđević 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; Dorđević 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

plus with probe Thermo Scientific Orion® (Beverly, Massachusetts, USA) was employed. For sulphates, a spectrophotometer UV–Vis Agilent®, model Cary 60 (Victoria, Australia) was used. For the potentiometric determination of fluoride a pH-ISE ion analyzer ORION® (Beverly, MA 01915 USA) model 710A plus with fluoride ISE (EPA approved) Thermo Scientific Orion® (Beverly, MA 01915 USA) model 9409 BN was used.

Welding Ar from Indura (Buenos Aires, Argentina) was used for ICP OES determinations. 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.

A cascade sieve (Zonytest EJR, Buenos Aires, Argentina) was used for the size fractionation of the samples.

2.2. Sampling collection and fractionation

Bahía Blanca is located between 38°45′–39°40′ S, and 61°45′–62°30′ W in the southwestern part of the province of Buenos Aires, Argentina, on the Atlantic Ocean. The geopolitical region covers an area of 2,300 km^2 with a population of 301,501 inhabitants.

Soil samples were collected in specific sites of high population density and in areas surrounding the city, covering a surface of approximately 10,000 km^2. Geological bibliography reports that this area belongs to Southern Pampa's geographical domain (Bidart, 1996). Specific sites selection for sampling collection was based on the variety of sources in the region 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. Based on this information, five main zones were selected: (i) agricultural activities, (ii) deserted zone, (iii) unpaved road shoulder in an industrial area, (iv) salt marsh soil, and (v) building construction. Twenty five soil samples were collected in 2013, as follows: 15 samples of raw top soils (0–10 cm depth) by using brush and spade and 10 samples of the corresponding sub-superficial undisturbed soils (50 cm depth) by using a hand screw auger of diameter 2.5 cm. No more sub-superficial soils were collected because the similarity between sub-superficial and topsoil.

Samples were placed in polyethylene bags and transported to the laboratory. Then, soil samples were dried in an oven, at a temperature of ~40 °C, for 24 h. Selected samples of each category (top soils and sub-superficial soils) collected in areas with similar characteristics were composited in proportions roughly similar to the proportions of the surface areas of the sites to form a single sample representative of the entire area. Then, they were dried at 100 °C for 24 h and sieved. After sieving, two fractions were obtained with the following particle diameter: $A < 37$ μm, $37 < B < 50$ μm. Table 1 shows the main characteristics of the soil and the mixtures done. Mixtures were identified as MII, MIII, MIV and MV. The different soils samples collected were identified with figures. Until analysis, sub-samples were weighed and stored in polyethylene flasks in a cool and dry place.

Table 1
Characteristics of the collected soils and the mixtures.

Category of soil	Sample ID (soils and mixture of soils)	Characteristics of the sampling zone
Top	5 + 7 (Mixture, M II)	Deserted zone
	23	Salt marsh soil
	28	Soil for pavement preparation
	25	Unpaved road shoulder in an industrial area
	27	Building construction
Sub-superficial	16 + 18+20 + 12+14 + 22 (Mixture, M III)	Agricultural activities
	6 + 8 (Mixture, M IV)	Deserted zone
	2 + 26 (Mixture, M V)	Unpaved road shoulder in an industrial area

2.3. Sample treatment

For ICP OES analysis it was necessary to digest the samples. In a multielemental study it is important to adopt a digestion procedure that represents the best compromise for a range of elements in terms of the wide range of elemental concentrations and result reliability. Chemical analysis of metals in soils requires matrix destruction particularly of siliceous material. This can only be ensured by using HF.

A 0.5 g portion of each sample was weighed into a PTFE beaker and 9 mL of an acid mixture containing HCl, HNO$_3$ 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 system. 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 anions determination it was necessary to obtain an aqueous fraction of the soils. To this end, an aliquot of ~0.5 g was carefully placed into a Falcon® tube and 10 mL of water were added. The soluble elements were extracted using an ultrasonic bath (Testlab, Argentina) for 60 min. After this period, the supernatant was placed in an acid-cleaned Falcon® tube. This solution was centrifuged for 3 min at 5000 rpm. An aliquot of 10 mL of this solution was taken with a micropipette and placed in an acid-cleaned Falcon® tube for subsequent determination of water-soluble anions and cations.

For checking accuracy a certified reference material namely, SRM 2711, Montana soil (NIST, USA) was treated as the samples and included in the over-all analytical process.

2.4. Sample analysis

2.4.1. Metals and metalloids

Inductively coupled plasma optical emission spectrometry (ICP OES) was employed for the determination of metals and metalloids in soil samples collected in Bahía Blanca. This technique can be applied to different matrices after a suitable dissolution procedure and is characterized by extended dynamic concentration ranges (4–6 orders of magnitude), is multielemental in nature and possesses high sensitivity and appropriate detection power.

For ICP OES determinations, four sets of multi-elemental calibrants were prepared by dilution of commercially available 1000 μg L^{-1} standard solutions of the individual elements. 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.

2.4.2. Cations and anions

Ions were identified and determined in the water-soluble extracts by HPLC. To analyze this kind of samples, HPLC has the following advantages: multiple-analyte detection, high resolving power and appropriate sensitivity. In addition, the separation of the ions does not require preliminary chemical modification of the anions and/or cations present in the sample.

For screening experiments, mixtures of anions (and cations) were prepared in order to select the optimum chromatographic parameters. For anions separation and determination by HPLC a Hamilton PRP-X100 column (polystyrene-divinylbenzene; 25 cm × 4.1 mm; id. 10 μm) was used. The mobile phase was a 4.5 mM potassium hydrogen phthalate solution (Merck) at a pH of 4.5. For cations separation and determination by HPLC a Hamilton PRP-X800 analytical column was selected. A 2 mM Cu(II) sulfate solution (Aldrich) at pH 2.5 was employed as mobile phase. Flow-rates of the mobile phases were tested between 0.5 and 1.2 mL min^{-1}. A flow rate of 1.2 mL min^{-1} was chosen for anion and 1.2 mL min^{-1} for cation determination.

Under optimized conditions, the calibration graph was obtained by injecting known concentrations of the ions in the range 1.0–40 mg L^{-1}. Daily calibrations were performed each the analysis of ten samples.

2.5. Evaluation of trueness and precision (repeatability)

2.5.1. Metals and metalloids

Table 2 summarizes the concentrations of the analytes in the Standard Reference Material® NIST 2709 (San Joaquin Soil) as determined by ICP OES. The overall picture can be considered satisfactory in terms of the recovery and the repeatability. The good recovery observed for Al (7.37 vs 7.50%) demonstrates that the selected procedure was suitable since this metal was not underestimated by the formation of complexes between HF and Al. No convincing explanation could be found for the high recovery of Mo (2 vs 3.6 μg g^{-1}) when it was quantified by ICP OES, as judged on the basis of value reported (non certified). To obtain recovery data, aliquots of the SRM were spiked with known concentrations of the

element studied. The experiments gave a final recovery ranged between 92 and 109% depending on the element.

2.5.2. Cations and anions in the soluble fraction of soils

In absence of an appropriated certified reference material for the target water-soluble ions in soil, the accuracy of the proposed HPLC method was assessed by international recommended methodology (Thompson et al., 2002). This methodology is based on comparing the accuracy of the HPLC method against the corresponding standard reference method for each ion. For this purpose, two homogeneous samples with different concentration levels of ions were analyzed, by duplicate, with both methods in repeatability conditions. Results are shown in Table 3. In the evaluation of the accuracy we included: (i) comparison of precisions, and (ii) comparison of the trueness of both methods. The variance of the means of both methods was compared by means of F-tests (Massart et al., 1997). All the experimental $F_{calculated}$ values were higher than those critical values ($F_{calculated} > F_{critical}$; $p < 0.01$), then the difference between the variance of the means of both methods was significant. Therefore, the HPLC method has repeatability precision better than the respective standard reference method for each ion. When comparing the precision of both methods, the trueness of the HPLC method was checked by using the paired sample Students' t-test for each ion (Massart et al., 1997). All the experimental $t_{calculated}$ values obtained for each analyte were minor than the corresponding two-sided $t_{critical}$ values, at a probability $\alpha = 0.05$. Then, bias was not statistically significant and the HPLC method was traceable to the standard reference method for each ion in the condition of repeatability precision studied.

3. Results and discussion

3.1. Metals and metalloids concentration in soils

Table 4 (**a** and **b**) summarizes the concentration of 17 metal and metalloids 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, crustal elements (earth's crust components) namely, Al, Ca, Fe, Mg and Ti are dominant and exhibited the highest concentrations in topsoils and sub-superficial soils as follows (in %): Al, 1.72–0.48; Ca, 0.4–11.8; Fe, 2.4–3.93; Mg, 0.04–0.99 and Ti, 0.15–0.41.

For Al, in general terms, concentrations resulted slightly higher in the small fraction in topsoils. For both fractions, Al concentrations were higher in sub-superficial soils than in topsoils and exhibited larger variability but a defined pattern was not observed.

Table 2
Results obtained in the analysis of the standard reference material NIST 2709 (San Joaquin Soil).

Element	Certified	Found[a]
Al	7.50 ± 0.06%	7.37 ± 0.15%
As	17.7 ± 0.8 μg g^{-1}	16.9 ± 0.9 μg g^{-1}
Ba	968 ± 40 μg g^{-1}	939 ± 44 μg g^{-1}
Ca	1.89 ± 0.05%	1.91 ± 0.07%
Cd	0.38 ± 0.01 μg g^{-1}	0.44 ± 0.02 μg g^{-1}
Cr	130 ± 4 μg g^{-1}	123 ± 7 μg g^{-1}
Cu	34.6 ± 0.7 μg g^{-1}	34.0 ± 1.6 μg g^{-1}
Fe	3.50 ± 0.11%	3.88 ± 0.16%
Mg	1.51 ± 0.05%	1.40 ± 0.07%
Mn	538 ± 17 μg g^{-1}	539 ± 25 μg g^{-1}
Mo	(2.0 μg g^{-1})	3.6 ± 0.2 μg g^{-1}
Ni	88 ± 5 μg g^{-1}	86 ± 5 μg g^{-1}
Pb	18.9 ± 0.5 μg g^{-1}	23.7 ± 1.5 μg g^{-1}
S	0.089 ± 0.002%	0.080 ± 0.004%
Sb	7.9 ± 0.6 μg g^{-1}	7.2 ± 0.4 μg g^{-1}
Ti	0.342 ± 0.024%	0.375 ± 0.018%
V	112 ± 5 μg g^{-1}	111 ± 5 μg g^{-1}
Zn	106 ± 3 μg g^{-1}	99 ± 5 μg g^{-1}

Data enclosed in brackets are noncertified values.
[a] Two set of replicates, each set consisting of ten measurements.

Table 3
Results obtained in the analysis of anions and cations using different analytical techniques.

Ion	HPLC (this work)[a]	Official method[a]
Chloride (mg g^{-1})	0.33 ± 0.02	0.36 ± 0.07
	8.0 ± 0.4	8.6 ± 1.5
Sulfate (mg g^{-1})	0.14 ± 0.02	0.19 ± 0.04
	3.12 ± 0.09	3.92 ± 0.80
Fluoride (μg g^{-1})	16.2 ± 1.0	12.2 ± 2.0
	29.6 ± 2.3	30.0 ± 6.0
Sodium (mg g^{-1})	3.8 ± 0.01	4.4 ± 0.8
	27.0 ± 0.01	23.9 ± 3.0
Potassium (mg g^{-1})	0.40 ± 0.01	0.44 ± 0.08
	2.48 ± 0.16	2.54 ± 0.50

[a] Two set of replicates, each set consisting of ten measurements.

Table 4
a) Concentration of 17 elements in size fractionated top soils. Fraction A: <37 μm and Fraction 37 < B < 50 μm (B). Concentrations are expressed as μg g^{-1} except Al, Ca, Fe, Mg and Ti (major elements) that are expressed as percentage. **b**) Concentration of 17 elements in size fractionated sub-superficial soils. Fraction A: <37 μm and Fraction 37 < B < 50 μm (B). Concentrations are expressed as μg g^{-1} except Al, Ca, Fe, Mg and Ti (major elements) that are expressed as percentage.

a)

Element	IIA	IIB	23A	23B	28A	28B	25A	25B	27A	27B
Major elements										
Al	0.97 ± 0.06%	0.84 ± 0.03%	1.89 ± 0.07%	1.72 ± 0.07	1.21 ± 0.05%	0.95 ± 0.04%	0.55 ± 0.03%	0.48 ± 0.02%	0.57 ± 0.03%	0.52 ± 0.03%
Ca	0.61 ± 0.04%	0.41 ± 0.02%	2.20 ± 0.13%	1.87 ± 0.09%	9.25 ± 0.39%	8.02 ± 0.40%	5.38 ± 0.21%	4.44 ± 0.19%	14.6 ± 0.6%	11.83 ± 0.41%
Fe	3.89 ± 0.14%	3.93 ± 0.13%	3.33 ± 0.14%	3.38 ± 0.12%	3.04 ± 0.11%	3.30 ± 0.15%	2.61 ± 0.13%	2.78 ± 0.15%	2.63 ± 0.11%	2.40 ± 0.13%
Mg	0.08 ± 0.004%	0.04 ± 0.002%	0.64 ± 0.03%	0.42 ± 0.02%	0.47 ± 0.02%	0.44 ± 0.02%	0.47 ± 0.02%	0.29 ± 0.01%	0.16 ± 0.01%	0.16 ± 0.01%
Ti	0.38 ± 0.02%	0.41 ± 0.02%	0.31 ± 0.01%	0.32 ± 0.02%	0.27 ± 0.01%	0.31 ± 0.01%	0.25 ± 0.01%	0.27 ± 0.01%	0.15 ± 0.01%	0.15 ± 0.01%
Minor elements										
Mn	1000 ± 39	995 ± 48	795 ± 36	787 ± 33	694 ± 33	698 ± 28	695 ± 24	666 ± 27	854 ± 39	745 ± 34
Trace elements										
As	2.73 ± 0.11	2.54 ± 0.12	2.72 ± 0.16	2.64 ± 0.15	7.26 ± 0.33	7.10 ± 0.33	10.8 ± 0.46	8.53 ± 0.46	5.41 ± 0.33	4.26 ± 0.18
Ba	74.4 ± 3.2	51.4 ± 4.4	100 ± 5	97.7 ± 4.3	169 ± 7	173 ± 8	121 ± 6	123 ± 7	303 ± 12	180 ± 8
Cd	0.40 ± 0.01	0.34 ± 0.02	0.30 ± 0.01	0.29 ± 0.02	0.32 ± 0.02	0.36 ± 0.02	0.32 ± 0.02	0.36 ± 0.02	0.35 ± 0.02	0.30 ± 0.01
Cr	16.6 ± 0.8	18.4 ± 0.8	14.3 ± 0.8	16.0 ± 0.8	10.8 ± 4.9	13.1 ± 0.7	11.5 ± 0.5	14.0 ± 0.6	10.5 ± 0.7	9.36 ± 0.8
Cu	25.8 ± 1.2	24.1 ± 0.9	16.3 ± 0.7	15.8 ± 0.9	17.9 ± 0.9	16.6 ± 0.6	14.3 ± 0.5	14.8 ± 0.6	15.2 ± 0.5	13.6 ± 0.6
Mo	0.69 ± 0.04	0.58 ± 0.04	0.10 ± 0.01	0.18 ± 0.01	0.10 ± 0.01	0.11 ± 0.01	1.92 ± 0.12	1.57 ± 0.08	0.27 ± 0.05	0.58 ± 0.05
Ni	9.01 ± 0.52	9.41 ± 0.43	5.10 ± 0.22	5.57 ± 0.27	4.93 ± 0.25	4.96 ± 0.51	5.22 ± 0.24	4.37 ± 0.29	4.35 ± 0.22	3.30 ± 0.25
Pb	7.05 ± 0.41	6.94 ± 0.39	4.28 ± 0.23	4.38 ± 0.19	9.18 ± 0.39	9.47 ± 0.45	16.2 ± 1.1	14.5 ± 0.7	16.2 ± 0.6	13.2 ± 0.7
V	65.4 ± 2.8	71.4 ± 3.3	67.2 ± 3.3	67.6 ± 3.2	73.7 ± 3.0	80.9 ± 2.9	99.8 ± 3.5	107 ± 3.7	51.4 ± 3.3	45.3 ± 2.0
Zn	49.5 ± 2.0	49.3 ± 1.8	36.8 ± 1.7	36.3 ± 1.7	32.4 ± 1.6	32.7 ± 1.7	53.4 ± 2.0	45.2 ± 1.7	99.9 ± 3.5	82.9 ± 3.4
Not detected										
Sb	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3

b)

Element	IIIA	IIIB	IVA	IVB	VA	VB
Major elements						
Al	0.66 ± 0.02%	0.88 ± 0.03%	3.17 ± 0.18%	0.88 ± 0.04%	1.77 ± 0.09%	2.12 ± 0.01%
Ca	4.23 ± 0.20%	3.49 ± 0.17%	4.91 ± 0.23%	3.01 ± 0.14%	3.24 ± 0.19%	3.06 ± 0.18%
Fe	3.66 ± 0.15%	3.36 ± 0.15%	3.40 ± 0.16%	3.34 ± 0.14%	3.33 ± 0.14%	3.25 ± 0.15%
Mg	0.53 ± 0.02%	0.42 ± 0.02%	0.99 ± 0.03%	0.44 ± 0.02%	0.51 ± 0.03%	0.52 ± 0.03%
Ti	0.30 ± 0.02%	0.28 ± 0.02%	0.24 ± 0.02%	0.24 ± 0.02%	0.29 ± 0.02%	0.29 ± 0.02%
Minor elements						
Mn	817 ± 37	715 ± 29	871 ± 41	852 ± 37	1200 ± 54	1100 ± 43
Trace elements						
As	5.93 ± 0.22	4.44 ± 0.19	6.69 ± 0.33	5.56 ± 0.21	9.14 ± 0.30	7.50 ± 0.25
Ba	221 ± 9	196 ± 8	297 ± 11	212 ± 9	171 ± 10	182 ± 9
Cd	1.15 ± 0.06	0.99 ± 0.06	0.56 ± 0.05	0.79 ± 0.06	0.64 ± 0.04	0.55 ± 0.05
Cr	14.3 ± 0.6	13.0 ± 0.7	19.8 ± 0.9	18.6 ± 0.8	17.2 ± 0.7	17.1 ± 0.7
Cu	29.2 ± 1.1	23.8 ± 1.1	23.2 ± 1.0	23.6 ± 1.0	15.9 ± 0.6	14.3 ± 0.6
Mo	<0.5	<0.5	0.97 ± 0.05	0.76 ± 0.05	1.70 ± 0.09	1.58 ± 0.08
Ni	9.64 ± 0.01	7.76 ± 0.01	12.2 ± 0.02	8.99 ± 0.01	4.94 ± 0.01	4.66 ± 0.01
Pb	15.3 ± 0.8	14.2 ± 0.8	26.6 ± 0.7	16.1 ± 0.8	21.3 ± 0.8	22.6 ± 0.9
V	74.9 ± 3.0	68.3 ± 2.3	96.7 ± 2.7	88.7 ± 2.4	126 ± 4.5	120 ± 3.9
Zn	56.0 ± 2.5	46.6 ± 2.2	66.9 ± 3.1	61.5 ± 3.0	57.5 ± 2.9	54.4 ± 2.8
Not detected						
Sb	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3

Calcium levels resulted higher in the smaller fraction of all samples. The high Ca concentration might be attributed to the high levels of calcium carbonate present in the soils of the area under study or to a possible redistribution of this element through pedogenic processes (Zárate, 2003). Calcium levels in samples 27A and 27B could be explained considering that Ca is an element present in asphalt and these samples were collected in soils where debris from construction materials are deposited.

Titanium and Fe were the major elements that exhibited a more homogeneous pattern in both fractions (A and B) and also in top and sub-superficial soils.

Table 4 depicts that a higher content of major elements was found in the 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 (Zárate, 2003). Concerning Mg levels, in general, higher concentrations were measured in the smaller fraction of both top and sub-superficial soils categories. Magnesium is an element abundant in cement and also abundant in asphalt (Galindo et al., 2011) and consequently high levels were measured in samples collected in urban areas. Manganese can be considered a minor element with similar concentrations in the fine and coarse fraction. The relationship between bulk concentrations of Mn *vs* Fe (normalized with respect to Al) in top soil and sub-superficial soil samples was used to give information on association patterns among the different category of soils. In our study, in all sub-superficial soils the ratio Mn/Fe exhibited a slope of 188 ($r = 0.96$; $p < 0.05$) that is similar to the ratio (171) found for this two elements in the earth's crust (Gaiero et al., 2003). On the other hand, the ratio Mn/Fe has a slope of 260 ($r = 0.95$; $p < 0.05$) for the top soil samples (except sample 27). This value might suggest that the earth's composition has been probably modified as a consequence of the fallout of the Chaitén volcano in 2009 that had a Mn-rich material.

Trace elements namely, As, Ba, Cd, Cu and Zn were mostly detected in the smaller fraction. This can be explained by considering that the presence of trace metals is controlled by small-sized mineral phases in each rock type (Smichowski et al., 2008).

Antimony is selective tracer of vehicular traffic associated with break wear. This metalloid was studied by our group in the atmosphere of Buenos Aires (Gómez et al., 2005). In this study, Sb was not detected in none of the samples analyzed even in those collected close to high traffic density areas (sample 25). Other trace elements of anthropogenic origin were detected albeit at concentrations close/below than those of the earth crust (Fig. 1). They are traffic and industry related elements such as Ba ($BaSO_4$ is common filler in brake linings), Cu and Mo (brake dust), Pb and V (diesel oil and gasoline), Cr (industries) and Ni and V as tracers for diesel and oil combustion. The only exceptions are Cd and Mn. With respect to Cd, its anthropogenic origin includes emissions from, non-ferrous metals manufactures and brake and tire rubber dust. In soils devoted to agricultural activities, Cd enrichment may be ascribed to the use of urban sludge, manure and phosphate enrichment fertilizers that are known to contain Cd, in addition to atmospheric deposition in any way. Manganese may have a traffic related origin associated with mechanical wear of automotive parts and the use of methylcyclopentadienyl Mn tricarbonyl (MMT) as fuel additive.

Minor variations in trace metals concentrations among the different topsoils analyzed reflect their domain-related geochemical differences.

The amount of As in both fractions ($4.3–8.3 \ \mu g \ g^{-1}$) were similar to those determined in sand fraction ($50–2000 \ \mu m$) of disturbed soils sampled in the same Pampean region (Blanco et al., 2012) and higher than earth crust levels. Furthermore, these authors reported higher As concentrations in the fine fraction than in the coarse fraction. Arsenic is removed from the sand fraction in view of the occurrence of mineral weathering reactions controlled by local geochemical factors (Blanco and Stoops, 2007). The lowest concentrations detected in both fractions of samples II and 23 ($2.54 \ \mu g \ g^{-1}$ to $2.73 \ \mu g \ g^{-1}$), closest to the estuarine tidal flat, were in the same concentration level of the upper continental crust ($\sim 2 \ \mu g \ g^{-1}$).

3.2. Cations and anions in the soluble fraction of soils

Table 5 (**a** and **b**) depicts the concentration of Cl^-, F^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+ in the soluble fraction of the analyzed soils. In general terms, the concentrations of individual ions in sub-superficial soils were in the order $Cl^- > Na^+ \cong SO_4^{2-} > K^+ > NO_3^-$. The cations content in the sub-superficial samples were in agreement with concentrations reported for the region (Blanco and Stoops, 2007).
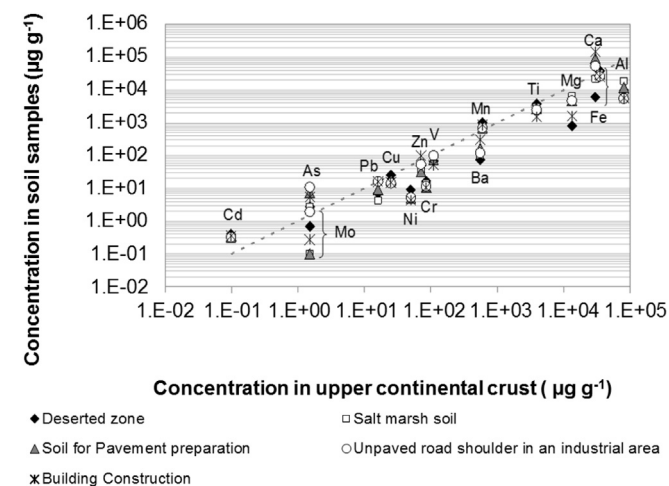

Fig. 1. Determined concentrations in the five types of soils analyzed against the elemental concentrations in the upper continental crust as reported by Taylor (1964).

As it can be seen in Table 5, chlorine, sodium and sulfate were the dominant species. Concentrations of NH_4^+ of $\sim 1.30 \ \mu g \ g^{-1}$ were detected only in some selected samples (not included in Table 4) of top soils (not detected in sub-superficial soils) collected in an area where agricultural activities are predominant. This fact could be explained by the generalized use of ammonia-based fertilizer in this region. These findings could indicate that NH_4^+ ion could be considered a marker of this kind of sources.

In order to evaluate the South Atlantic oceanic influence in the ambient air of Bahía Blanca and as a consequence of its effects on the chemical composition of soils, the sea-salt ratios were calculated for each inorganic ion using Na^+ as a reference element and a typical marker of marine aerosols, assuming all Na^+ to be of marine origin. For samples 25 and V (the closest to the marine tidal influences) the average calculated ratio for K^+/Na^+ was consistent (same order of magnitude) with the average ratios for each ion in seawater, while in the case of samples belonging to groups 23, II and IV (salt marshes and desert zones) the average calculated ratio for Cl^-/Na^+ was the most consistent with the seawater values (Millero, 2002). On the contrary, the average ratios for SO_4^{2-}/Na^+ in all samples were larger than the seawater ratio for these ions, indicating a contribution of non-marine sources. Summarizing, some characteristics of the chemical composition of the analyzed soils (e.g., NH_4^+ content and ionic elemental ratios) can be associated with the soil characteristics and others with the soil uses.

3.3. Enrichment factors

To evaluate the contribution of the studied elements to local environment, enrichments factor of the analyzed samples with respect to crustal average were calculated. Values informed by Taylor (1964) were taken as reference profile. Silicon, Al, or Fe are generally used as the reference elements because they are abundant in soils. In this study, Ti was adopted as a reference element because it is a major element that exhibited a more homogeneous pattern in both fractions (A and B) as well as in top and sub-superficial soils.

It has to be remarked that the analysis of the EF furnish only qualitative information because the wide variation of the elemental concentration of the upper crust has to be considered. It is assumed that elements having a EF > 20 can be considered mainly of anthropogenic origin (elements enriched) while elements having EF < 10 can be considered mainly of crustal origin while those with EFs between 10 and 20 can be considered of mixed origin: crustal and anthropogenic.

Calculation has not been performed for Sb because this metalloid presented in all samples concentration under the detection limit and this does not allow a reliable calculation of EF. The calculated EFs showed that only As and Cd are not significantly enriched in both, superficial and sub-superficial soils. In spite of the low EFs exhibited this data is of special concern if we take into account that these elements are particularly toxic. In the sub-superficial soils, in the agricultural, desert and unpaved road shoulder (industrial areas) soils, EFs of As ranged from 6.26 to 9.98 (Fraction A) and between 5.02 and 8.19 (Fraction B). For Cd, EFs ranged from 6.29 to 10.93 (Fraction A) and from 5.41 to 10.08 (Fraction B). For superficial soils, the highest values were found in Fraction A (~ 10) for As and ~ 11 to ~ 15 for Cd. The highest levels of Cd were detected in samples collected close to a highway. For elements that are more enriched in the smallest size fraction (Fraction A), it is important to highlight that these elements may be considered as chemical markers of soil resuspension in receptor model analysis. For Cd, EFs differ according to the area under study. Vehicular emissions (e.g., brake linings, tire rubber) and industrial activities

Table 5
Concentration of water soluble anions in soil samples collected in Bahía Blanca. **a**) Concentration of water soluble ions in size fractionated top soils. Fraction A: <37 μm and Fraction 37 < B < 50 μm (B). **b**) Concentration of water soluble ions in size fractionated sub-superficial soils. Fraction A: <37 μm and Fraction 37 < B < 50 μm (B).

a)

Sample	Unit	IIA	IIB	23A	23B	28A	28B	25A	25B	27A	27B
Chloride	(mg/g)	8.0 ± 0.4	8.0 ± 0.4	34.2 ± 0.91	41.9 ± 1.6	0.50 ± 0.04	0.49 ± 0.03	14.5 ± 0.5	19.8 ± 0.4	0.39 ± 0.03	0.36 ± 0.02
Fluoride	(μg/g)	25.8 ± 1.9	29.6 ± 2.3	ND	27.7 ± 1.5	22.0 ± 1.1	18.3 ± 0.9	93.1 ± 3.2	25.4 ± 2.0	10.9 ± 1.6	<LOD
Nitrate	(μg/g)	131 ± 5	82.3 ± 6	215 ± 10	370 ± 29	169 ± 14	178 ± 5	151 ± 12	175 ± 10	162 ± 14	143 ± 10
Sulfate	(mg/g)	3.26 ± 0.08	3.12 ± 0.09	9.79 ± 0.80	10.1 ± 0.4	2.01 ± 0.06	1.94 ± 0.13	18.6 ± 0.8	14.1 ± 0.9	1.57 ± 0.07	1.53 ± 0.08
Sodium	(mg/g)	4.02 ± 0.17	3.80 ± 0.12	14.8 ± 0.7	17.3 ± 0.7	1.15 ± 0.09	1.02 ± 0.06	14.3 ± 0.5	15.5 ± 0.9	1.39 ± 0.07	1.30 ± 0.09
Potassium	(mg/g)	0.78 ± 0.06	0.76 ± 0.06	1.39 ± 0.09	1.23 ± 0.07	0.12 ± 0.01	0.11 ± 0.01	0.68 ± 0.04	0.71 ± 0.05	0.83 ± 0.06	0.76 ± 0.05
Ammonium	(μg/g)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

b)

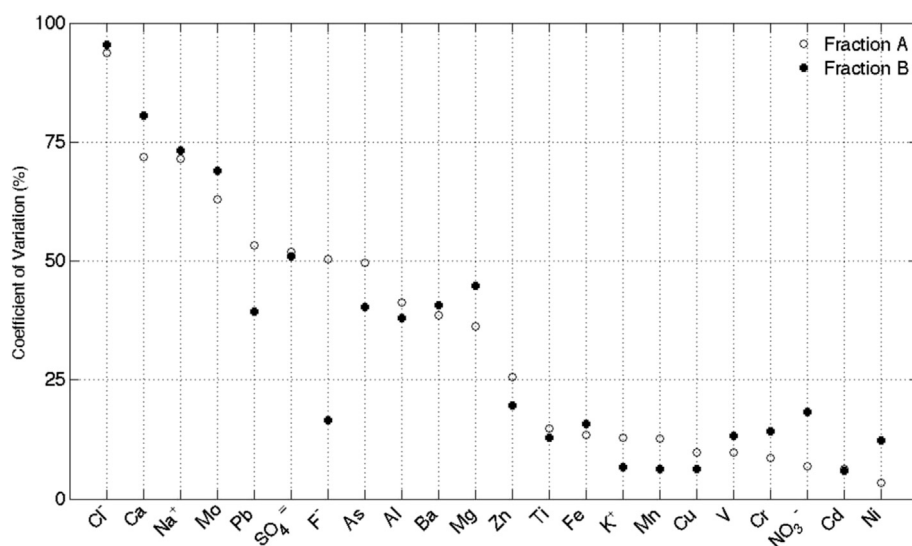| Sample	Unit	IIIA	IIIB	IVA	IVB	VA	VB
Chloride	(mg/g)	0.45 ± 0.02	0.33 ± 0,02	2.0 ± 0.1	2.3 ± 0.1	7.2 ± 0.1	7.3 ± 0.1
Fluoride	(μg/g)	15.3 ± 1.2	16.2 ± 1.0	15.4 ± 1.6	<LOD	18.4 ± 1.2	16.5 ± 0.9
Nitrate	(μg/g)	43.7 ± 4.5	69.2 ± 5.1	<LOD	<LOD	<LOD	<LOD
Sulfate	(mg/g)	0.20 ± 0.01	0.14 ± 0.02	2.61 ± 0.02	2.71 ± 0.15	7.39 ± 0.33	6.46 ± 0.26
Sodium	(mg/g)	0.37 ± 0.03	0.27 ± 0.02	1.35 ± 0.07	1.44 ± 0.07	6.77 ± 0.18	6.34 ± 0.28
Potassium	(mg/g)	0.38 ± 0.02	0.40 ± 0.02	0.35 ± 0.02	0.36 ± 0.02	0.44 ± 0.02	0.45 ± 0.02
Ammonium	(μg/g)	ND	ND	ND	ND	ND	ND

Fig. 2. Coefficient of variation for all elements and ions determined in fraction A and B of the five samples considered.

(e.g., metallurgic industry) may contribute to Cd contamination, especially in topsoils (Bourennane et al., 2010).

3.4. Chemical and site-to-site variability

For each chemical component (*f*) determined in the top soil samples, the variability of each element/ion concentration ($x_{c,f}$) within the overall region comprising the five representative zones (IIA, 23A, 25A, 27A and 28A) was calculated by means of the co-efficient of variation ($CV_{c,f}$) defined in Eq. (1). Where $median_j \{|x_j − median_i(x_i)|\}$ is the median absolute deviation about the median. This estimator, also known under the shorter name of median absolute deviation (MAD), is calculated as the median value of the deviation of all individual concentrations x_j from the median concentration. The MAD is a robust measure that is not significantly affected by the presence of outliers.

$$CV_{c,f} = \frac{median_j\left\{\left|x_{c,f_j} − median_i\left(x_{c,f_i}\right)\right|\right\}}{median_i\left(x_{c,f_i}\right)} \times 100 \left(\%\right) \quad (1)$$

The variability of the concentrations of the measured components in fractions A and B over the region of interest is depicted in Fig. 2. Nine out of 23 components determined (*i.e.*, Al, As, Cu, F⁻, K⁺, Mn, Pb, Ti and Zn) exhibited relatively larger variability in the fine fraction. Chloride > Ca > Na⁺ > Mo > SO₄²⁻ are the components with the largest variability (CV > 50%) in both fractions while As, F⁻ and Pb only had CV > 50% for fraction A. The highest concentrations of Cl⁻ (34–42 mg g⁻¹) and Na⁺ (15–17 mg g⁻¹) were detected at site 23 (estuarine salt marsh) which confirms that this soil receives input from the ocean at high tide while the lowest concentrations (~0.5 mg g⁻¹ for Cl⁻ and ~1 mg g⁻¹ for Na⁺) were detected in site 28 (soil for pavement preparation). Calcium, the metal with the highest variability (CV ~75%), was detected at levels from ~0.5% in the dry sandy soil of the deserted area to much higher concentrations ~12–15%. The last one is an area of active construction where

typical Ca-rich materials like cement, lime and their derivatives are routinely used. In the case of SO_4^{2-}, fractions A and B had similar CV values, >50%. Highest concentrations of this anion (~14–19 mg g^{-1}) were detected in samples collected in an industrial area close to a highway. In spite of being the metal with the second highest variability, measured Mo concentrations ranging from ~0.1 to 2.0 µg g^{-1} were within normal background levels of this metal in soils (Lavado et al., 2004). Because of the detected concentrations and considering that Mo is an essential element for plants and grazing ruminants, it is plausible to ascribe the estimated variability to different rates of plant uptake.

As Ca exhibited the largest variability of all elements (Fig. 2), the concentration ratios between each element X$_i$ and Ca (X$_i$/Ca) may be used as an indicator to differentiate the five chemical profiles of interest by site. These ratios for the finer fraction in topsoils are depicted in Fig. 3. The focus on this soil layer and its finer fraction is of prime importance within the framework of receptor model analysis because these particles would be most likely put into suspension by wind action, becoming potential sources of PM.

The X$_i$/Ca profile calculated for the deserted area exhibited the largest values for all elements, except Mg. Arid and semi-arid regions of Argentina such as Bahía Blanca are sources of aerosols. In these areas, when dust storms occur, depending to their intensity may be reduced visibility to zero and the dust may be transported through the atmosphere over long distances. Therefore, it is important to estimate the contribution of the deserted area surrounding Bahía Blanca to the high levels of PM observed in this area. The considerable differences between the X$_i$/Ca values for the deserted zone and the remaining areas provide a valuable tool for this purpose.

To compare the determined chemical profiles of soils at different sites we recurred to the use of the coefficient of divergence (COD) as expressed in Eq. (2) (Wongphatarakul et al., 1998).

$$COD_{jk} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}}\right)^2} \qquad (2)$$

In Equation (2), x_{ij} represents the average concentration for a chemical component i at zone j; j and k represent two different sampling sites; and n is the number of chemical components. If the two monitoring sites are similar in chemical composition, the COD approaches zero. Values of CODs lower than 0.2 indicates a
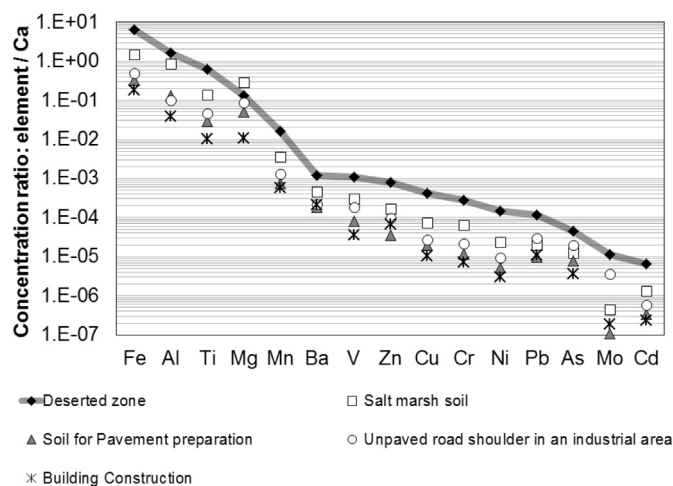
relatively homogeneous spatial distribution (Contini et al., 2012). If they are very different, the COD approaches one.

Three categories of CODs were calculated using different sets of chemical components to assess whether they have different impact in the spatial variability of the determined concentrations. We defined COD_{Global} as that comprising the 17 elements and six ions (n = 17 elements + 6 ions = 23), NH$_4^+$ was not included because it was not detected in any of the samples. The other CODs, consider only one type of component, $COD_{Elements}$ accounts for the 17 elements and COD_{Ions} refers to the ions measured. All CODs calculated are reported in Table 6, for top and sub-superficial soils and the two size fractions considered. This Table shows that both, coarse and fine fractions, exhibit significant spatial variability, with COD_{Global} varying from ~0.4−0.5 for the top soils and within the range ~0.3−0.4 for the sub-superficial soils. The slightly higher values of COD_{Global} associated with the top soil samples may be attributed to the fact that this layer is subject to more perturbations including removals (resuspension, diggings, etc.) and deposit from different causes. In all cases CODs are in the order: $COD_{Ions} > COD_{Global} > COD_{Elements}$, which is consistent with the variability, expressed by the coefficient of variation (Fig. 2) that has been observed for each chemical component of the soils under study.

4. Conclusions

Elemental concentrations in topsoils of Bahía Blanca are in general below crustal values, except for As, Ca and Cd. The levels of As were similar to those determined in sand fraction in the same Pampean region, indicating its predominant natural origin. Calcium exhibited the largest variability; lowest levels were detected in the dry sandy soil of the deserted area while the highest levels were

Fig. 3. Concentration ratios for topsoils (fractions A) between each element X$_i$ and Ca (X$_i$/Ca).

Table 6
Coefficients of divergence (COD) calculated according to Eq. (1), based on different sets of elemental and ion concentrations. The global COD values consider the determined concentrations of the entire set under study, while the other reported COD values are based either on the chemical elements alone or on the ions only. **a)** Top soils. **b)** Sub-superficial soils.

a)

Sites	23A	28A	25A	27A	Sites	23B	28B	25B	27B
COD$_{Global}$ (elements and ions)									
IIA	0.43	0.44	0.40	0.42	IIB	0.39	0.46	0.40	0.47
23A	–	0.46	0.40	0.51	23B	–	0.43	0.32	0.51
28A	–	–	0.45	0.30	28B	–	–	0.42	0.37
25A	–	–	–	0.45	25B	–	–	–	0.45
COD$_{Elements}$									
IIA	0.34	0.40	0.38	0.39	IIB	0.34	0.42	0.40	0.40
23A	–	0.24	0.37	0.40	23B	–	0.25	0.34	0.37
28A	–	–	0.28	0.28	28B	–	–	0.27	0.30
25A	–	–	–	0.32	25B	–	–	–	0.26
COD$_{Ions}$									
IIA	0.59	0.53	0.45	0.48	IIB	0.52	0.57	0.43	0.61
23A	–	0.80	0.48	0.74	23B	–	0.71	0.25	0.76
28A	–	–	0.72	0.34	28B	–	–	0.68	0.52
25A	–	–	–	0.70	25B	–	–	–	0.74

b)

Sites	IIA	IIIA	Sites	IIB	IIIB
COD$_{Global}$ (elements and ions)					
IIA	0.41	0.46	IIB	0.44	0.47
IIIA	–	0.28	IIIB	–	0.33
COD$_{Elements}$					
IIA	0.27	0.28	IIB	0.15	0.27
IIIA	–	0.21	IIIB	–	0.19
COD$_{Ions}$					
IIA	0.64	0.76	IIB	0.80	0.77
IIIA	–	0.41	IIIB	–	0.55

detected at zones where typical Ca-rich materials are customarily used. Anthropogenic Cd is the only element that can be considered as a sensitive marker of the presence of industrial facilities, non-exhaust traffic and agricultural activities.

Chemical and spatial variability was assessed using robust indicators namely, the coefficients of variation and divergence, respectively. The variability of chemical profiles is dominated by five out of 23 components determined namely, $Cl^- > Ca > Na^+ > Mo > SO_4^{2-}$, indicating that these are key chemical markers for future assessment of PM in the area. Both, coarse and fine fractions exhibit significant overall spatial variability with COD_{Global} of ~0.5.

The ratios X_i/Ca were used as indicators to differentiate chemical profiles by site for the top soil layer and its finer fraction. These ratios proved to be particularly useful to discriminate the soil of the deserted area and, since these particles are susceptible to be put into suspension by wind action, they can be employed as a tool to estimate the contribution of the semi-arid region surrounding Bahía Blanca to the high levels of PM normally found in this area.

Our findings, lead to confirm the importance of investigating metal and ion content in topsoils and sub-superficial soils as part of the characterization of areas impacted by multiple particle sources of natural and anthropogenic origins as a first step to identify natural and anthropogenic sources of airborne particulate matter.

Acknowledgments

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