Multielemental chemical characterisation of fine urban aerosols collected in Buenos Aires and Tokyo by plasma-based techniques

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ABSTRACT

In the framework of a collaborative project, a comprehensive chemical characterisation of urban fine aerosols collected in the antipodal cities of Buenos Aires and Tokyo was performed. Twenty three elements namely, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V and Zn were determined by plasma-based techniques after microwave-assisted digestion of the airborne particulate matter. An acid mixture containing HNO_3, H_2O_2 and HF (6:1:3) was used for sample treatment. In samples collected in Buenos Aires concentrations varied between 0.1 µg g^{-1} equivalent to 0.001 ng m^{-3} (Be) and 36,000 µg g^{-1} equivalent to 480 ng m^{-3} (Na) while in Tokyo minimum and maximum determined concentrations varied from 0.6 µg g^{-1} equivalent to 0.01 ng m^{-3} (Co) to 52,000 µg g^{-1} equivalent to 1200 ng m^{-3} (Na). For both cities, significantly high enrichment factors (EFs > 100) were identified for Se > Sb > Cd > Zn > Pb > As, indicating the anthropogenic origin of these elements.

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1. Introduction

The increasing concern about air pollution and climate change has attracted the interest of researchers all over the world for assessing the presence, as well as the health and environmental impacts, of a diversity of pollutants including atmospheric aerosols. Airborne particulate matter (APM) is a complex matrix composed of metals, metalloids, ions, organic compounds, biogenic material, black carbon; being metals and metalloids unequivocal chemical markers of air quality. During many years research was focused on the determination of metals in particles with aerodynamic diameter > 10 µm (PM10). Progressively, more attention has been paid to the characterisation of smaller fractions. Epidemiological studies have revealed consistent association between ambient concentrations of inhalable and respirable particles and their elemental composition with adverse respiratory health effects [1] Particle size and shape are critical factors controlling the extent to which airborne particles penetrate into the respiratory tract [2].

Studies on the characterisation of atmospheric aerosols were carried out during many years by different groups worldwide. In the last years, special attention was paid to the called traffic-related elements (TREs). Many elements (mainly released as particulate matter) such as Ca, Ce, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Pd, Pt, Rh, S, Sb, V and Zn have been ascribed

to vehicular traffic and were detected not only in APM but also in road dust, soil, grass plants growing near roads, as well as river sediments and other matrices [3].

Several studies were focused on the chemical characterisation of APM in the atmosphere of Buenos Aires and Tokyo including specific research on several TREs [4–9]. Furuta and his group by using anion-exchange chromatography (AEC) and/or size-exclusion chromatography (SEC) in combination with plasma-based techniques and hydride generation (HG) reported the separation and quantification of inorganic and organic Sb species in APM samples [10]. In other study, Iijima et al. studied the predominant emission sources of Sb in APM and estimated their effects on the atmosphere of Japan [11]. The fractionation and speciation analysis of Sb in atmospheric aerosols and related matrices was reported by Smichowski in a book chapter [12]. A quantitative real-time monitoring of 15 elements in airborne particles by direct introduction into an ICP-MS was reported by Suzuki [13].The chemical profile of Buenos Aires city was reported by the Argentinean researchers, based on the determination of 13 elements in an early study for PM10 and later for PM2.5 and PM2.5-10 [4,9]. Broadening the scope, in this research a new profile was established for fine particles on the basis of the determination of 23 elements, including in this case key elements such as As, Be, Cd, Co, K, Li and Na that have not been considered in previous studies.

This brief description of the research done evidences the mutual interests, since more than a decade, of researchers of Argentina and Japan in the application of analytical techniques to study and characterise

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atmospheric aerosols. In the framework of a collaborative research project between Argentina and Japan, a study was undertaken to (*i*) gain knowledge about the chemical profiles of fine urban aerosols collected in Buenos Aires and Tokyo, and (*ii*) infer potential contributing sources using groups of specific elements as chemical markers.

2. Experimental

2.1. Instrumentation and reagents

An inductively coupled Ar plasma optical emission spectrometer (ICP OES) was used for determining major elements (SPS-5100, SII NanoTechnology Inc., Tokyo, Japan). Instrumental details and operating conditions are summarised in Table 1. For minor and trace elements determination an inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent 7500ce, Agilent Technologies, Tokyo, Japan) was used and the characteristics and instrumental conditions adopted are depicted in Table 2.

All reagents were of analytical grade. Nitric acid (70%, electronic laboratory grade, Kanto Chemical Co., Tokyo, Japan), HF (50%, semiconductor grade, Daikin Industries Co., Tokyo, Japan), and H_2O_2 (30%, electronic laboratory grade, Kanto) were used for sample treatment and preparation of the standards. Multielemental standard solutions for standardisation of calibration curves were prepared by mixing single-element standard stock solutions (1000 mg L^{-1}) of each element purchased from Kanto Chemicals (Tokyo, Japan) and Wako Chemicals (Osaka, Japan). Diluted working solutions were prepared daily by serial dilutions of those stock solutions. Purified water used throughout the present study was prepared by a Milli-Q system (Millipore Gradient, Millipore, Tokyo, Japan).

All glassware and plastic bottles used were cleaned by rinsing with Milli-Q water, soaking with a 10% (v/v) nitric acid solution for 24 h and then rinsing several times with Milli-Q water. All samples and standards were stored in polypropylene bottles (50 mL) or tubes.

2.2. Sample collection

Samples were collected simultaneously during 15 days, from 20th October to 4th November 2014 (spring in Argentina and autumn in Tokyo). Samples were collected as follows:

Buenos Aires: samples were collected at one sampling site on the roof of a building at Comisión Nacional de Energía Atómica (CNEA) at an elevation of ~12 m. It is at approximately 250 km from the sea and influenced mainly by emissions from residential sources and urban vehicular traffic. Aerosol samples were collected on Teflon® filters with a diameter of 37 mm with a PQ200 ambient air particulate sampler (Butler, NJ, USA) with PM2.5 sampling head. The sampling flow rate used was 16.7 L min^{-1} and the sampling period was 15 days to achieve a concentration of trace metals sufficient for their quantification. The average air volume collected daily was 24.04 m^3. Each filter was placed in a clean polyethylene bag during transport and storage.

Table 1
Instrumental characteristics and settings for ICP OES.

Instrument	SPS-5100, SII NanoTechnology
rf Power	1.0 kW
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.5 L min^{-1}
Carrier gas flow rate	0.9 L min^{-1}
Solution delivery	1.0 mL min^{-1}
Nebulizer	Concentric pneumatic nebulizer
Polychromator	Echelle spectrometer
Detector	CCD
Measurement mode	Continuous nebulization
Wavelengths (nm)	Fe, 261.187; Mg, 285.213; Ca, 317.933; Al, 394.401; Na, 568.821 K, 766.491

Table 2
Instrumental characteristics and settings for ICP-MS.

Instrument	7500ce, Agilent technologies
Frequency of rf generator	1400 W
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.00 L min^{-1}
Carrier gas flow rate	0.93 L min^{-1}
Makeup gas flow rate	0.32 L min^{-1}
He gas flow rate (CRC)	3.0 mL min^{-1}
Nebulizer	Concentric pneumatic nebulizer
Data acquisition	0.3 s
Mode	Quantitative
Isotopes	^{7}Li, ^{9}Be, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{95}Mo, ^{111}Cd, ^{121}Sb, ^{137}Ba, ^{208}Pb, (^{115}In, ^{185}Re as internal standard)

Tokyo: samples were collected on the rooftop (~45 m height) of a building on the Chuo University campus. The airborne particulate matter samples were classified into six size ranges (>11, 2.1–11, 1.1–2.1, 0.65–1.1, 0.43–0.65, and <0.43 μm) and collected on quartz glass fiber filters by using an Andersen low-volume air sampler (Model AN-200; Tokyo Dylec Co., Tokyo, Japan) with a sampling flow rate of 28.3 L min^{-1}. After sampling, filters were stored in a desiccator.

2.3. Sample pre-treatment and analysis

Once in the laboratory, filters loaded with APM and blank filters were placed into high pressure Teflon® vessels to which an acid mixture of HNO_3 (6 mL), H_2O_2 (1 mL) and HF (3 mL) was added (Ultrapure grade, Kanto Chemicals, Japan). The digestion was carried out in a microwave oven (Ethos TC, Milestone General, Kawasaki, Japan). After digestion, the HF was removed by heating the Teflon® vessels until dryness on a hot plate at 210 °C. An aliquot of 10 mL of 2 mol L^{-1} of HNO_3 was added and heated at 140 °C to dissolve the residues to reach a transparent solution without visible particles. Then, samples were diluted to 50 mL of with Milli-Q water.

About 20 mg of the certified reference material NIST SRM 1648 (urban particulate matter) were weighed and subject to the same treatment that the samples.

An ICP OES (JY24; Jobin Yvon, France) was used to determine major elements (Al, Ca, Fe, K, Mg and Na). For the determination of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Ti, V and Zn) an ICP-MS (7500ce-Agilent Technologies, Hachioji, Japan) was employed.

3. Results and discussion

The analytical methodology adopted in this research has demonstrated to be robust and suitable for the determination of major, minor and trace elements present in different types of aerosol samples and related matrices [4,8]. To this end, samples collected in the two antipodal megacities of Buenos Aires and Tokyo were analysed by the same procedure to identify levels of metals and metalloids in the APM of both air basins.

3.1. Metals and metalloids in the atmosphere of Buenos Aires and Tokyo

Analysis of filters by plasma-based techniques requires a careful sample preparation that involves the digestion of deposited particulate matter. Atmospheric aerosols are difficult to digest samples, which contain a variety of components including oxides, sulfides, nitrates, carbonates, silicates, and organic compounds. Generally, HNO_3 in conjunction with other acids like $HClO_4$, HF, HCl or with H_2O_2 in different proportions were used for this purpose. In this study, an acid mixture of HNO_3 (6 mL), H_2O_2 (1 mL) and HF (3 mL) was adopted. The selection of these acids is based on the following considerations: (*i*) HNO_3 was chosen to destroy organic compounds and to oxidise metals and

hence, breaks down the complex hydrocarbons into H_2O and CO_2. In addition, it forms water-soluble salts with most elements and consequently losses due to precipitation are not expected; (*ii*) H_2O_2 is a very efficient oxidising agent because of its strong oxidation power and constitutes a safer alternative to $HClO_4$ that is more dangerous, and (*iii*) because silicates are present in the sample, the addition of HF is necessary to break up the silica matrix and dissolve mineral constituents.

Samples were collected in each city according to the particulate matter samplers available. Samples of PM2.5 were collected in Buenos Aires whereas size fractionated samples classified into six size ranges (>11, 2.1–11, 1.1–2.1, 0.65–1.1, 0.43–0.65, and <0.43 μm) were collected in Tokyo. It is important to remark that in spite of the difference in fraction sizes, we judge of interest to apply the same methodology at the same time to samples collected in both cities since our primary focus resided in the role played by different subsets of elements (especially those present in the respirable fractions) as chemical markers of contributing sources to the load of APM.

The analytical results of the multielemental analysis of APM samples collected in Buenos Aires and Tokyo are depicted in Tables 3 and 4, respectively.

In Buenos Aires, the median elemental concentrations varied within a wide range, encompassing six orders of magnitude, from 0.2 μg g^{-1} (Be) to 15,000 μg g^{-1} (Na) (Table 3). Such high Na levels in Buenos Aires were observed previously, especially in the coarse fraction (aerodynamic diameter > 2.5 μm) as a consequence of marine intrusion even when the city is located at ~250 km from the Atlantic Ocean [14]. These results confirm the presence of sea-salt aerosols even in the PM2.5 fraction. Beryllium concentrations in Buenos Aires were measured for the first time in this study. Even for a relatively short sampling period of 15 consecutive days, temporal variability was observed for all elements with a difference of one order of magnitude between extreme values for each element (Fig. 1). Furthermore, Mn (52–1700 μg g^{-1}), Mo (7.9–1500 μg g^{-1}), Pb (12–1900 μg g^{-1}) and V (5.1–1000 μg g^{-1}) varied significantly. Geological elements such as Al, Ca and Fe exhibited the highest level after Na even in the PM2.5 fraction under this study. Good pairwise correlations among these three elements ($0.90 \leq r \leq 0.95$) were observed, which are indicative of a common origin. Traffic-related elements (TREs) namely, those coming from brake wear (Ba,

Cu, Mo and Sb) and those arising mainly from vehicle exhaust (As, Cd, Mn, Pb and Zn) did not show significant pairwise correlations as a consequence of the contribution of other emission sources.

In all fractions of Tokyo samples (Table 4) a great variability of concentrations was observed. In each fraction, the following elements exhibited the highest concentration: Fe in fractions E (43 mg g^{-1}), K resulted to be the element with the highest concentration in fraction E (6.6 mg g^{-1}), Na in fraction E (52 mg g^{-1}) and Ca in fraction F (39 mg g^{-1}). As expected, the group of earth–crustal elements (i.e., Al, Ca, Fe, Mg and Ti) was most abundant in the largest size fractions (E and F).

The variation of concentration according to the six fractions analysed could be grouped in two main patterns (Fig. 2). Several elements showed increasing concentrations with increasing particle size being the highest concentration in fractions E and/or F. Cobalt, Cr, Cu, Fe, Li and Na exhibited the highest concentration in fraction E and a relatively smaller level in fraction F while the concentrations in the other fractions were considerably lower. Distinct geological elements such as Al, Ca and Ti exhibited the highest concentrations in fraction F. Sodium is an unequivocal marker of marine aerosols and as expected it was also detected in the coarse fraction, exhibiting a similar size distribution of crustal elements. Sea salt spray is one of the potential sources of K and Mg. Other group is comprised by As, Pb, Sb, Se and V, showing an increasing trend in concentrations with decreasing particle size. These toxic and potentially toxic elements were present mainly in the finer size fractions (A to D), which represents a concern from the health point of view. Cadmium, K, Ni and Zn showed unique behaviour which did not allow identifying a common pattern.

3.2. Enrichment factors in Buenos Aires and Tokyo

To evaluate the contribution of the studied elements to the local environment of both cities, enrichment factors (EFs) of all analysed samples with respect to crustal average were calculated. It has to be remarked that the analysis of EFs furnishes only qualitative information because the wide variation of the elemental concentration of the upper crust has to be considered. In this study, values informed by Wedepohl were taken as reference profile [15]. Enrichment factors constitute useful indicators comparing concentrations of an element in APM

Table 3
Descriptive statistics of measured concentrations of PM2.5 collected in Buenos Aires.

Element	μg g^{-1}				ng m^{-3}			
	Minimum	Median	Average	Maximum	Minimum	Median	Average	Maximum
Al	1800	6600	8013	24,000	27	130	118	230
As	3.8	23	27	66	0.06	0.4	0.5	1.4
Ba	490	1800	2503	5900	11	28	41	140
Be	0.1	0.2	0.4	1.5	0.001	0.003	0.006	0.02
Ca	2600	9000	13,093	37,000	71	210	186	350
Cd	1.6	8.7	15	45	0.03	0.17	0.23	0.84
Co	1.9	5.6	8	16	0.04	0.09	0.13	0.46
Cr	39.0	100.0	185	810	0.6	2.1	2.7	8.6
Cu	230	510	682	1700	3.7	9.7	11	29
Fe	2300	9900	11,947	35,000	35	170	180	350
K	2200	5000	6307	16,000	46	91	94	160
Li	0.9	3.2	4.3	10	0.01	0.06	0.07	0.15
Mg	880	3200	3539	9100	16	55	53	82
Mn	52	210	364	1700	0.78	4.1	5.0	14
Mo	7.9	480	541	1500	0.12	8.5	8.4	13
Na	3100	15,000	14,936	36,000	67	205	233	480
Ni	31	190	200	500	0.67	2.0	3.5	15
Pb	12	330	526	1400	0.18	4.5	9.5	39
Sb	17	58	60	120	0.34	0.77	1.1	2.8
Se	5.9	31	32	76	0.09	0.52	0.5	0.85
Ti	110	445	641	1700	1.7	9.0	9.2	15
V	5.1	110	212	1000	0.08	1.2	4.1	21
Zn	1200	2800	4527	14,000	22	54	69	150

Table 4
Concentrations of major, minor and trace elements in size–fractionated airborne particulate matter collected in Tokyo.

Element	Fraction A (<0.43 μm) $\mu g\,g^{-1}$	$ng\,m^{-3}$	Fraction B (0.43–0.65 μm) $\mu g\,g^{-1}$	$ng\,m^{-3}$	Fraction C (0.65–1.1 μm) $\mu g\,g^{-1}$	$ng\,m^{-3}$	Fraction D (1.1–2.1 μm) $\mu g\,g^{-1}$	$ng\,m^{-3}$	Fraction E (2.1–11 μm) $\mu g\,g^{-1}$	$ng\,m^{-3}$	Fraction F (>11 μm) $\mu g\,g^{-1}$	$ng\,m^{-3}$
Al	<114	<71	<114	<71	26	0.14	3000	11	14,000	144	14,000	44
As	34	0.16	35	0.17	32	0.17	14	0.05	10	0.10	<0.07	<0.04
Ba	46	0.21	<3.1	<2.0	76	0.14	450	1.6	980	10	410	1.2
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	950	4.4	160	0.78	930	5.0	6600	24	31,000	320	39,000	120
Cd	5.0	0.02	3.0	0.02	5.3	0.03	<0.38	<0.24	1.2	0.01	<0.38	<0.24
Co	1.2	0.01	<0.04	<0.03	0.6	0.01	2.2	0.01	13	0.13	7.0	0.02
Cr	120	0.55	27	0.13	96	0.53	120	0.42	230	2.4	180	0.54
Cu	370	1.7	250	1.2	250	1.3	500	1.8	1000	11	340	1.0
Fe	5000	23	4500	22	7300	40	19,000	67	43,000	450	33,000	100
K	4400	20	5800	29	6000	33	4100	15	6600	68	3300	10
Li	1.5	0.01	1.2	0.01	1.5	0.01	1.9	0.01	3.9	0.04	2.2	0.01
Mg	96	0.40	<29	<18	460	2.5	2700	9.8	12,000	120	6800	21
Mn	280	1.3	530	2.6	760	4.2	730	2.6	930	9.6	720	2.2
Mo	<43	<27	<43	<27	<43	<27	<43	<27	<43	<27	<43	<27
Na	2700	12	2100	10	2900	16	9700	35	52,000	540	18,000	54
Ni	130	0.61	<10	<6.2	<10	<6.2	<10	<6.2	94	0.97	10	0.01
Pb	440	2.0	410	2.0	550	3.0	420	1.5	220	2.3	140	0.43
Sb	120	0.54	94	0.46	81	0.44	71	0.26	88	0.91	18	0.06
Se	79	0.37	95	0.46	110	0.60	58	0.21	20	0.20	2.6	0.01
Ti	50	0.23	18	0.09	120	0.64	610	2.2	1700	18	1600	4.8
V	370	1.7	250	1.2	130	0.70	84	0.31	86	0.89	63	0.19
Zn	1300	6.2	1700	8.2	3000	16	4300	16	2900	30	1400	4.3

(M(APM)) respect to its concentration in Earth crust (M(Earth crust)). They were calculated according to Eq. 1, using Al as reference element.

$$EF = \frac{M(APM)\big/Al(APM)}{M(Earth\ crust)\big/Al(Earth\ crust)} \qquad (1)$$

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 of crustal origin while those with EFs between 10 and 20 are of mixed origin: crustal and anthropogenic.

As depicted in Fig. 3, the calculated EFs showed the diversity of composition levels in the samples collected in both cities as discussed below.

(*i*) Buenos Aires: For PM2.5 samples, EFs varied from 0.23 (Be) to 12,000 (Se). The high EFs calculated for Se may be due to the fact that up to 90% of Se content in ambient air is emitted during the burning of fossil fuels. Selenium dioxide is formed during combustion of elemental Se present in fossil fuels [16]. The elements that exhibited the highest values were Se (1300–12,000) > Mo (2200–11,000) > Sb (570–10,000) > Cd (430–4600). Copper, Mo and Sb are components of the brake pads and this research corroborates the values calculated for Buenos Aires in our previous studies [5]. Other typical traffic related elements (TREs) such as Pb and Zn, showed EFs > 1000 in selected samples.
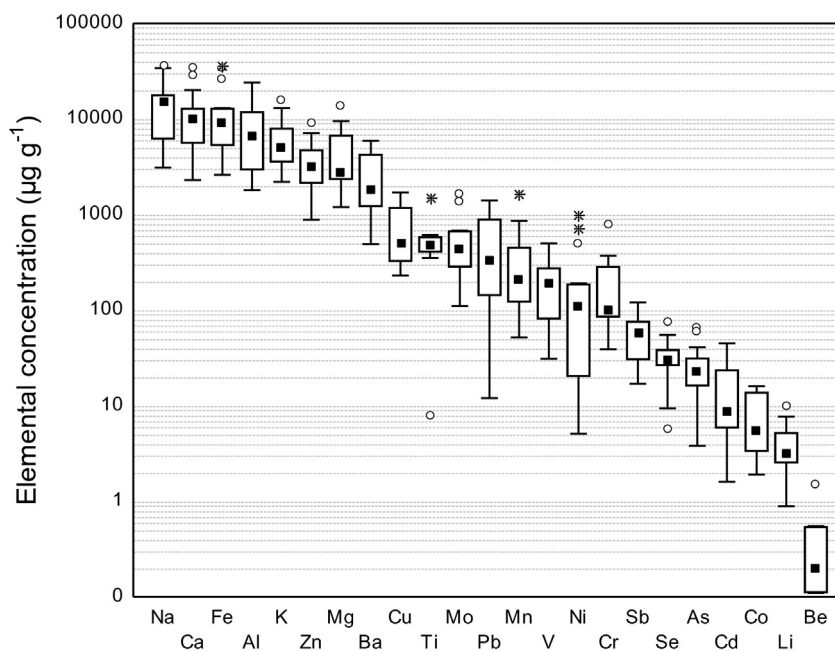

Fig. 1. Levels of metals and metalloids in PM2.5 samples collected in Buenos Aires. Black dot represents the median, the box indicates the range 25–75% of the distribution, whiskers represent minimum and maximum values, empty circles indicate outliers and asterisks extreme values.
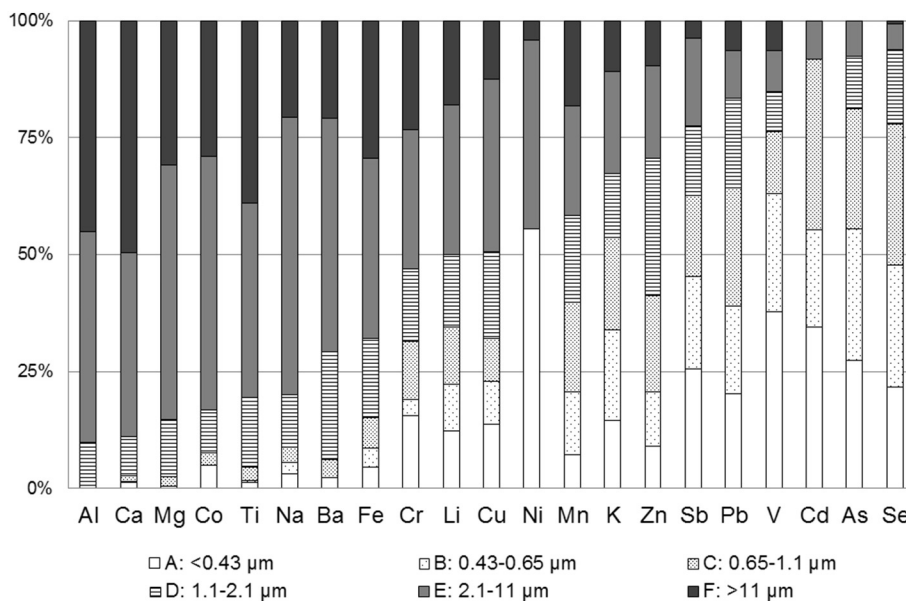
Fig. 2. Distribution of elemental concentrations by size fraction (A to F) of samples collected in Tokyo. Depicted distribution is based on concentrations expressed as µg g^{-1}.

(*ii*) Tokyo: EFs were calculated for fractions C to F while those for the finest fractions (A and B) were not included because Al concentrations for these samples were below the detection limit. The element that exhibited a surprisingly high enrichment was Se (EF: 3,300,000) for the fraction of 0.65–1.1 µm, followed by Sb (800,000) > Cd (160,000) > Zn (140,000) > Pb (110,000) > As (55,000). For these elements, EFs resulted significantly lower in fractions of larger particle size, from 15,000 (EF: Se) to 5.0 (Pb). Enrichment factors decreased systematically with the particle size fraction considered. The highest values in the particles with the smallest aerodynamic diameter, which are likely to reach alveolar level is a matter of concern from the health standpoint of view. Fig. 3 shows that in general terms, EFs of PM2.5 in Buenos Aires were between those of fractions C and F collected in Tokyo. Only five elements, namely Ca, Fe, Mg, Mn and Ti exhibited a different pattern, being the EFs in Buenos Aires lower than those in Tokyo. It is plausible to attribute this fact to a higher contribution of geological elements in Buenos Aires PM2.5. To corroborate this attribution, the results of Al,

Ca and Fe concentrations determined in the samples collected in both cities were compared to the concentration of these elements in the crustal rock. To this end, a ternary graph of Al-Ca-Fe concentrations, free of other elements, was used. Fig. 4 depicts these results, which clearly shows that concentrations of the three elements in PM2.5 of Buenos Aires are closer to their concentrations in the Earth crust in comparison to those in Tokyo. In addition, Fig. 4 shows that the concentrations of the finest fraction in Tokyo (A to C, see Table 4), which are depleted in Al, lie far from the levels of these elements in Earth crust, indicative of a negligible presence of geological contribution.

3.3. Evaluation of trueness and precision (repeatability)

Table 5 summarises the concentrations of the elemental analysis of the Standard Reference Material NIST 1648 (Urban Particulate Matter) as determined by ICP OES and ICP-MS. This SRM was used to verify analytical procedures including sampling digestion. The overall picture
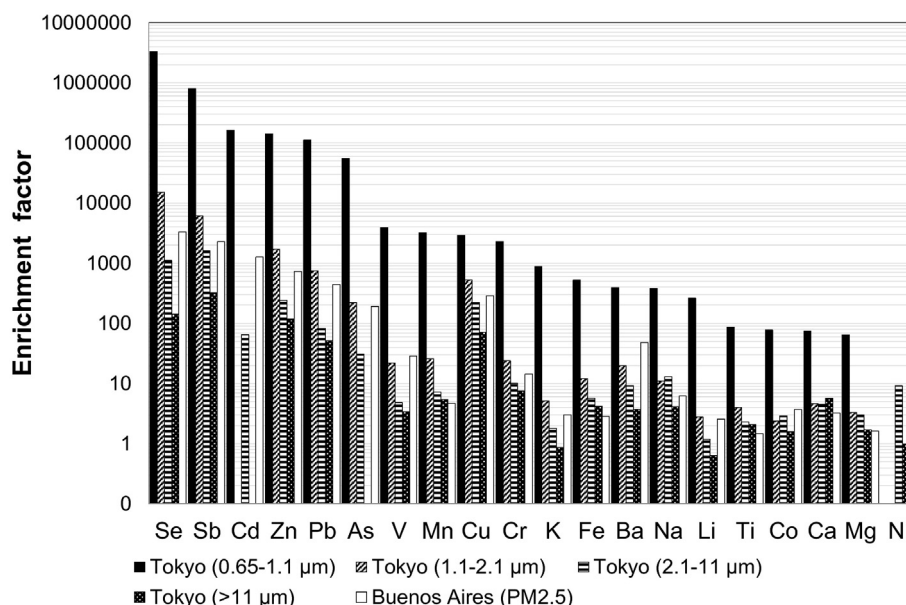

Fig. 3. Enrichment factors of size–fractionated samples collected in Tokyo and PM2.5 samples collected in Buenos Aires. Aluminium was taken as reference elements for EF calculation.
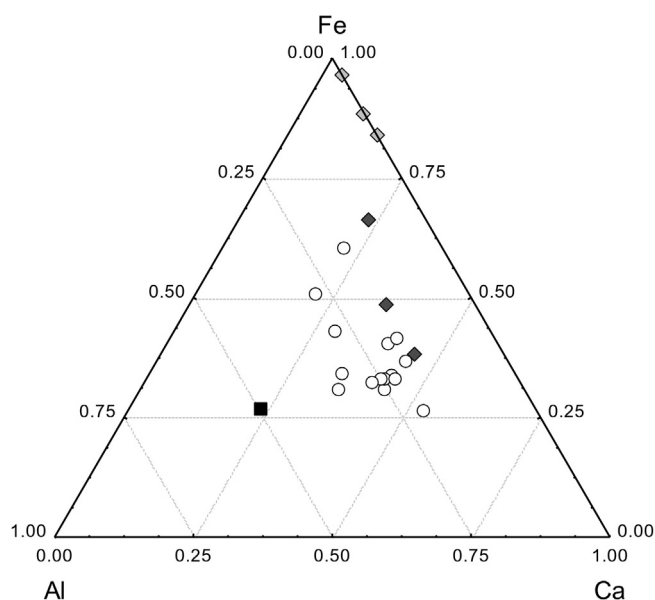
Fig. 4. Three component Al-Ca-Fe plot for size-classified APM samples collected in Tokyo, PM2.5 samples collected in Buenos Aires. The concentration of the continental crust is taken as reference value. ○ Buenos Aires PM2.5 samples; ◇ Tokyo size classified samples A, B or C; ◆ Tokyo size-classified samples D, E or F; ■ Earth crust.

can be considered satisfactory in terms of the recovery and the repeatability.

4. Conclusions

Even when the objective of this research was not strictly focused on the comparative assessment of the air quality in Buenos Aires and Tokyo, some conclusions can be reached from the results obtained.

Considering the average concentrations ($\mu g\,g^{-1}$) of PM2.5 in Buenos Aires with respect to the concentration of PM2.1 (sum of the determined concentrations in fractions A to D) in Tokyo some relevant

analogies and differences can be set forth. In general terms, concentrations of metals and metalloids are higher in Tokyo, except for Al, Ba, Ca, Co and Ni. Concentrations in Tokyo were 10% (Mg) to >1000% (Se) higher than those in Buenos Aires.

The enrichment factors evaluated for the analysed samples are indicative of the significant levels of toxic and potentially toxic elements in the atmosphere of both coastal megacities. The results obtained for the finest fraction in Tokyo raised particular concern from the environmental and health standpoint and pave the way to the need of considering the finest fraction for future studies in Buenos Aires.

References

[1] C.A. Pope III, M. Ezzati, D.W. Dockery, Fine-particulate air pollution and life expectancy in the United States, N. Engl. J. Med. 360 (2009) 376–386.
[2] P. Smichowski, D.R. Gómez, Analysis of atmospheric aerosols, Encyclopedia of Analytical Chemistry, Wiley Online Library, John Wiley & Sons Ltd., New York, 2012 http://dx.doi.org/10.1002/9780470027318.a9338.
[3] G. Weckwerth, Verification of traffic emitted aerosol components in the ambient air of cologne (Germany), Atmos. Environ. 35 (2001) 5525–5536.
[4] P. Smichowski, D.R. Gómez, L.E. Dawidowski, M.F. Giné, A.C.S. Bellato, S.L. Reich, Monitoring trace metals in urban aerosols from Buenos Aires city. Determination by plasma-based techniques, J. Environ. Monit. 6 (4) (2004) 286–294.
[5] D.R. Gómez, M.F. Giné, A.C.S. Bellato, P. Smichowski, Antimony: a traffic-related element in the atmosphere of Buenos Aires, Argentina, J. Environ. Monit. 7 (12) (2005) 1162–1168.
[6] B. Bocca, S. Caimi, P. Smichowski, D. Gómez, S. Caroli, Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina, Sci. Total Environ. 358 (1) (2006) 255–264.
[7] A. Iijima, H. Tago, K. Kumagai, M. Kato, K. Kozawa, K. Sato, N. Furuta, Regional and seasonal characteristics of emission sources of fine airborne particulate matter collected in the center and suburbs of Tokyo, Japan as determined by multielement analysis and source receptor models, J. Environ. Monit. 10 (9) (2008) 1025–1032.
[8] K. Sato, T. Tamura, N. Furuta, Partitioning between soluble and insoluble fractions of major and trace elements in size-classified airborne particulate matter collected in Tokyo, J. Environ. Monit. 10 (2) (2008) 211–218.
[9] M. Dos Santos, D. Gómez, L. Dawidowski, E. Gautier, P. Smichowski, Determination of water-soluble and insoluble compounds in size classified airborne particulate matter, Microchem. J. 91 (1) (2009) 133–139.
[10] A. Iijima, K. Sato, T. Ikeda, H. Sato, K. Kozawa, N. Furuta, Concentration distributions of dissolved Sb(III) and Sb(V) species in size-classified inhalable airborne particulate matter, J. Anal. At. Spectrom. 25 (2010) 356–363.
[11] A. Iijima, K. Sato, Y. Fujitani, E. Fujimori, Y. Saito, K. Tanabe, N. Furuta, Clarification of the predominant emission sources of antimony in airborne particulate matter and estimation of their effects on the atmosphere in Japan, Environ. Chem. 6 (2) (2009) 122–132.
[12] P. Smichowski, Fractionation and speciation analysis of antimony in atmospheric aerosols and related matrices, Speciation Studies in Soil, Sediment and Environmental Samples, CRC Press, Boca Raton 2013, pp. 341–362 (ch. 8).
[13] Y. Suzuki, H. Sato, K. Hiyoshi, N. Furuta, Quantitative real-time monitoring of multielements in airborne particulates by direct introduction into an inductively coupled plasma mass spectrometer, Spectrochim. Acta Part B 76 (2012) 133–139.
[14] M. Dos Santos, L. Dawidowski, P. Smichowski, A.G. Ulke, D. Gómez, Factors controlling sea salt abundances in the urban atmosphere of a coastal South American megacity, Atmos. Environ. 59 (2012) 483–491.
[15] K.H. Wedepohl, Geochemistry, Holt, Rinehart and Winston Inc., New York 1971, p. 65.
[16] HSDB, U. S., National Library of Medicine, Hazardous Substance Database, Online-Datenbank, Stand: März, 1991.

Table 5
Results obtained in the analysis of the SRM NIST 1648 (Urban particulate matter) by ICP OES and ICP-MS.

Element	Certified value	Found by ICP OES [%]	Found by ICP-MS [mg kg^{-1}]
Al	3.42 ± 0.11%	3.40 ± 0.05	–
As	115 ± 10 mg kg^{-1}	–	122 ± 1.0
Ba	(737 mg kg^{-1})	–	758.7 ± 3
Be	NDR	–	ND
Ca	NDR	5.72 ± 0.10	–
Cd	75 ± 7 mg kg^{-1}	–	70.2 ± 0.7
Co	(18 mg kg^{-1})	–	17.7 ± 0.0
Cr	403 ± 12 mg kg^{-1}	–	388 ± 7.1
Cu	609 ± 27 mg kg^{-1}	–	551 ± 8.9
Fe	3.91 ± 0.10%	3.91 ± 0.05	–
K	1.05 ± 0.01%	1.00 ± 0.01	–
Li	NDR	–	25.5 ± 0.2
Mg	(0.8%)	0.78 ± 0.02	–
Mn	786 ± 17 mg kg^{-1}	–	820 ± 6.0
Mo	NDR	–	18.8 ± 0.6
Na	0.425 ± 0.002%	0.42 ± 0.01	–
Ni	82 ± 3 mg kg^{-1}	–	78.4 ± 0.2
Pb	6550 ± 80 mg kg^{-1}	–	6228 ± 60
Sb	(45 mg kg^{-1})	–	46.8 ± 0.6
Se	27 ± 1 mg kg^{-1}	–	26.7 ± 0.6
Ti	(0.40%)	–	4110 ± 83
V	127 ± 7 mg kg^{-1}	–	138 ± 0.8
Zn	0.476 ± 0.014%	–	4250 ± 38

Noncertified values are in brackets. NDR: no data reported. ND: not detected.