Chemical markers of biomass burning: Determination of levoglucosan, and potassium in size-classified atmospheric aerosols collected in Buenos Aires, Argentina by different analytical techniques

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A B S T R A C T

A study concerning the identification and quantification of key chemical markers of biomass burning namely, levoglucosan and potassium in size-fractionated airborne particulate matter was conducted. To perform a complete characterization of PM2.5 and PM10 samples collected in Buenos Aires, Argentina black carbon, metals and metalloids were also determined. Due to the particularly complex chemical composition of atmospheric aerosols several analytical techniques were employed. Levoglucosan was extracted from filters and determined by gas chromatography–mass spectrometry (GC–MS). It was detected in a wide range of concentrations, from 2.0 ng m^{-3} to 4.90 μg m^{-3} (PM2.5) and 6.0 ng m^{-3} to 1.86 μg m^{-3} (PM10). Equivalent black carbon concentrations were determined by reflectromety and varied between 3.3 and 8.9 μg m^{-3}. Other tracer of biomass burning such as Potassium was determined by flame atomic absorption spectrometry (FAAS). Potassium was mainly detected in the coarse fraction varying from <0.56 to 3.51 μg m^{-3}. In addition, 17 minor, major and trace elements (Al, As, Ba, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Sn, Ti, V and Zn) were determined by plasma-based techniques namely, inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma-mass spectrometry (ICP-MS). Mean concentrations (in ng m^{-3}) of metals and metalloids varied from 1.57 (Hg) to 1688 (Al) for PM2.5 and 1.5 (Al) to 1502 (Hg) for PM10.

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1. Introduction

Atmospheric aerosols are ubiquitous in the earth's atmosphere and are associated with many well-known environmental problems such as climate change, stratospheric ozone depletion and air quality deterioration. The chemical composition of airborne particulate matter (APM) varies dramatically in different localities. In urban environments, aerosol particles can affect human health through their inhalation. In the last years, aerosol science has been benefiting more and more from studies focused to assess the chemical composition of aerosols as well as the contribution of the main sources. Even though considerable progress has been made concerning the characterization of atmospheric aerosols, this topic still represents a major research challenge because there are many aspects that require further investigation.

Chemical tracers/markers are single species or a group thereof and/or concentration ratios that are able to distinguish between APM sources. Specific trace elements such as K and distinct organic molecules (e.g., levoglucosan) have been widely used as efficient chemicals markers of biomass burning. Levoglucosan exhibits favorable properties to be used as a biomass marker of combustion processes for its good photochemical stability in the atmosphere and also in the liquid phase as reported by Caseiro et al. [1] and references therein.

In this context, the study of organic aerosol (OA) components is of prime importance because they constitute a large and/or dominant fraction of the atmospheric particulate matter. Although the total mass of organic compounds can comprise a significant part of the overall mass of particles, it is made up of a very large number of individual organic compounds, each of which is present at a very low concentration [2]. Among the key components, levoglucosan deserves special attention as a chemical marker of biomass burning.

Biomass burning of natural and anthropogenic origin is an important source of gases and aerosol particles to the atmosphere which produce an impact on global climate by absorbing radiation but also by acting as cloud condensation nuclei [3] as well as to influence, precipitation and climate on both global and regional scales. The monosaccharide anhydrides (MAs) are among the important compounds that have been

used for monitoring of biomass burning emissions, being levoglucosan (1,6-anhydro-â-ᴅ-glucopyranose) and its isomers galactosan and mannosan the most known representatives [4]. The use of levoglucosan as a tracer for biomass burning was introduced by Simoneit et al. in 1999 [5] because it can only be generated by the degradation of cellulose and hemicellulose when the burning temperature is higher than 300 °C. In addition, it is emitted in large quantities and is stable in the atmosphere. Tracer compounds are important tools in tracking the transport of particles produced during biomass burning. According to Calvo et al. [6], the biomass burning is listed as a primary source of levoglucosan resulting from the decomposition of cellulose.

The chemical complexity of atmospheric aerosols requires the use of different analytical techniques to get an overview of its composition. In the case of levoglucosan, the more used analytical techniques for sugar compounds determination, including levoglucosan (LEV), are gas chromatography (GC)-based methods after derivatization, high-performance liquid chromatography (HPLC)-based methods and in less extent, capillary electrophoresis (CE)-based methods [7]. Due to high polarity, hydrophilicity and low volatility, saccharides have to be converted into volatilizable and stable derivatives (e.g., trimethylsilyl or acetate derivatives, before GC analysis). In spite of the series of steps necessary for analytes extraction and derivatization, GC–MS has been extensively used for levoglucosan determination. In addition, this technique is readily available in many analytical laboratories, also provides a higher chromatographic resolution with a capillary column and a greater sensitivity. For studying the seasonal variation of levoglucosan and other compounds in aerosols collected in the western North Pacific, Fu et al. [8] performed the GC separation on a fused silica capillary column with an optimized GC oven temperature program. Various silylating agents, were compared and the effects of different concentrations of trimethylchlorosilane (TMCS) were assessed to optimize the conditions for detecting levoglucosan and related monosaccharide anhydrides in atmospheric aerosols by GC–MS [9]. For aerosols collected in São Paulo, Brazil, Vasconcellos and coworkers employed and compared two extraction procedures. For the derivatization step, levoglucosan was converted to the trimethylsilyl derivative by reaction with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine [10].

Even when less used, high-performance liquid chromatography (HPLC) was employed with various detectors including high-resolution mass spectrometry. Dixon and Baltzell [11] reported the determination of levoglucosan in atmospheric aerosols using HPLC with an ion exchange column and water as eluent reaching a limit of detection (LOD) of ~90 ng mL^{-1}. Liquid chromatography (LC) combined with electrospray ionization mass spectrometry (ESI-MS) has become in a useful method for the determination of different saccharides in aerosol samples [12,13]. Recently, using ultra-performance liquid chromatography combined with triple tandem quadrupole mass spectrometry (UPLC-MS/MS) a concentration of levoglucosan as low as 0.11 ng L^{-1} was measured in snow and ice samples [14].

Ahmed et al. [15] reported the application of a simple ultrasonic assisted extraction procedure coupled to HPLC and GC–MS for the determination of surface active compounds in APM. The result obtained showed that a variety of organic compounds, including levoglucosan, are the main surface active compounds in APM because of their surface active potential. Both analytical techniques resulted suitable since they provide low detection limits.

The combination of negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI(−)-FT-ICR MS) and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC × GC-TOFMS) techniques provided comprehensive characterization of bio-oil samples from the flash-pyrolysis of empty palm fruit and pine wood chips. The presence of levoglucosan was identified with both techniques [16].

Potassium is another well-known marker of biomass burning. During cultivation of cereals, nitrogen, phosphorus and potassium are supplemented in the soil with fertilization purposes to increase the crop production. In the absence of other important sources, such as soil dust, sea salt and meat charbroiling, water soluble K can be a satisfactory biomass marker [17].

Another compound determined in this study was black carbon (BC), being the most refractory and polymerized part of the aerosol. Carbonaceous components of atmospheric aerosols arising from combustion processes have been conceived as a transition that starts in slightly charred products and culminates in black carbon [18,19].

The aim of this study was to identify and measure two key chemical markers of biomass burning such as levoglucosan and potassium. In addition and to perform a complete characterization of the samples under study, Al, As, Ba, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Sn, Ti, V and Zn as well as black carbon were determined in size-fractionated airborne particulate matter collected in Buenos Aires.

To the best of our knowledge, this is the first time that levels of levoglucosan in airborne particulate matter are reported for a city of Argentina.

2. Experimental

2.1. Instrumentation and reagents

Qualitative and quantitative determinations of levoglucosan were performed by gas chromatography–mass spectrometry (Agilent 7820A). Separation was performed with an inert 5% phenyl – methyl column, VF – 5 ms (30 m × 0.250 mm, 0.25 μm film thickness) with a temperature program: isothermal at 120 °C for 2 min, 5 °C min^{-1} to 200 °C held for 2 min, then 20 °C min^{-1} to 300 °C held for 2 min. The total analysis time was 27 min. The splitless injector was maintained at 250 °C, with He as carrier gas at a flow rate of 1.3 mL min^{-1}. The temperature of the transfer line was 300 °C. The mass spectrometer was operated in the electron impact mode at 70 eV ion source energy, and at a temperature of 220 °C. Data acquisition was performed with the full scan mode in the 30–400 m/z range. Levoglucosan was identified by GC retention index, mass spectra (base peak at m/z 204 and 217 in mass fragmentograms) and comparison with an authentic standard of levoglucosan (Sigma-Aldrich).

All reagents were of analytical grade. Dichloromethane, methanol and pyridine (Labsynth, São Paulo, Brazil) were used for sample treatment and preparation of standards. The standard of levoglucosan and N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) was obtained from Sigma-Aldrich (St. Louis, MO, USA).

Elemental composition was determined by plasma-based techniques namely, inductively coupled plasma optical emission spectrometry (ICP OES) and/or inductively coupled plasma-mass spectrometry (ICP-MS). A Perkin Elmer (Norwalk, CT, USA) ICP Optima 5100 DV, 40 MHz (axial view) simultaneous ICP OS provided with a Model AS 90 autosampler and a Perkin Elmer Q-ICP-MS model NexIon 300× provided with a CETAC AXS-520 autosampler were used. Instrumental details and operating conditions for both instruments are summarized in Table 1 and Table 2.

Welding and 99.998% (minimum purity) Ar from Indura (Buenos Aires, Argentina) were used for ICP OES and ICP-MS determinations, respectively.

Potassium was determined by flame atomic absorption spectrometry (FAAS) using a spectrometer Perkin Elmer PinAAcle 900 T. All measurements were carried out using an air-acetylene flame and La 1000 μg mL^{-1} was added as ionization suppressor. The K analytical line of 766.49 nm was selected.

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 (Merck, Darmstadt, Germany), hydrofluoric and nitric acids (Baker, Center Valley, PA, USA) were used for sample treatment and standards preparation. Commercially available 1000 mg L^{-1} standard solutions

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

(Chem-Lab, Zedelgem, Belgium) 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).

The content of black carbon was determined by reflectometry using a Digital Smoke Stain Reflectometer (Model EEL 43D, Diffusion Systems Ltd., London, UK).

2.2. Aerosol collection

Airborne particulate matter, fine-respirable (PM2.5) and coarse-inhalable (PM10) size ranges was collected during a sampling campaign carried out between September and October 2016 (spring in the Southern Hemisphere). Samples were collected at one sampling site on the yard of a building at Comisión Nacional de Energía Atómica (CNEA), located at ~15 m distance from a highway (34° 38′S, 58° 28′W). This site is located at ~200 km from the open sea in a region influenced mainly by vehicular and residential sources.

Samples (*n* = 11) were collected on quartz-fiber filters (Sartorius Stedim Biotech, Germany) using a medium-volume air sampler (PQ200, BGI Incorporated, MA USA) equipped with a size-selective inlet. The average air volume daily collected was 24 m^3. Before collection, each filter was placed in an oven at 800 °C by 5 h to eliminate any impurity. Then, all filters were placed under controlled temperature (~25 °C) and relative humidity (<40%) for 24 h before weighing. Mass concentrations were obtained gravimetrically using an electronic microbalance with a readability of 0.1 μg (Mettler Toledo, model UMX2).

Table 2
Instrumental characteristics and settings for quadrupole ICP-MS.

Instrument	PerkinElmer NexIon 300×
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 10–06 Torr
Isotopes	^{75}As, ^{138}Ba, ^{53}Cr, ^{63}Cu, ^{202}Hg, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{82}Se, ^{118}Sn (^{115}In, as internal standard)

After sampling, all filters were wrapped in aluminium foil and stored in a dry and dark place at 4 °C until analysis.

2.3. Sample preparation

Each filter was cut in four pieces of approximately the same area (~4.34 cm^2). For levoglucosan extraction one piece was extracted three times for 30 min with 20 mL of a mixture of dichloromethane-methanol (4:1 *v*/v) under ultrasonic agitation in a 25 mL Pyrex glass flask. Extraction efficiencies from quartz-fiber filters were in the range 102 ± 7%.

Then, the extracts were dried by rotatory evaporation (300 Torr; 35 °C) until 3 mL; the residue was filtered through a membrane Millex LCR (PTFE 0.22 μm pore size; 13 mm diameter). After dryness, the extract was dissolved in 200 μL of a mixture of dichloromethane-methanol (1:1) Levoglucosan was converted to its trimethylsilyl derivative by reaction with 40 μL *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) containing 1% trimethylchlorosilane (TMCS) and pyridine (2:1 *v*/v) at 70 °C for 1 h in sealed vials. After reaction and cooling, aliquots of 1 μL were analyzed by gas chromatography.

For multielement analysis, samples were subjected to acid digestion. Chemical analysis of metals in APM requires destruction of siliceous material and consequently, an acid mixture containing HF was adopted. An area of ~4.34 cm^2 of each filter sample was placed into a PTFE vessels and a mixture of 3 mL of HF and 8 mL of aqua regia was added. The mixture was left overnight at room temperature and finally subjected to microwave (MW)-assisted acid digestion. The digestion cycle was repeated twice as follows: (step 1), 2 min, 250 W; (step 2), 2 min, 0 W; (step 3), 6 min, 250 W; (step 4), 5 min, 400 W; (step 5), 6 min, 650 W. The final solution was filtered through a 0.45 μm nylon filter, transferred into a 50 mL volumetric flask and diluted to a final volume of 20 mL. For checking accuracy aliquots of the certified reference material NIST SRM 1648, Urban Particulate Matter (NIST, Gaithersburg, MD, USA) were subjected to the same procedure as the samples and included in the over-all analytical process.

For K extraction, each filter piece was carefully placed into an evaporating dish (vertical wall) of 100 mL (i.d., 6.5 cm) and 10 mL of water were added. The soluble K was extracted using an ultrasonic bath (Testlab) for 60 min. After this period, the supernatant was placed in an acid-cleaned Falcon® tube while the filter remained in the dish. This solution was centrifuged for three minutes at 5000 rpm. An aliquot of 10 mL of this solution was taken with a micropipette and placed in an acid-cleaned Falcon® tube. The pH was measured in all aqueous filtrates.

2.4. Analysis

Levoglucosan determination was carried out on an Agilent 7820A gas chromatography connected to a mass spectrometer. Separation was performed with an inert 5% phenyl – methyl column, VF – 5 ms (30 m × 0.250 mm, 0.25 μm film thickness). For analysis, a sample volume of 1 μL was injected into a split/splitless injector, operated in the splitless mode (splitless time: 0.5 min) at 250 °C. The carrier gas was He at a flow rate of 1.3 mL min^{-1}. The temperature of the transfer line was 300 °C. The temperature program was as follows: (i) initial temperature of 120 °C, for 2 min, (ii) a gradient of 5 °C min^{-1} up to 200 °C for 2 min, (iii) then, 20 °C min^{-1} to 300 °C for 2 min. The total analysis time was <20 min. The mass spectrometer was operated in the electron ionization (EI) mode at electron energy of 70 eV and an ion source temperature of 220 °C. The data acquisition was performed with the full scan mode in the 30–400 *m/z* range. Levoglucosan was identified by GC retention index, mass spectra (base peak at m/z 204 and 217 in mass fragmentograms) [20]. A GC–MS chromatogram of levoglucosan determined in one of the collected PM10 samples is depicted in Fig. 1.

Plasma-based techniques namely, ICP OES and ICP-MS were employed for the determination of metals and metalloids in PM2.5 and PM10 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 APM samples. In particular, Al, Fe, Mg, Ti, V and Zn were determined by ICP OES while As, Ba, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sb and Sn were measured by ICP-MS.

In both cases, five sets of multi-elemental calibrants were prepared by dilution of commercially available 1000 μg 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.

Unlike levoglucosan and chemical elements, BC is not a single component but a carbonaceous condensate of unknown chemical composition and the determination of BC concentration is operationally defined. In this context, as optical absorption methods were used for determination, we report our results in terms of equivalent black carbon (EBC) following the recommendations of Petzold et al. (2013) [21]. The determination of the equivalent black carbon content (EBC), in all samples was performed by reflectometry using a Smokestain Reflectometer M43D. This instrument allows the estimation of the concentration of EBC in the collected particulate material by measuring light absorption through the filter-sample assembly. Blank filters were used to set reflectance at 100%, and the sampled filter was measured three times on different locations; the average of these three measurements was used in the calculations. For the calculation of EBC, expressed in μg m^{-3} (Eq. 1) was used, where A is the effective particle collection area in cm^2, EBC$_A$ is the concentration in area A, determined on the basis of the reflectance of the blank filter and the reflectance of the sample filter and V is the sampled air volume (m^3).

$$EBC(\mu g\ m^{-3}) = EBC_A\ (\mu g\ m^{-2}) \times A/V \qquad (1)$$

3. Results and discussion

3.1. Levoglucosan extraction and derivatization

The derivatization process is a critical step for subsequent analysis of levoglucosan by GC–MS. Attempts to analyze levoglucosan directly by GC–MS, without prior derivatization of the analyte resulted unsatisfactory. The chromatographic behavior was always poor, and the response was lower than that obtainable for the pertrimethylsilyl derivative. According to Hsu and coworkers [9] the formation of a single derivative with a mass spectrum of ions of high diagnostic value is necessary to reach a maximum sensitivity as well as specificity. Due to the three hydroxyl groups present in the molecule that may originate numerous derivatives it is required the formation of a single derivative with a mass spectrum of ions of high diagnostic value to maximize both, the specificity and the sensitivity. Screening experiments with different silylating agents demonstrated that BSTFA containing 1% TMCS (10% v/v), either at room temperature or at 70 °C for up to 6 h showed a multiple silylation products [22]. In contrast, other authors reported successful derivatization of levoglucosan with BSTFA [5]. This apparent contradiction may be caused by differences in the nature of the organic solvent, the volume ratio of solvent to silylation reagent, and the presence/absence of a catalyst or basic co-solvent for the derivatization reaction (e.g., TMCS or pyridine). According to previous studies it was observed that to increase derivative efficiency, the conversion of levoglucosan
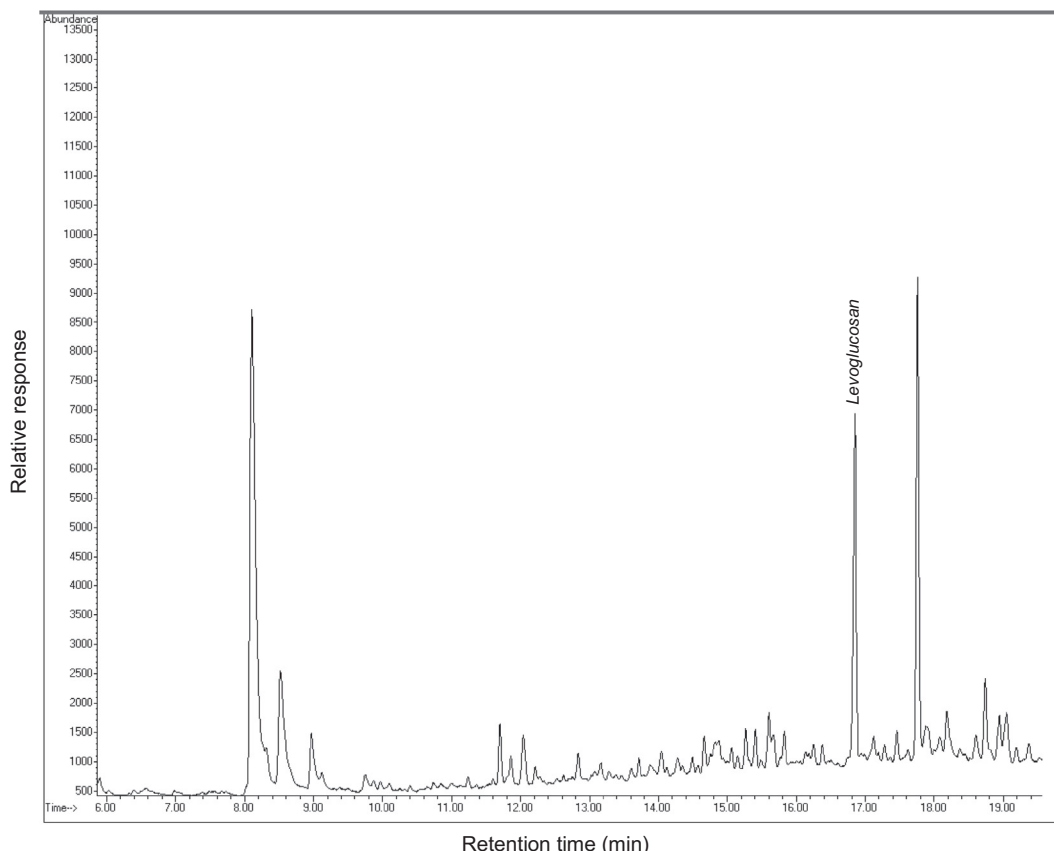

Fig. 1. Mass chromatogram at m/z 204 + 217 obtained from the analyses of a PM10 sample collected on aTeflon® filter. Levoglucosan concentration: 5.61 ng m^{-3}.

with MTSFA at optimized temperature conditions was the best alternative [9]. In this study, a temperature of 70 °C during 60 min was employed. To increase the derivative efficiency, MSTFA agent was added. According to Hsu et al. [9] the presence of the TMCS plays an important role for these analytes because >40% of bis-*O*-TMS derivatives abundance is reduced when 1% TMCS solution was added to MSTFA. Finally, MSTFA with 1% TMCS as derivatization solution with pyridine (2:1) was selected for further work. The study of the effect of reaction time and temperature showed that 70 °C during 60 min resulted to be adequate to avoid that the abundances of bis-*O*-TMS derivatives that decrease at higher temperatures.

3.2. Levoglucosan in Buenos Aires PM2.5 and PM10

Eleven samples were collected for levoglucosan determination by GC–MS. In seven samples of PM2.5, levoglucosan was detected in five of these samples. For PM10, only in two out of six samples levoglucosan was quantified. In general terms, the levels of levoglucosan detected in Buenos Aires PM2.5 and PM10 samples resulted of the same order of magnitude of those reported in the literature [23–25].

Table 3 provides concentrations of APM and levoglucosan in the collected samples. The mass collected (average concentrations) for both fractions resulted quite similar, 39.7 μg m^{-3} for PM2.5 and 45.4 μg m^{-3} for PM10, indicative that the fine fraction PM2.5 was predominant in the Buenos Aires APM.

Levoglucosan concentration varied between 0.002 μg m^{-3} and 4.90 μg m^{-3} for PM2.5 and from 0.006 μg m^{-3} to 1.86 μg m^{-3} for PM10. The similitude of concentrations of both particle sizes may be explained for the fact that carbonaceous particles are primarily present in the fine fraction which is included in the PM10 fraction. Our findings showed that LEV contribution to APM mass concentration ranged from negligible levels to ~10%. Even when the number of samples analyzed was small, they provide evidence that emissions from biomass burning as identified by the selected tracer exhibited a significant variability; however when present they showed to be a relevant contributor to the aerosols load in the Buenos Aires atmosphere.

Caseiro et al. [1] measured levoglucosan in urban aerosols in three Austrian regions. The authors found that levoglucosan varied with the seasons, ranging from 40 to 50 ng m^{-3} (summer) to 500–1500 ng m^{-3} in winter. On the basis of these values, the proposed method is sensitive enough for the determination of very low levels (<10 ng m^{-3}) of levoglucosan in atmospheric aerosols.

Open air biomass burning of agricultural residues and/or activities associated with deforestation is not typically carried out in the area under study. However, biomass burning occurs in some other regions of South America during the dry season (June to October) and depending on burnt area, fire intensity and meteorological conditions, the APM arising from these activities may be transported and reach Buenos Aires. In an effort to get a better understanding of the extent and patterns of burning in the area under study we analyzed the likelihood that regional emission from biomass burning would have impacted the monitoring site during the sampling period. To corroborate our hypothesis of regional impact, we used the fire database from Fire Information for Resource Management System (FIRMS) and HYSPLIT backtrajectories to determine whether air masses that reached the city in that period crossed fire regions. Although there were some regional fires during the sampling period, the backtrajetories did not connect the fires with

the sampling point. Therefore, we concluded that the determined levoglucosan in the APM samples did not arise from regional sources and we postulate that mainly local sources were responsible for the presence of this compound in the collected samples.

As an attempt to elucidate whether barbecue grilling, a widespread activity throughout the country, was responsible for the presence of levoglucosan in the analyzed samples, we carried out some combustion tests. We examined the emissions from burning different types of wood and charcoal, simulating typical grilling conditions of Argentinean barbecues, which are allegedly the main local source of emissions from biomass burning. More specifically we combusted charcoal and wood from *acacia caven*, *pinus* and *salix* bought from a local supplier. To this end, we collected a limited number of samples of total particulate matter from the exhaust fumes and we observed that levoglucosan was found in a wide concentration range (<83 ng m^{-3} to 3.28 μg m^{-3}). Concentrations of the other selected markers also exhibited wide variations: K was found in the range 235–1150 μg m^{-3} and EBC content was between 55 μg m^{-3} (charcoal) and 3600 μg m^{-3} (*salix*). The combined evidence provided by the presence of the markers under consideration in the emissions from the combustion of charcoal and wood together with the likely absence of regional sources, could indicate that biomass burning sources during the sampling period were dominated by local burning, particular barbecue grilling.

3.3. Elemental composition of the PM2.5 and PM10 samples

This study was also focused on a full characterization of the sample under study. To this end, plasma-based techniques (for metals and metalloids) and reflectometry (for black carbon) were used. Table 4 depicts the concentrations measured in PM2.5 and PM10 samples. Concentrations found in this research were compared with those reported in previous studies. For PM2.5, the element that exhibited the minimum concentration was Sb (0.34 ng m^{-3}) [26] vs 0.24 ng m^{-3} (this study). The most abundant element was Al with a maximum concentration of 4405 ng m^{-3} (this study), which was in the range of previous studies [27] that reported a large range of variation for this element with maximum concentrations ranging from 35 ng m^{-3} to 23,658 ng m^{-3}. For PM10, Sb and Al were the elements with the minimum and maximum concentrations. The levels of both elements were similar to those reported previously Sb: (0.9 ng m^{-3}) [28] vs 1.65 ng m^{-3} (this study) and Al: 2058 ng m^{-3} (this study) vs 2541 ng m^{-3} [28].

Table 3
Levoglucosan in PM2.5 and PM10 samples collected in Buenos Aires.

	Gravimetric concentration/μg m^{-3}			Levoglucosan/μg m^{-3}		
	Mean	Maximum	Minimum	Mean	Maximum	Minimum
PM2.5	39.7	50.4	24.3	1.65	4.90	0.002
PM10	45.4	51.8	31.4	0.93	1.86	0.006

Table 4
Metals, metalloids, K and black carbon in PM2.5 and PM10 collected in Buenos Aires. Results are expressed in ng m^{-3}.

	PM2.5			PM10		
	Minimum	Mean	Maximum	Minimum	Mean	Maximum
Al	1035	1688	4405	1273	1502	2058
As	32.2	61.4	99.2	58.0	88.0	136
Ba	56.0	164	258	116	183	424
Cr	44.4	57.0	63.5	67.3	94.5	144
Cu	21.5	30.5	37.3	16.6	52.0	36.6
Fe	584	672	815	969	1245	1974
Hg	0.52	1.57	2.49	1.00	1.50	2.12
Mg	305	371	554	391	517	712
Mn	14.3	16.2	19.5	18.9	28.9	42.9
Ni	12.0	16.5	22.3	16.2	23.8	32.7
Pb	3.98	8.67	16.4	3.29	8.98	12.3
Sb	0.34	0.77	2.8	1.65	2.92	4.75
Se	0.06	6.89	14.8	<0.05	1.71	2.16
Sn	7.16	9.92	14.0	8.13	12.2	20.2
Ti	77.8	93.4	102	89.8	154	272
V	26.9	53.1	37.1	37.6	60.0	78.5
Zn	248	274	306	270	204	476
BC	2950	4970	7860	3200	5280	8870
K	<66	109	562	<66	1165	3507

During cultivation of cereals, nitrogen, phosphorus and potassium are supplemented in the soil with fertilization purposes to increase the crop yield. In the absence of other important sources, such as soil dust and sea salt, water soluble K can be a satisfactory biomass marker. In this study, in the aqueous fraction K was only detected in PM10 samples with concentrations varying from <0.08 to 0.44 µg mL^{-1}, equivalent to <562 to 3500 ng m^{-3}.

No significant correlation between soluble K and levoglucosan concentrations was found. This poor correlation may be attributed to the presence of K in sea salt and road dust, which are also components of the Buenos Aires APM [29,30].

3.4. Multicomponent profile of PM2.5 and PM10 samples

Fig. 2 provides an overall view of the measured concentrations of levoglucosan, black carbon and K, together with the 17 elements considered. The figure depicts the wide range of concentrations found for both particle sizes, spanning five orders of magnitude.

The analysis of Fig. 2 within the framework of the contribution patterns of different APM sources shows:

(i) Levoglucosan exhibited the widest concentration range attributable to the spotty and unsteady nature of the postulated local emission sources (barbecue grilling);

(ii) EBC concentrations were very similar for both, PM2.5 and PM10, denoting that the finer fraction is more enriched in this component;

(iii) Soluble K (K$^+$) exhibited higher levels in PM10, which may be associated with sea-salt intrusion and road dust resuspension in the atmosphere of Buenos Aires as was demonstrated in previous studies [29,30].

(iv) As expected, concentrations of geological elements such as Al, Fe, Mg and Ti in PM10 were clearly higher than those in PM2.5, which is indicative of their abundance in the coarser particles as a consequence of road dust resuspension;

(v) Very similar concentrations of some traffic related elements (TREs), namely Zn, Ba, Cu, Mn, Pb and Hg in both size fractions point out to the prevalence of these elements in the fine fraction, most likely associated with vehicular exhaust [31];

(vi) Other TREs (V, Cu, Ni, Sn and Sb) exhibited higher concentrations in the coarse fraction. According to previous studies it is due to their predominance in the coarser wear particles [30].

3.5. Analytical figures of merit

The limits of detection for levoglucosan were assessed as those concentrations giving a peak signal equivalent to three times the standard deviation of the blank signal. Special attention was paid to obtain the lowest LOD through a careful control of contamination and a continuous check of the blanks. For the calibration curve standards 0.05, 2, 3, 5 and 7 µg mL^{-1} were used (R^2 = 0.9814). Limits of detection (LOD) and quantification (LOQ) resulted to be 100 ng µL^{-3} (equivalent to 0.083 µg m^{-3}) and 300 ng µL^{-3} (equivalent to 0.25 µg m^{-3}), respectively. To assess the repeatability of the method, five filter pieces, each of 4.5 cm^2 were subjected to the developed procedure and injected into the GC–MS instrument. The good precision of the results (varying between 1.6 and 3.1%) demonstrates the homogeneity of the collected samples. There was no significant difference in the repeatability between injections of the same extract and injections from different extractions. For estimating the
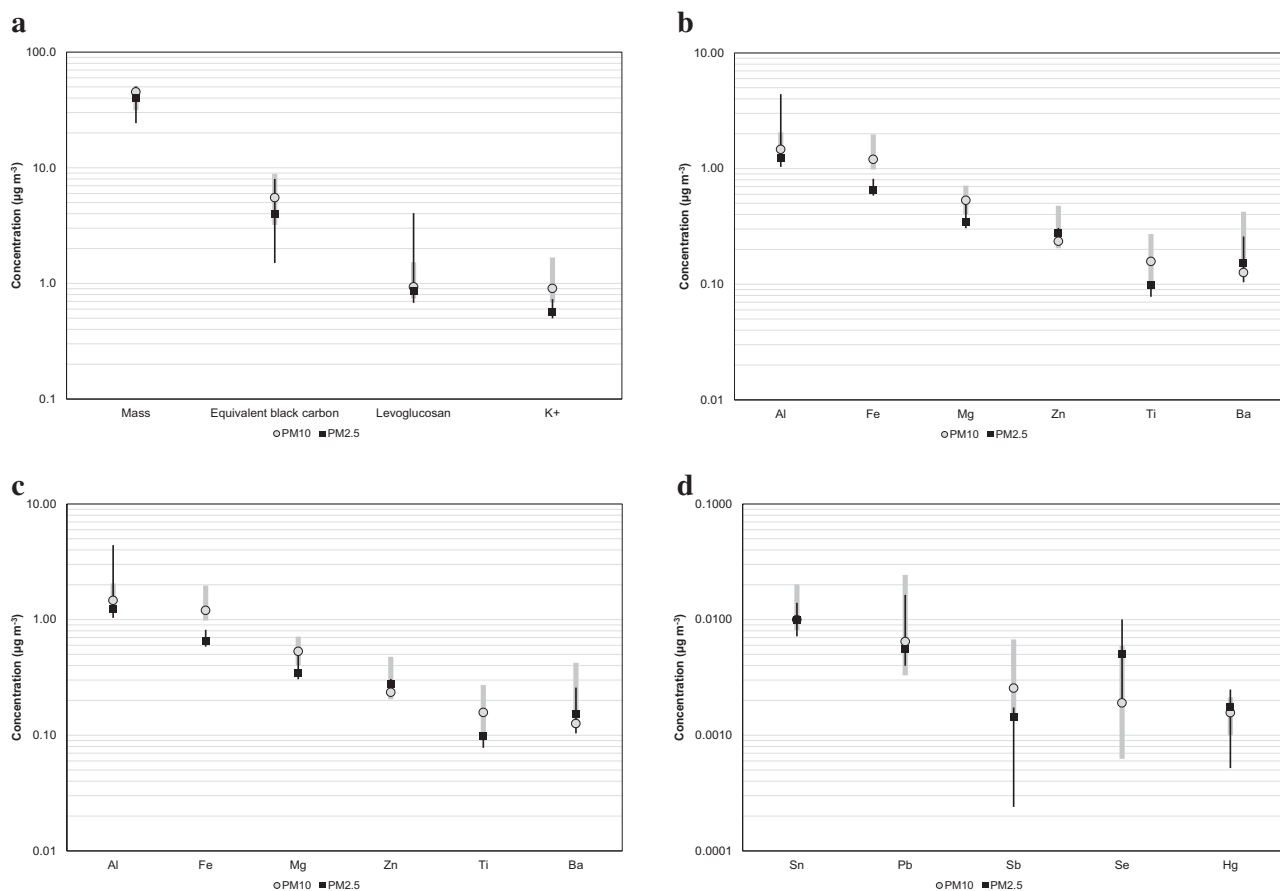

Fig. 2. Concentrations of components of PM2.5 and PM10 samples collected in Buenos Aires. (a) Mass, equivalent black carbon, levoglucosan and potassium; (b) Major elements; (c) Minor elements; (d) Trace elements.

accuracy of the method and due to the lack of a certified reference material (CRM), recovery tests were carried out by spiking standards of levoglucosan in blank filters. The recovery of levoglucosan was ~104% ($n = 5$).

4. Conclusions

Derivatization is a crucial step in the determination of levoglucosan by GC–MS. The derivatization conditions adopted in this investigation based on the use of MSTFA (+ 1% TMCS as a stimulator to increase derivatization efficiency) and pyridine resulted reliable because the formation of numerous derivatives compounds with multiple hydroxyl groups (i.e., monosaccharide anhydrides) was avoided. In addition, the derivatization efficiency was increased. The results obtained demonstrate a stronger trimethylsilylation power.

The anhydrosaccharide levoglucosan was confirmed as a reliable marker of the contribution of biomass burning to the Buenos Aires APM. The low detection limits reached allowed distinguishing between the presence and the absence of the contribution of emission sources.

The technique used for EBC measurements resulted simple and reliable when other more sophisticated techniques are not available. The results confirmed that black carbon biomass is a major contributor of the local APM.

Because of the presence of other contributing sources of K in the atmosphere of Buenos Aires, particularly sea-salt and road dust, K did not result an efficient marker of biomass burning for this city.

The multielemental profiles of PM2.5 and PM10 for the analyzed samples resulted in good agreement with our previous studies, indicating similarity of contribution sources.

To the best of our knowledge the levels of levoglucosan reported in this study are the first measured for this air basin.

Acknowledgements

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