



Meteoric ^{10}Be in aerosol filters in the city of Seville

S. Padilla^{a,b,*}, J.M. López-Gutiérrez^{a,c}, G. Manjón^{a,d}, R. García-Tenorio^{a,d}, J.A. Galván^{a,d},
M. García-León^{a,e}



^a Centro Nacional de Aceleradores (Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Junta de Andalucía), Thomas Alva Edison 7, 41092, Seville, Spain

^b LEMA. Instituto de Física, Universidad Nacional Autónoma de México (UNAM), CP 045010, Ciudad de México, México

^c Dpto. de Física Aplicada I, Escuela Universitaria Politécnica, Universidad de Sevilla. Virgen de África 7, 41011, Seville, Spain

^d Dpto. De Física Aplicada II, Escuela Superior de Arquitectura, Universidad de Sevilla. Av. Reina Mercedes 2, 41012, Seville, Spain

^e Dpto. de Física Atómica Molecular y Nuclear, Universidad de Sevilla. Reina Mercedes s/n, 41012, Seville, Spain

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ABSTRACT

Cosmogenic radionuclides in the one-million-year half-life range, like ^{10}Be , find application fields in several Sciences. They are powerful tools in Geology and Geochronology, as they are very important tracers on the Earth, being utilized as chronometer. Meteoric ^{10}Be ($T_{1/2} = 1.39 \times 10^6$ y) associated to aerosols can be used as a tracer of atmospheric processes and specifically as indicators of the cosmogenic interactions in lower Stratosphere, upper Troposphere, the air exchange between both and deposition processes on the Earth surface. The applications of ^{10}Be are even more relevant when combined with other radionuclides such as ^{26}Al . In order to provide new data about concentration ^{10}Be in this type of samples, the first atmospheric air filters in Spain have been analysed. Values around 10^4 at/m³ (atoms per cubic meter of air) for ^{10}Be have been obtained. Due to the location and the features of the sampling site (urban area, at sea level and mid latitude), a new radiochemical procedure was designed and developed in our laboratory for the Accelerator Mass Spectrometry (AMS) measurement of ^{10}Be in this kind of samples. The samples were measured in SARA, the 1 MV AMS system at Centro Nacional de Aceleradores (CNA).

1. Introduction

The main constituents of earth's atmosphere are Nitrogen (78%), Oxygen (21%) and Argon (1%). The interaction of cosmic rays with isotopes of these elements produces ^{10}Be mainly by spallation reactions with Nitrogen due to its higher concentration. ^{10}Be is a potential tracer operating over time scales of up to 10^7 years (Graly et al., 2010). This radionuclide is very scarce in nature and is found in the same places where it is produced as consequence of cosmic rays in the atmosphere, water, soil or rocks. It is primarily produced in the lower stratosphere and upper troposphere. The average residence time in the atmosphere ranges from the order of two weeks in the troposphere to several years in the stratosphere depending on the altitude where it is produced (troposphere or stratosphere). As a result of stratosphere-troposphere exchange as well as deposition, the ^{10}Be concentrations on the surface and the deposition fluxes can be influenced. Once deposited on the surface, meteoric ^{10}Be is adsorbed onto particles only if the coexisting solution pH exceeds a value of 6 (von Blanckenburg et al., 2012).

Sedimentary systems can therefore record both the long term deposition of meteoric ^{10}Be and the subsequent fate of the isotope due to the chemical leaching, illuviation, erosion or soil mixing. The meteoric ^{10}Be concentration on the earth's surface is the result of the production, transport in atmosphere and its deposition (Ebert et al., 2012; Graly et al., 2010; Masarik and Beer, 1999). The advantages of the meteoric variety of ^{10}Be over the in situ-produced nuclide lie in its higher concentrations, requiring smaller sample amounts, its applicability to quartz-free lithologies, and the possibility to determine denudation rate time series in fine-grained sedimentary deposits (Padilla et al., 2018; von Blanckenburg et al., 2012; Willenbring and von Blanckenburg, 2010).

Meteoric ^{10}Be has been applied extensively to different problems in the last decades. The study in rain waters, surface firns, ice cores and atmospheric or aerosols filter samples provides important information related with to production and distribution in the atmosphere. Beryllium-10 is also used to study atmospheric mixing, stratosphere-troposphere exchange and seasonal variations, which can provide the

* Corresponding author. Laboratorio Nacional de Espectrometría de Masas (LEMA), Dpto. Física Nuclear y Aplicaciones de la Radiación, Instituto de Física, Universidad Nacional Autónoma de México (UNAM), CP 045010, Ciudad de México, México.

E-mail address: spadilla@fisica.unam.mx (S. Padilla).

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transport time from the production until the deposition on the surface of this radionuclide (Auer et al., 2009, 2007; Graham et al., 2003; Jordan et al., 2003). A very useful tool is the analysis of the isotopic ratio $^{10}\text{Be}/^{7}\text{Be}$. Both radionuclides have a similar production process in the stratosphere, but ^{7}Be has a much shorter half-life ($T_{1/2} = 53$ days). In fact, due to its short half-life the presence of ^{7}Be in the atmosphere is almost exclusively due to the production from cosmic rays without any relevant contribution from re-suspension. When no other source of beryllium is present, the isotopic ratio would increase with time, modified also by the presence of aerosol ^{10}Be . For that reason, $^{10}\text{Be}/^{7}\text{Be}$ is a very good tracer of stratospheric and resuspended ^{10}Be , respectively.

The knowledge of the variation of ^{10}Be concentrations is also relevant for the combined use with ^{26}Al in climatic and atmospheric research (Auer et al., 2007). The aim of this work is to provide data for meteoric ^{10}Be from measurements of aerosol filters samples through atmospheric filters taken from an urban location as Seville (Spain).

2. Sampling and radiochemical procedure

The samples were taken on the roof of the Faculty of Physics building at University of Seville ($37^{\circ}21'33''\text{N}$; $5^{\circ}59'12''\text{W}$), about 30 m high. Samples were taken weekly throughout the year 2013, within a Nuclear Security Council surveillance program. Air was pumped through propylene filters with an approximate surface of $43 \times 43 \text{ cm}^2$ in an Aerosol Sampling Station ASS-500, with an average flow of $100\,000 \text{ m}^3/\text{week}$. These filters are routinely used to study radionuclides such as ^7Be , ^{214}Pb , ^{214}Bi and to evaluate the presence of some fission products such as ^{95}Nb , ^{131}I and ^{137}Cs , using gamma spectrometry. The filters are stored for other purposes, for instance determination of Pu isotopes (^{239}Pu y ^{240}Pu) (Chamizo et al., 2010).

After collection, the filter is immediately sent to the laboratory where it is folded, pressed and covered by a plastic film to obtain the adequate measurement geometry for gamma spectrometry. ^7Be activity was determined by gamma-spectrometry using a ReGe detector, with 30% relative efficiency. Decay correction of ^7Be corresponding to the sampling period was applied (Jiménez-Ramos et al., 2006).

The purpose of the sample preparation procedure is to extract Be from the aerosol filter and precipitate it as BeO , which can then be used as target for the AMS measurement. In previously published studies, this kind of samples for ^{10}Be measurement have been taken in high latitude and altitude zones such as Antarctic, Alps or from aircrafts flying in the stratosphere (Auer et al., 2009; Zanis et al., 2003). For these samples, the radiochemical procedure is described in (Auer et al., 2007) and consists of: a) leaching in 1M HCl for two hours b) filtering through $0.45 \mu\text{m}$ pore size filters, c) pouring the sample through an anion exchange resin Bio-Rad AG1-X8, in order to remove Fe and Mg, d) separating Be and Al by cation exchange resin AG50W-X8, extracting $\text{Be}(\text{OH})_2$ and finally e) oxidizing by calcination to BeO . Afterwards, measurement with Accelerator Mass Spectrometry (AMS) is carried out. As AMS requires high currents of the stable isotope, ^9Be carrier is added at the start of the leaching procedure.

Preliminary tests performed applying the procedure of Auer et al. (2009) to our filter samples were not successful. Analysing the different steps of the procedure we observed that the Be and Al isolation in the anion resin did not function properly. Traces of Fe and/or organic matter remains in the solution after passing through the anion resin and thus affecting the final recovery of Be and Al.

The procedure of Auer et al. (2009) is valid for clean air zones. However, in our case, the sampling zone is located in an urban area. Therefore, the amount of organic material is expected to be higher than in samples taken from Antarctic or Alps (high altitude and no urban areas). This fact led to the need of developing a new radiochemical procedure, in which a new step to remove the organic material at the beginning of the procedure was included. In the first tests carried out in our laboratory, the sample was lost. The radiochemical procedure

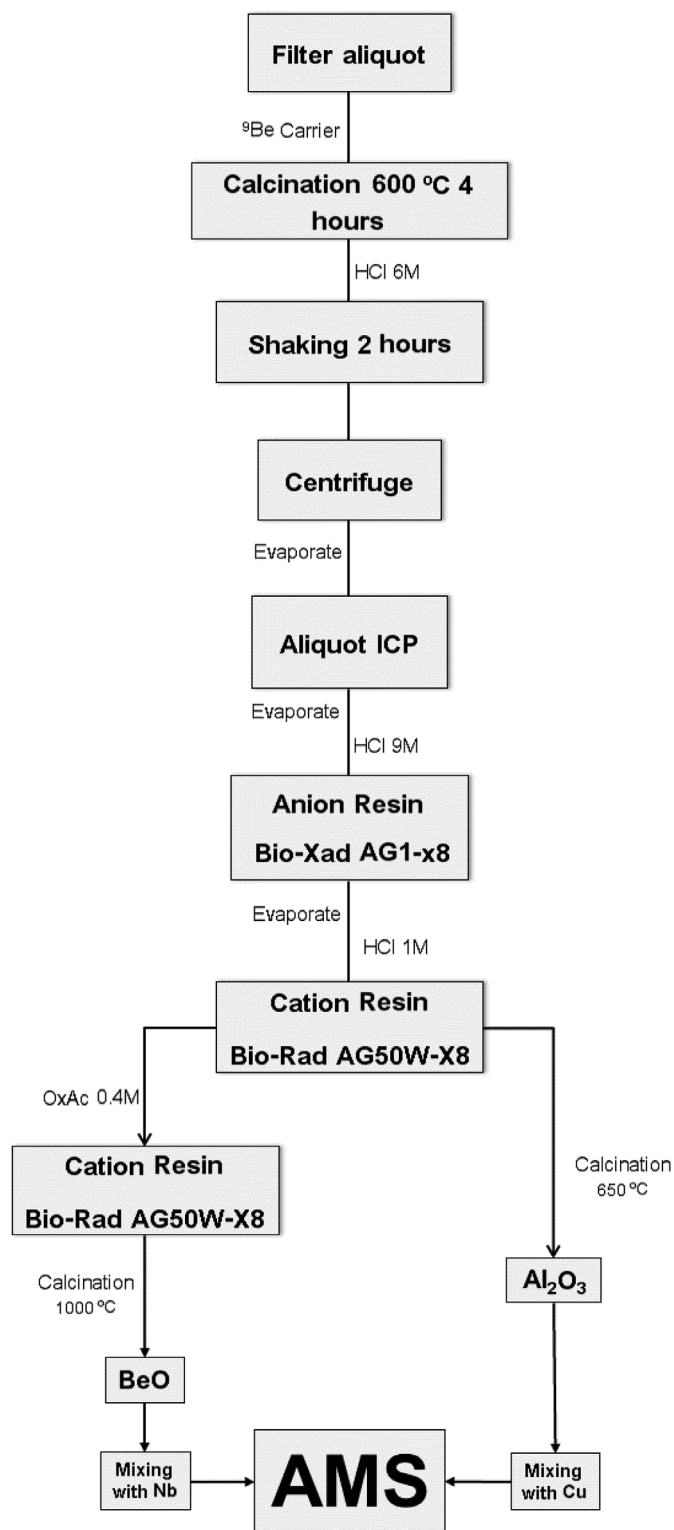


Fig. 1. Scheme for separation of the Al and the Be with ion exchange resins.

presented below is a modification of the procedure reported by (Auer et al., 2007), designed by (Padilla Domínguez, 2015) (Fig. 1).

An amount of $250 \mu\text{l}$ of ^9Be carrier ($\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ standard, 1000 mg/l for ICP-MS, Merck) was added into ceramic crucibles. An aliquot of the aerosol filter (about $15 \times 15 \text{ cm}^2$, corresponding to approximately 10000 m^3 of air) was cut into small pieces and put into the crucible. In order to homogenize the sample and carrier, HCl 6M was added totally covering the sample and standing for one hour. After

drying the sample on a hot plate, it was calcined in an oven at 600 °C for four hours before leaching, hence removing the organic material. In Auer's procedure, the sample is directly leached in a centrifuge tube. As commented before, due to the nature of our samples it is necessary to remove the organic material, obtaining a cleaner sample. Once the sample was at room temperature, it was cleaned and poured in a centrifuge tube with HCl 6M and shaken for two hours. The sample was then centrifuged at 4000 r.p.m for ten minutes discarding the solid material, avoiding filtering (Auer et al., 2007), and therefore the possibility of any loss of the sample. An aliquot was taken from the liquid to determine by ICP-MS the amount of ^9Be and ^{27}Al in the sample. The liquid was then evaporated completely in a glass beaker and then dissolved again in 9M HCl.

In order to remove remaining Fe and Mg from the sample, the liquid was passed through an anion exchange resin (Bio-Rad AG1-X8) (Larchner et al., 2013). Afterwards, Be was recollected with 20 ml of HCl 1M. This solution contains also the Al originally present in the sample.

In order to perform parallel measurements of both ^{10}Be and ^{26}Al (Auer et al., 2009; Kim and Englert, 2004), both radionuclides were separated. For this purpose, the sample was evaporated, again dissolved in HCl 1 M and poured onto a cation exchange resin (Bio-Rad AG50W-x8) separating Al and Be. Be was eluted using 20 ml of HCl 1M and Al in 10 ml of HCl 4.5M. Both liquids were evaporated and dissolved in water. Beryllium was then precipitated in Ammonia and subsequently dissolved in Oxalic acid 0.4M, to prevent the possibility that some Calcium was contained into the sample. It was then finally purified pouring the solution onto a cation exchange resin (Bio-Rad AG50W-x8) and eluting with 16 ml of HNO_3 0.5 M and 26 ml of HNO_3 1 M. The solution of Be was then evaporated and dissolved in water.

The result at this step was a set of two purified fractions containing the Be and the Al dissolved in water respectively. From the solutions, Al was precipitated as $\text{Al}(\text{OH})_3$ and Be as $\text{Be}(\text{OH})_2$ by addition of Ammonia. Both solids were calcined to Al_2O_3 and BeO in an oven at 650 and 1000 °C, and then mixed with Cu and Nb respectively. Finally the samples were pressed into sample holders and measured by AMS at CNA Sevilla (Padilla Domínguez, 2015).

3. AMS and radiometric measurements

^{10}Be samples were measured for one hour each using the 1 MV AMS system installed at the Centro Nacional de Aceleradores (CNA, Seville, Spain), called SARA (Spanish Accelerator for Radionuclide Analysis).

Accelerator Mass Spectrometry (AMS) is an accelerator technique in which ions are separated when they pass through magnetic and electrostatic fields. The ions are injected typically by a magnetic deflector into a tandem accelerator that is operated at a high terminal voltage (up to 1 MV for SARA). In the accelerator, ions acquire high energies and the beams are later analysed by another magnetic deflector and an electrostatic deflector so only ions with fixed m/q arrive at the ion detector, which is usually an ionization chamber. Two characteristics make AMS an ultrasensitive tool: first, molecules with the same mass as the isotope of interest are deflected in the stripper of the tandem accelerator, where the ion beam interacts with a gas (He in these measurements). Second, the use of high energies gives the possibility of discriminating the ions that arrive at the final detector not only by their total energy but also by their stopping power (dE/dx). As this property is related not only to the mass and the energy but also to the nuclear charge, it can help discriminating ions with the same or similar energy and m/q .

For AMS measurement of ^{10}Be , it is necessary to separate it from its stable isobar: ^{10}B . In spite of the sample preparation, many more atoms of ^{10}B than ^{10}Be are present in any sample. In order to reduce the intensity of the ^{10}B beam, a thin SiN layer (passive absorber) is placed behind the high energy magnetic analyser so that the difference in energy loss when passing through the absorber makes the ^{10}Be and the

^{10}B beams follow slightly different paths in the subsequent electrostatic deflector, and eventually leads to a strongly reduced intensity of the ^{10}B beam in the detector.

The AMS facility SARA in Seville has a very compact design ($3.8 \times 6.3 \text{ m}^2$) (Calvo et al., 2015). On the low energy side, a Cs-Sputter SO110 ion source produces the negative ion beam. It is initially mass-analysed by a 40 cm radius 90° sector magnet (low energy magnet), and accelerated in a 1 MV Tandemtron accelerator using He gas in the terminal stripper. The beam is then analysed for mass and energy by an 85 cm radius 90° sector magnet (high energy magnet) and by a 120° electrostatic analyser (ESA). The ions are finally counted and identified in a two-anode gas ionization chamber with a 40 mm silicon nitride entrance window (Calvo et al., 2015). Measurements were carried out in charge state +1 for the Be after the accelerator, and +2 after the passive absorber. The average currents obtained on the measurements in the high-energy zone were 1 μA for $^9\text{Be}^+$. The energy of the $^{10}\text{Be}^+$ beam after the accelerator was 1403.61 keV. All measured isotopic ratios $^{10}\text{Be}/^9\text{Be}$ were normalized to a standard sample with $^{10}\text{Be}/^9\text{Be} = 2.709 \times 10^{-11}$ (Nishiizumi et al., 2007).

Typical isotopic ratios for the samples were in the order of 10^{-11} with more than 10000 ^{10}Be counts, except for the November sample, which gave about 3000 counts. The uncertainties were calculated including statistics, deviation of the different run results and standard correction. The final uncertainties include the AMS measurement, the ^9Be concentration measured by ICP-MS and the amount of air corresponding to the filter aliquot and are typically between 8 and 10%. Three chemical blank samples were prepared with 0.25 g of ^9Be following the same chemical process from the calcination step and measured together with the samples. These blanks showed final $^{10}\text{Be}/^9\text{Be}$ ratios between 1.66×10^{-13} and 3.61×10^{-13} , much lower than the real samples.

^{26}Al measurements were also carried out in the samples. However, the low ratios obtained implied large errors. For that reason, ^{26}Al results are still under analysis in order to establish reliable conclusions and will be presented in future publications.

4. Results and discussion

^{10}Be results are presented in Table 1. All the concentrations are in the order of 10^4 at/m^3 (atoms per cubic meter of air) ranging from $(1.67 \pm 0.13) \times 10^4 \text{ at/m}^3$ in the filter taken in November to $(7.57 \pm 0.42) \times 10^4 \text{ at/m}^3$ in the one taken in August.

A reference work about the presence of ^{10}Be in the atmosphere is the one by Auer et al. (2009) in which both ^{26}Al and ^{10}Be are measured in air filters from different locations: at high altitude ($> 15000 \text{ m}$) and at sea level in the Antarctica (Neumayer) and at two locations in the Alps and the Black Forest, Sonnblick and Schauinsland, at 3100 and 1200 m above sea level, respectively. No strong differences are found between these locations, except for the stratospheric samples. While typical ^{10}Be concentrations in tropospheric samples are in the order of 10^4 at/m^3 (or low 10^5 at/m^3 in a few samples from Sonnblick), stratospheric values are in the order of 10^6 at/m^3 . This is in very good agreement with our results. The slightly higher values in Sonnblick could be due to the higher altitude of this location (3100 m). A very good agreement with the results presented in this paper is also found with the results obtained by (Yamagata et al., 2010), who presented data on ^{10}Be and ^7Be in Tokyo, Fukuoka and the Sea of Japan in 2004 and 2005. ^{10}Be concentrations are in the order of 10^4 and 10^5 at/m^3 , with all values under $2 \times 10^5 \text{ at/m}^3$.

^7Be was also measured in our samples in order to evaluate the $^{10}\text{Be}/^7\text{Be}$ atom ratio. In most of the studies with results on this ratio found in literature, samples were directly taken from the lower stratosphere or upper troposphere during flight, close to the tropics (Jordan et al., 2003), at high latitudes (Dibb et al., 1994), in the Antarctic (Elsässer et al., 2011), or on mountains at high altitude stations (Zanis et al., 2003). The concentrations of both radionuclides and the $^{10}\text{Be}/^7\text{Be}$

Table 1
 ^{10}Be and total Al concentration in air filters from Sevilla.

Year 2013	From	To	m ³ air (aliquot)	^{10}Be (10^4 at/m ³)	1σ (10^4 at/m ³)	Al (ng/m ³)
January	31-Dec-12	7-Jan-13	10454	2.10	0.20	160.0
February	28-Jan-13	10-Feb-13	8179	5.35	0.27	295.7
March	4-Mar-13	10-Mar-13	11744	4.16	0.30	125.6
April	1-Apr-13	7-Apr-13	11944	6.06	0.52	209.1
May	13-May-13	19-May-13	11281	4.78	0.35	660.3
June	10-Jun-13	16-Jun-13	10609	5.96	0.66	869.6
July	22-Jul-13	28-Jul-13	10526	6.15	0.28	500.9
August	12-Aug-13	18-Aug-13	10854	7.57	0.42	867.4
September	16-Sep-13	22-Sep-13	12898	3.43	0.26	461.9
October	7-Oct-13	13-Oct-13	10675	4.27	0.36	485.9
November	18-Nov-13	24-Nov-13	7859	1.67	0.13	320.1
December	2-Dec-13	8-Dec-13	8525	2.93	0.19	438.1

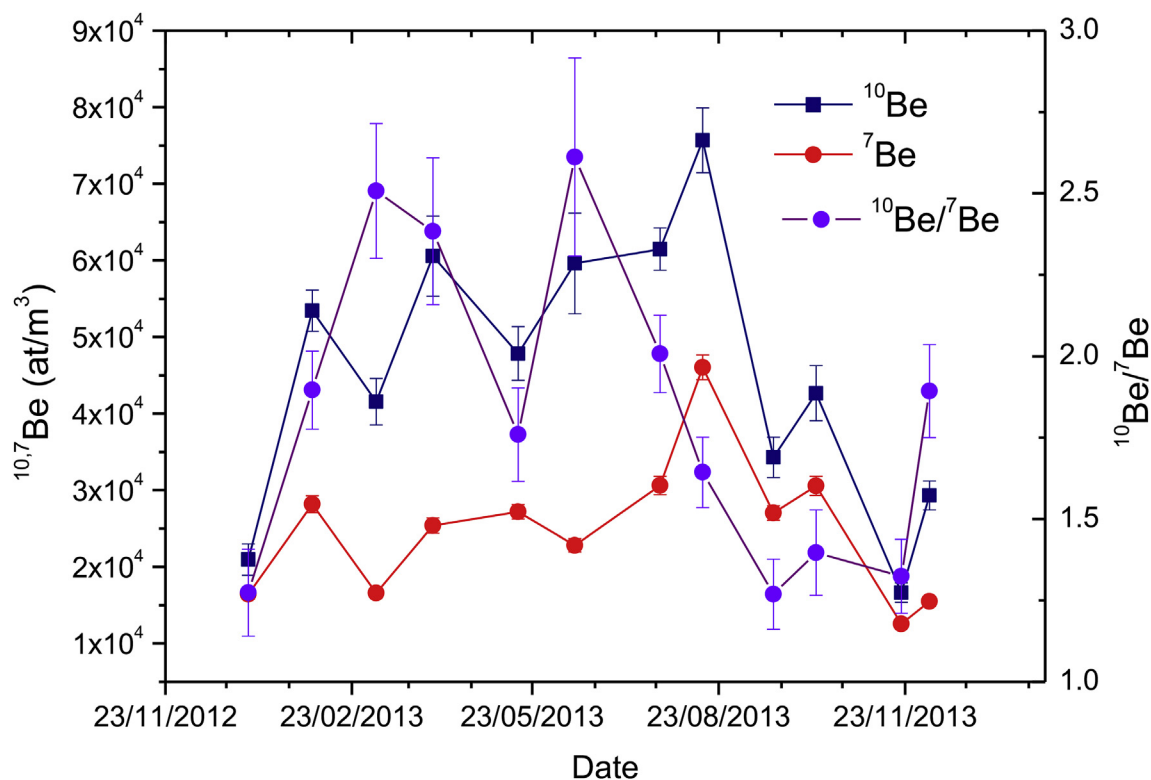


Fig. 2. Evolution of the isotopic ratio $^{10}\text{Be}/^7\text{Be}$, ^7Be and ^{10}Be concentration for aerosols samples, in Seville city in 2013.

ratio in our study are shown in Fig. 2. Isotopic ratios range from 1.3 to 2.6. Jordan (Jordan et al., 2003) found that isotopic ratios around 0.6 are typical of the troposphere while increasing values show the influence of stratospheric air. The results obtained in our study are in good agreement with the ones reported by (Zanis et al., 2003) for the concentrations of both radionuclides ^{10}Be and ^7Be as well as for the ratio $^{10}\text{Be}/^7\text{Be}$, in aerosols collected at high altitude stations such as Jungfraujoch (Switzerland) and Zugspitze (Germany), in the Alps. They measure concentrations in the order of 10^4 at/m³ for both ^{10}Be and ^7Be and ratios between 1.6 and 2.1. Our results can also be compared to the ones measured by Yamagata (Yamagata et al., 2010). $^{10}\text{Be}/^7\text{Be}$ ratios in Tokyo and Fukuoka were found to be between 2 and 7, with higher values in Tokyo. However, when these values are corrected by subtracting the ^{10}Be contribution by resuspension, ratios are in most cases around 2, in good agreement with our results.

It is also possible to correct the $^{10}\text{Be}/^7\text{Be}$ ratio in our samples. The aforementioned correction is known to be small in areas covered by ice or vegetation because the samples collected there are expected to not show high quantities of resuspended sand particles, but the correction

can be higher and variable over time in urban areas due to the potential higher contribution of resuspended particles.

Based on the considerations reported by Yamagata equation (1), the difference between the initial concentration of ^{10}Be in the sample (bulk) and the ^{10}Be supplied by re-suspension of particles is denoted by $^{10}\text{Be}_{\text{corr}}$, and calculated through

$$^{10}\text{Be}_{\text{corr}} = ^{10}\text{Be}_{\text{Bulk}} - Al_i/Eff/S_{Al} \times S^{10}_{\text{Be}} \quad (1)$$

where $^{10}\text{Be}_{\text{Bulk}}$ is the concentration of ^{10}Be measured in the sample (at/m³), Al_i is the concentration of Al measured by ICP-MS (g/m³), Eff is the average leaching efficiency (0.51 ± 0.06), determined by comparing bulk samples analysed by NAA with leached samples analysed by ICP-AES, S_{Al} is the typical concentration of Al in soil in Japan (8.93%) (Imai et al., 2004) and S^{10}_{Be} is the average concentration of ^{10}Be in soil (3×10^8 at/g) (Shen et al., 1992). A comparison between the uncorrected and corrected ^{10}Be concentrations is shown in Fig. 3. The difference between the isotopic ratios corrected and uncorrected for resuspension is small, typically between 5 and 10%. This means that most of the ^{10}Be detected in the samples from Seville is of atmospheric

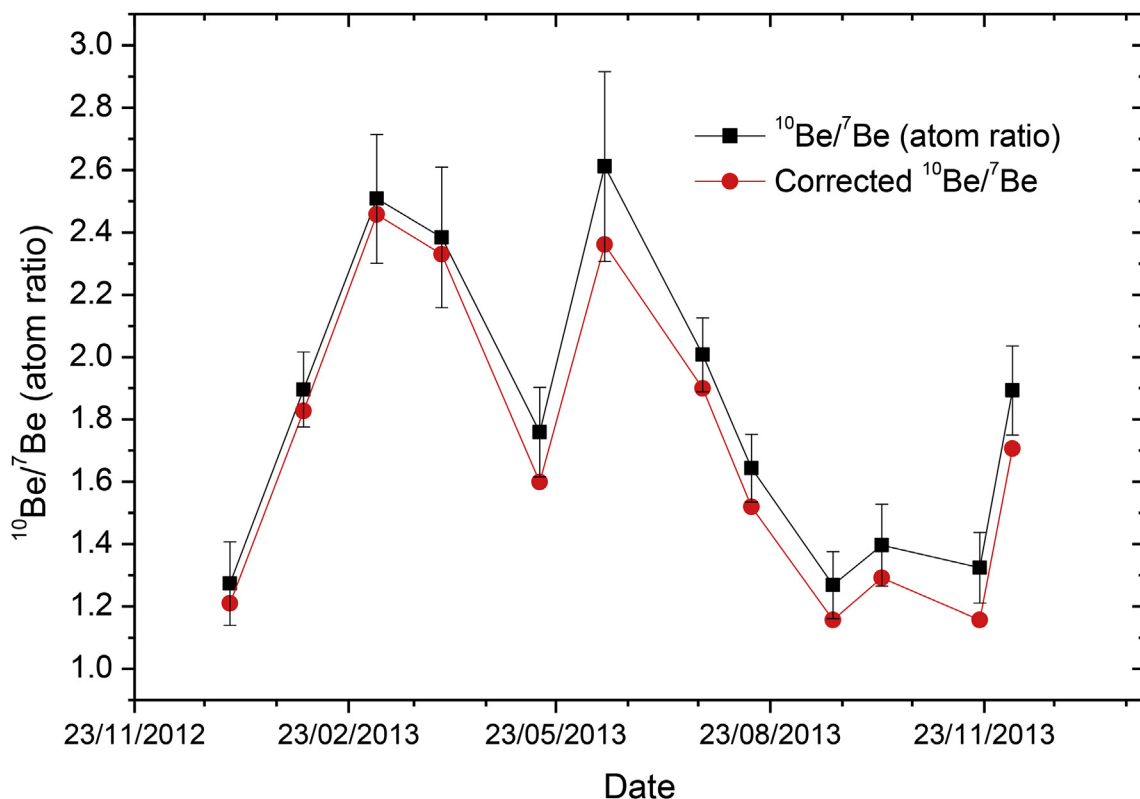


Fig. 3. Comparison of the $^{10}\text{Be}/^7\text{Be}$ and the $^{10}\text{Be}_{\text{corr}}/^7\text{Be}$ atom ratios, this last one estimated from equation (1).

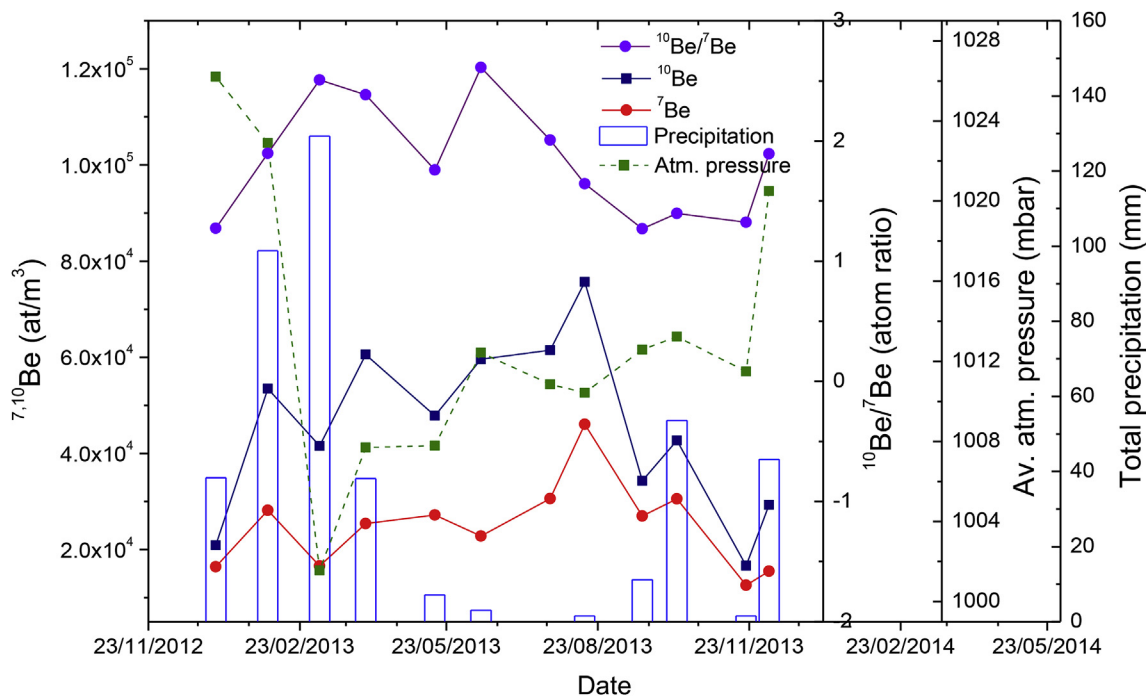


Fig. 4. ^{10}Be , ^7Be concentrations and $^{10}\text{Be}/^7\text{Be}$ isotopic ratios in aerosol samples in Seville plotted together with the total precipitation and the average atmospheric pressure in each period.

origin and the contribution of resuspended ^{10}Be is low. In Yamagata et al. (2010), a relatively important contribution of resuspended ^{10}Be is found in some of the measured samples. This could be expected in our measurements, as they correspond to samples taken in an urban zone. However, the contribution of resuspended ^{10}Be seems to be low in Seville in contrast to it was thought in the beginning. This is an

unexpected result for an urban zone as well as the high content in organic matter, which led to the modification of the sample preparation method. The reasons for this are unknown. It could be possible that it is related to the concrete location of the sampling point, close to a river and an urban park. In any case, this fact will be investigated in future sampling campaigns.

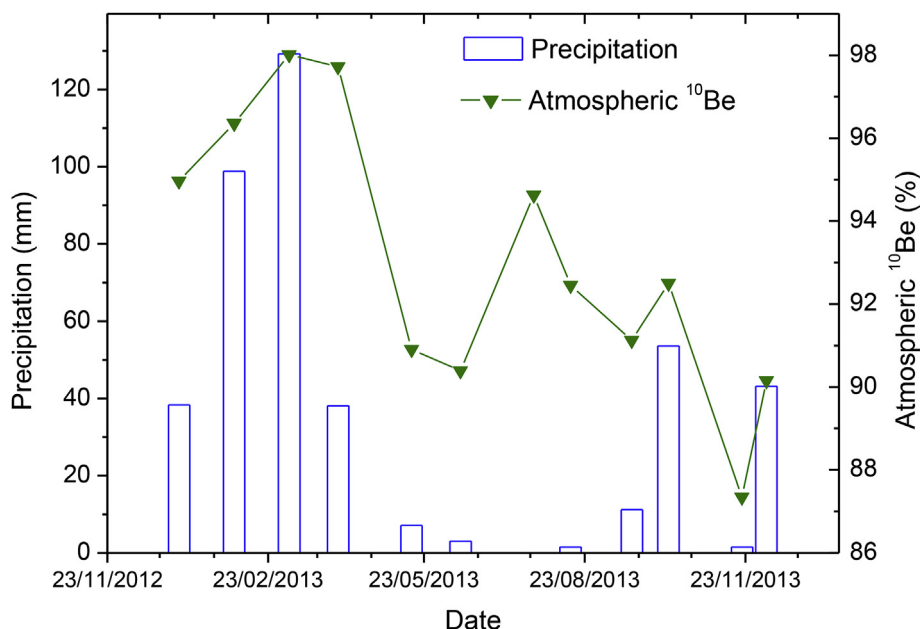


Fig. 5. Proportion of purely atmospheric ¹⁰Be and total precipitation in aerosol samples in Seville during the sampling period.

There is a good agreement between the temporal evolution of the ¹⁰Be and ⁷Be concentrations. This reinforces the previous conclusion that most ¹⁰Be is of atmospheric origin and not resuspended. In both cases (⁷Be and ¹⁰Be), concentrations drop abruptly in autumn. Nagai (Nagai et al., 2000) calculated production rates for ¹⁰Be and ⁷Be and ¹⁰Be/⁷Be ratios in the atmosphere based on a box model. They estimated isotopic ratios typically between 1.5 and 2 for the Northern Hemisphere, increasing at the beginning of summer, and decreasing during autumn with the minimum values in winter. The evolution of the ¹⁰Be/⁷Be ratio in our samples shows typically higher values in spring and the beginning of summer (between 1.8 and 2.4), followed by lower values in autumn and winter (1.3–1.9, this last value for the December sample). In spite of the delay, the variation of the ¹⁰Be/⁷Be ratio in our samples reflects quite well the expected behaviour, based on the known injection of stratospheric air in late spring or early summer. This air, due to the short half-life of ⁷Be and the relatively long residence time of Beryllium in the stratosphere, has a higher ¹⁰Be/⁷Be ratio. This would also explain the increase on the ¹⁰Be and ⁷Be concentrations in spring and summer.

Yamagata et al. (2010) find a correlation between the ¹⁰Be concentration and atmospheric pressure in samples taken every 12 h for a few days. Also in (Heikkilä et al., 2008), the authors find a strong influence of local effects in the ¹⁰Be/⁷Be ratio measured in rain samples taken at Dübendorf and at Jungfraujoch, Switzerland. In Fig. 4, the ¹⁰Be and ⁷Be concentrations and the isotopic ratio are plotted together with the total amount of precipitation and the average atmospheric pressure in each period. No obvious relationship can be found between meteorological conditions and the beryllium concentrations. The variability of the isotopic ratio for samples taken between May and December seems to be linked to the atmospheric pressure, but no correlation is found in earlier samples. The similar profiles can potentially be explained as a large period of anticyclone conditions. This suggests a transportation effect from higher (where the air is more enriched in ¹⁰Be against ⁷Be) to lower altitudes, as observed in Yamagata et al. (2010).

In Fig. 5 we compare the percentage of atmospheric ¹⁰Be (calculated from equation (1)) as ¹⁰Be_{corr}/¹⁰Be_{bulk} and total precipitation. The correlation is probably related to the influence of rain on the proportion of resuspended ¹⁰Be present in the atmosphere (which is between 2 and 12% only).

5. Conclusions

The characteristics of urban environments make it difficult to directly apply methods previously developed for samples taken in cleaner zones, such as the Antarctic or high altitudes. A method for the extraction of ¹⁰Be and ²⁶Al in particulate filters in urban zones has been presented, and results for ¹⁰Be concentrations were reported. Although ²⁶Al results are still under evaluation, our ¹⁰Be concentrations are in good agreement with previously published values, showing that 10⁴ at/m³ seems to be the typical order of magnitude of particulate ¹⁰Be in the atmosphere in Seville. The isotopic ¹⁰Be/⁷Be ratios are between 1.2 and 2.6, the temporal evolution of both radionuclides showing a good agreement. This suggests that the proportion of resuspended ¹⁰Be is low and can be estimated between 2% and 12% from the measured stable Al concentration. The concentrations of both radionuclides seem to be governed by stratosphere-troposphere exchange, which starts in spring in our samples. The proportion of resuspended ¹⁰Be is influenced by the amount of precipitation.

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