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Depositional fluxes and concentrations of ^{7}Be and ^{210}Pb in bulk precipitation and aerosols at the interface of Atlantic and Mediterranean coasts in Spain

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[1] Bulk depositional fluxes of ^{7}Be and ^{210}Pb in precipitation measured over a period of 16 months (April 2009–July 2010) in Huelva, Spain varied between 5.6 and 186 Bq m^{-2} month^{-1} (annual mean: 834 Bq m^{-2} year^{-1}) and 0.8 and 8.1 Bq m^{-2} month^{-1} (annual mean: 59 Bq m^{-2} year^{-1}), respectively, with the lowest depositional fluxes occurring during dry summer months. Quantitative evaluation of the precipitation-normalized seasonal depositional fluxes of ^{7}Be and ^{210}Pb indicates that the enrichment factor in winter is < 1.0 while in 2010 spring, it is significantly higher than 1, possibly indicating input of air from the stratosphere-troposphere exchange (for ^{7}Be). The specific activities of ^{7}Be and ^{210}Pb varied from 0.03 to 7.42 Bq L^{-1} (mean = 2.5 Bq L^{-1}) and 0.005 to 1.07 BqL^{-1} (mean = 0.23 Bq L^{-1}), respectively, with the highest values corresponding to the spring season. The spatial and temporal variations of ^{7}Be and ^{210}Pb in aerosols from three stations are evaluated and compared to their monthly depositional fluxes. The mean depositional velocity of aerosols using ^{7}Be and ^{210}Pb are similar, ~0.5 cm s^{-1} and are compared to other published values. This is the first time the fractional amounts of ^{7}Be and ^{210}Pb in monthly bulk precipitation are compared to the fractional amount of precipitation and provides insight on how the amount of precipitation plays a key role on the scavenging of these nuclides. The importance of dry fallout is evaluated for the study site which has direct implications for other areas in the Mediterranean Climate Zone.

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1. Introduction

[2] Utility of ^{7}Be (half-life = 53.3 days) and ^{210}Pb (half-life = 22.1 yrs) as tracers for quantifying sediment dynamics in estuarine, coastal, lacustrine and riverine systems, soil erosion studies and in other environmental studies require the depositional fluxes of these nuclides [*Robbins*, 1978; *Krishnaswami et al.*, 1980; *Dominik et al.*, 1989; *Baskaran et al.*, 1997; *Sommerfield et al.*, 1999; *García-Orellana et al.*, 2006; *Church and Sarin*, 2008; *Jweda et al.*, 2008; *Kaste and Baskaran*, 2011; *Matisoff and Whiting*, 2011]. The variations in the concentrations of ^{7}Be and ^{210}Pb in aerosols have been modeled using modified versions of the global circulation models to determine the vertical transport and residence times of aerosols [*Turekian et al.*, 1977; *Brost et al.*, 1991; *Balkanski et al.*, 1993; *Koch et al.*, 1996]. These two radionuclides have distinctly different source functions. ^{7}Be is produced in the upper and middle atmosphere (5–30 km) as a product of spallation of oxygen and nitrogen nuclide by energetic cosmic rays [*Lal et al.*, 1958]. Due to its short mean life (77 days) and longer residence time of aerosols in the stratosphere (about 1–2 years), most of the ^{7}Be produced in the stratosphere does not readily reach the troposphere, except when there is a seasonal thinning of the tropopause taking place at midlatitudes, resulting in transport of ^{7}Be-containing aerosols into the troposphere. Like any other cosmogenic-nuclide, its flux to the Earth's surface is latitude-dependent. Due to its source, its concentration is expected to increase with height above the planetary boundary layer (PBL). During summer months, the air mass at the PBL gets heated and the lower-density air mass depleted in ^{7}Be starts rising while it is replaced by sinking colder air mass enriched in ^{7}Be from aloft. The flux of ^{7}Be is expected to be independent of longitude.

[3] ^{210}Pb is produced in the atmosphere by radioactive decay from its progenitor, ^{222}Rn [e.g., *Poet et al.*, 1972; *Tokieda et al.*, 1996]. It has been estimated that about 1 to 10% of the ^{222}Rn produced from the decay of ^{226}Ra in the upper one meter of the soil is released into the atmosphere. The average concentration of ^{226}Ra in the upper crust is 31 Bq kg^{-1} while the concentration in surface ocean water is ~1.3 mBq kg^{-1}. It has been estimated that the global ^{222}Rn flux from continent ranges from 1300 to 1800 Bq m^{-2} d^{-1}, but ~17 mBq m^{-2} d^{-1} from oceanic areas [*Samuelsson et al.*,

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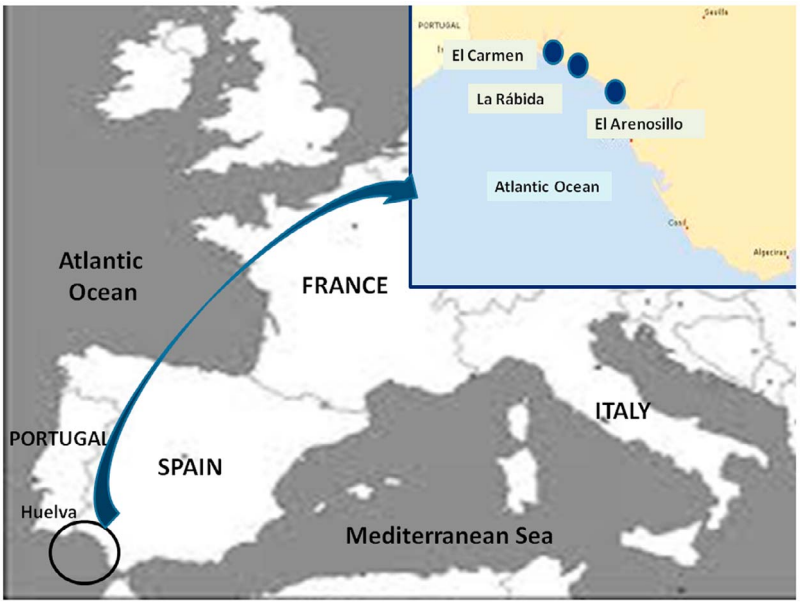

Figure 1. Station locations.

1986; *Nazaroff*, 1992; *Baskaran*, 2010]. As a consequence, the standing crop of ^{210}Pb in the atmosphere strongly depends on the longitude, depending on whether it is above the ocean or a continent. After its production in the atmosphere, it is removed primarily by precipitation (both rain and snow) and dry deposition processes. In coastal areas, the depositional fluxes of ^{210}Pb are expected to depend on the relative portion of the continental and maritime air masses. Furthermore, the ^{222}Rn emanation depends on several other factors, including concentration and distribution of ^{226}Ra in the mineral grains, the porosity of the soils, the water content, among others. Combining these two radionuclides that have two different source functions, one can obtain information on the mechanisms and rates of removal of aerosols in the atmosphere, including chemical species injected in to the troposphere, elevation at which cloud condensation takes place, and source(s) of air masses.

[4] The location of Huelva province at the edge of European Continent makes it as a suitable station for the measurement of ^{210}Pb and ^{7}Be in surface air under the influence of air masses of different origins. In particular, the present study intend to quantify the role of different air masses, in this case continental versus maritime (Atlantic and Mediterranean), on the temporal variability of the concentrations in the air and depositional fluxes of these nuclides in this area. Furthermore, scanty rainfall in the summer months will aid in quantifying the role of dry deposition of aerosols at the study site, and by analogy other sites in the Mediterranean climate zones.

2. Materials and Methods

2.1. Area of Study

[5] The province of Huelva is located in the Iberian Peninsula, at halfway along the southwestern coast of Spain (Figure 1). The Tinto and Odiel Rivers cross part of the province and flow from the north to the south. In the north of the province (80 km far from the coastline) are the Sierra Morena Mountains, with an altitude of 940 m. Furthermore, there are three chemical industrial complexes in the surroundings of the city of Huelva (Figure 1) which started operating after the extensive industrialization process that began in the year 1960. Due to the wide spectrum of types of emission sources near the industrial complex of the city of Huelva and the coastal location, a study of air pollution is of great interest in this region.

[6] Monitoring network sampling formed by three stations was utilized for aerosol sampling: 1) "El Arenosillo," 2) "El Carmen" in Huelva town, and 3) "La Rábida" (Figure 1). El Arenosillo station (37°05′58″N, 6°44′15″W) is located in a fairly flat area away from industrial activities and is considered to be a reference (background) site. This site is located inside a pine forest in the Atmospheric Sounding Station, which belongs to the National Institute of Aerospatiale Technology, and it is at ~1 km distance from the coastline and 35 km southeast of the city of Huelva, and 5 km from the National Park of Doñana. Air samples were collected from about 6 m above ground. The second sampling station was chosen at an urban site, at the border of the city of Huelva (population ~150,000). Aerosol samples were collected from ~10 m above the ground, at the El Carmen campus of the University of Huelva (37°16′07″ N, 6°55′27″ W). In addition, on the roof of Huelva station four drums were deployed for the collection of the bulk deposition samples. The third sampling station is sited at "La Rábida" at the campus of the University of Huelva, (37°11′60″N, 6°55′6″W), and close to the chemical industrial complex. Aerosol samples were collected in this station at ~10 m above the ground.

2.2. Samplings and Radionuclide Measurements

[7] Aerosol samples (PM10, < 10 μm) were collected onto quartz fiber filters (QF20 Schleicher & Schuell, 25.4 cm × 20.3 cm) with high volume samplers at a flow rate of 40 cfm (68 m^3 h^{-1}) in each of the three stations. Samples were collected for 48 h every fifteen days, from July 2004 to April 2010. The filters were weighed before aerosol collection

(precision 0.1 mg) several times until mass remained constant, inside a chamber with controlled humidity. In order to evaluate the collection efficiency of the filters, we put two filters on the inlet of the sampler. The ^{7}Be and ^{210}Pb concentrations in the second filter were below the minimum detectable activity (MDA), which are 0.10 mBq m^{-3} and 0.14 mBq m^{-3}, respectively. Taking these detection limits into account, a retention efficiency of > 96% is estimated for these filters. This is in contrast with the earlier studies where collection efficiency of Whatman 41 filters for ^{210}Pb was found in the range of 70–80%, with ~25% of the ^{210}Pb in the first filter was found in the second filter (back-up filter) [*Stafford and Ettinger*, 1972; *Turekian and Cochran*, 1981; *Turekian et al.*, 1989]. The reasons of these discrepancies are not clear, but could be due to differences in the sizes of aerosols (PM10 versus PM1 by earlier groups) or the differences in the composition of the filters used to collect aerosols.

[8] Total deposition samples (also called bulk) were collected using 4 drums with 200 L of total capacity, and a total surface area of 4120 ± 30 cm^2 (1030 cm^2 each), from April 2009 up to July 2010. The precipitation record was obtained from a meteorological station close to the sampling site. The drums were cleaned three times by repeated washings with 10% HNO_3 at the beginning of the bulk deposition collection. Prior to each deployment, 1 mg of stable Be and Pb in 100 mL of 10% HNO_3 were added into the drums. The addition of acid is to prevent adsorption of particle-reactive radionuclides onto the polyethylene drum surfaces. At the end of the collection period, the collectors were emptied into a container; and their walls were rinsed twice with 50 mL of 8 M HNO_3 (each), which were then added to the sample. In the summer months, the solution completely evaporated and we rinsed the rain collector in the same way as described above. Following this thorough acid cleaning and a distilled water rinsing, the collectors were deployed again after the addition of dilute acid and stable Pb and Be carriers. The sample is evaporated to about 50 mL and then to dryness. Then, it is dissolved with a mixture of strong acids (5 mL of 65% HNO_3, 2 mL of 37% HCl, 15 mL of 40% HF), and finally the residue was re-dissolved in dilute 5% HNO_3 (5 mL) and the solution was quantitatively transferred into a 5-mL gamma spectrometry vials. We assumed that there is no loss of ^{7}Be and ^{210}Pb (due to repeated rinsing with strong acids as given above) during the collection, evaporation and in the transfer of the solution to the counting vials. The vials are counted on a high-purity Ge well detector coupled to a multichannel analyzer. The MDA for ^{7}Be and ^{210}Pb are 0.06 Bq and 0.09 Bq, respectively.

[9] On the other hand, the aerosol filters were cut in two halves, and both were weighed (0.1 mg precision). One half is wrapped, pressed in a plastic bag and measured by gamma spectrometry. The other half is totally dissolved with a mixture of strong acids (65% HNO_3, 37% HCl, 40% HF), and the final solution was used for the determination of ^{210}Po and other alpha emitting U and Th-isotopes (the results are not discussed in this paper).

[10] Typically, the samples were counted by gamma spectrometry for about 48 h, depending on the activity of ^{210}Pb in the sample, since all of the samples have relatively high activities of ^{7}Be. The detectors with its shielding are located in a room with walls and ceiling made of 75 cm thick concrete at the basement of a four-story building.

[11] Beryllium-7 and ^{210}Pb concentrations in bulk deposition samples were quantified using a well Ge detector (Canberra), that has a full-width at half-maximum (FWHM) of 1.33 keV at 122 keV (^{57}Co) and 2.04 keV at 1332 keV (^{60}Co), and a peak/Compton ratio of 56.2/1. The detector was coupled to a multichannel analyzer and the detector was shielded with 10 cm lead shield. In order to avoid interferences from X-rays from the Pb in the shield, a layer of 2 mm thick of Cu layer is placed as a shield between the Pb shield and the detector. The full energy peak efficiency calibration for the peaks of interest was conducted using the solid RGU-1 Standard Reference Material, obtained from IAEA, with a known amount of ^{238}U (4940 ± 30 Bq kg^{-1}, and with all its daughter products in secular equilibrium). Absorption corrections were made for the measurements of ^{210}Pb or ^{7}Be, following the method of *Appleby et al.* [1992]. Absolute efficiencies for the standard geometry of the samples used in this study for ^{210}Pb and ^{7}Be were calculated to be about 46% and 13%, respectively.

[12] Lead-210 and ^{7}Be measurements in atmospheric filters were performed using an XtRa coaxial Ge detector (Canberra), with 38% relative efficiency and FWHM of 0.95 keV at the 122 keV (^{57}Co) and 1.9 keV at the 1333 keV (^{60}Co). The detector is coupled to a set of standard electronics components, including a multichannel analyzer, and was shielded with 15 cm thick Fe shield. The peak analysis of ^{7}Be (branching ratio (BR) = 10.3%, Eγ = 477.7 keV) and ^{210}Pb (BR) = 4.05%, Eγ = 46.5 keV) was conducted. Details on the efficiency calibration for ^{210}Pb (counting efficiency 14.3%) and ^{7}Be (counting efficiency 3.7%) determination in air filters are given elsewhere [*Martínez-Ruiz et al.*, 2007].

[13] The atmospheric flux of ^{7}Be and ^{210}Pb are calculated using the expression

$$F = \frac{A}{St}\left(Bq\ m^{-2} month^{-1}\right) \quad (1)$$

where A is the activity in the sample (Bq), S is the surface area of the collector and t is the duration of deployment (months). The activity of the sample is obtained from the gamma spectra.

3. Results and Discussion

3.1. Variations of Monthly Precipitation and Bulk Depositional Fluxes of ^{7}Be and ^{210}Pb

[14] The amount of rainfall, collection interval and depositional fluxes of ^{7}Be and ^{210}Pb for the 16 monthly bulk deposition (wet + dry) samples collected between April 2009 and July 2010 are given in Table 1. The monthly amount of precipitation is plotted in Figure 2. The year 2009 was the wettest in the last 40 years. The historic annual average rainfall in Huelva is about 550 L m^{-2} (=550 mm/yr), while for 12 months (April 2009 to March 2010), the total rainfall was ~10^3 L m^{-2} (1000 mm). About 80–90% of the precipitation is confined to October–April, with very little rainfall in the remaining months. During this sampling period, the highest amount of precipitation was observed in December, January and February (~200 mm/month, with 69.3% of the total in three months), although this amount may vary from October to February. There are many other climate regions similar to coastal Mediterranean climate region (e.g., San Francisco,

Table 1. Sampling Time, Amount of Precipitation, Specific Concentrations and Bulk Depositional Fluxes of ^{7}Be and ^{210}Pb in Huelva (Spain) From April 2009 to August 2010[a]

	Date In	Date End	Days in Collection[b]	Rainfall (mm)	^{7}Be (Bq L^{-1})	^{210}Pb (Bq L^{-1})	^{7}Be/^{210}Pb	^{7}Be Flux (Bq m^{-2} month^{-1})	^{210}Pb Flux (Bq m^{-2} month^{-1})	^{210}Pb Velocity (cm s^{-1})	^{7}Be Velocity cm (s^{-1})	^{210}Pb Washout Ratio	^{7}Be Washout Ratio
DA 1	18/04/2009	27/04/2009	9 (3)	39	0.03	0.005	5.14	27.5 ± 1.4	5.3 ± 0.4	0.91	0.25	28	8
DA 2	27/04/2009	15/05/2009	18 (2)	2.4	0.82	0.065	12.50	25.9 ± 1.1	2.1 ± 0.2	0.09	0.14	90	139
DA 3	15/05/2009	25/06/2009	41 (4)	1.2	7.42	1.068	6.95	13.8 ± 0.9	2.0 ± 0.3	0.20	0.07	3285	1203
DA 4	25/06/2009	31/07/2009	36 (0)	0	—	—	5.46	5.6 ± 0.6	1.0 ± 0.1	0.25	0.05		
DA 5	31/07/2009	01/09/2009	32 (0)	0	—	—	6.79	9.6 ± 0.3	1.4 ± 0.1	0.06	0.06		
DA 6	01/09/2009	01/10/2009	30 (3)	10.2	3.44	0.259	13.28	75 ± 5	5.6 ± 0.5	0.28	0.41	401	583
DA 7	01/10/2009	04/11/2009	34 (12)	25.1	4.52	0.318	14.21	114 ± 4	8.0 ± 0.3	0.63	1.30	775	1604
DA 8	04/11/2009	01/12/2009	27 (16)	28.8	1.33	0.093	14.40	42.7 ± 1.3	3.0 ± 0.1	0.11	0.36	107	351
DA 9	01/12/2009	22/12/2009	21 (14)	202	0.13	0.007	19.04	50.4 ± 2.0	2.6 ± 0.2	0.64	0.54	52	44
DA 10	03/01/2010	01/02/2010	29 (16)	196	0.40	0.034	11.99	97 ± 3	8.1 ± 0.3	1.33	0.52	171	67
DA 11	01/02/2010	01/03/2010	28 (21)	227	0.04	0.003	13.19	11.1 ± 0.4	0.8 ± 0.1	0.26	0.12	30	13
DA 12	01/03/2010	01/04/2010	31 (15)	109	1.59	0.099	16.04	174 ± 5	10.9 ± 0.4	0.78	0.97	221	277
DA 13	01/04/2010	01/05/2010	30 (8)	42.3	3.93	0.169	23.31	186 ± 6	8.0 ± 0.4	1.09	1.77	719	1162
DA 14	01/05/2010	01/06/2010	31 (5)	3.6	7.42	0.630	11.78	39.1 ± 1.8	3.3 ± 0.3			—	—
DA 15	01/06/2010	01/07/2010	30 (3)	15	2.04	0.183	11.17	30.7 ± 0.9	2.7 ± 0.2			—	—
DA 16	01/07/2010	01/08/2010	31 (0)	0	—	—	5.36	20.4 ± 0.6	3.8 ± 0.2			—	—
Range										(0.06–1.33)	(0.05–1.77)	28–3285	8–1604
Mean										0.51 ± 0.12	0.50 ± 0.15	534 ± 300	496 ± 180

[a]Flux and washout ratios for ^{7}Be and ^{210}Pb are also shown.
[b]Number of rain days given in parentheses.

Los Angeles in USA). The amount of precipitation in these places also is negligible in the warmer months (June, July, August, and September) (Figure 2). Taking into account Figure 2 and the specific activities (Bq L^{-1}) shown in Table 1, it can be seen the dilution effect of the rainfall: when a high amount of precipitation occurs, the specific activities are lower than in periods with less precipitation.

[15] The monthly depositional flux of ^{7}Be ranges from 5.6 to 186 Bq m^{-2} month^{-1} (Table 1) with the lowest deposition occurring during the summer months (June and July) when there is no precipitation. The depositional flux during these two months is completely due to dry deposition. The average dry depositional flux for these months is 7.5 Bq m^{-2} month^{-1}. If we assume that the dry deposition has remained constant throughout the year, the dry deposition would account for 11% of the bulk fallout. It is likely that this is an overestimate, because the precipitation will efficiently strip-off the aerosols and hence the dry fallout in rainy months is likely much less than the dry months. The dry depositional flux is spatially and temporally variable. For example, the dry fallout in Galveston, Texas varied between 3.0 and 7.4% of the bulk depositional flux in October 1990, but it accounted for ~87% during October 1991 and this was attributed to very low rainfall [*Baskaran et al.*, 1993]. This value of 11% is in agreement with values obtained in others studies at similar latitudes [*Olsen et al.*, 1985; *Todd et al.*, 1989; *McNeary and Baskaran*, 2003].

[16] The monthly depositional flux of ^{210}Pb varied between 0.8 and 10.9 Bq m^{-2} month^{-1}. The average dry depositional flux of ^{210}Pb during dry months is 1.2 Bq m^{-2} month^{-1}. If we assume that the dry deposition has remained constant throughout the year, the dry deposition would account for 24% of the bulk fallout. *Benitez-Nelson and Buesseler* [1999] reported that dry deposition accounts for less than 1% of the ^{7}Be flux, but accounts for 12% of the ^{210}Pb flux. In our study, the dry deposition for ^{210}Pb is significantly higher than that of ^{7}Be and the differences are attributed to the differences in their sources and their half-lives. The expected inventories ^{210}Pb in the upper 2–3 cm of the soil layer are expected to be much higher than that of ^{7}Be. When soil dust from the upper 2–3 cm layer is resuspended, the dust is expected to have

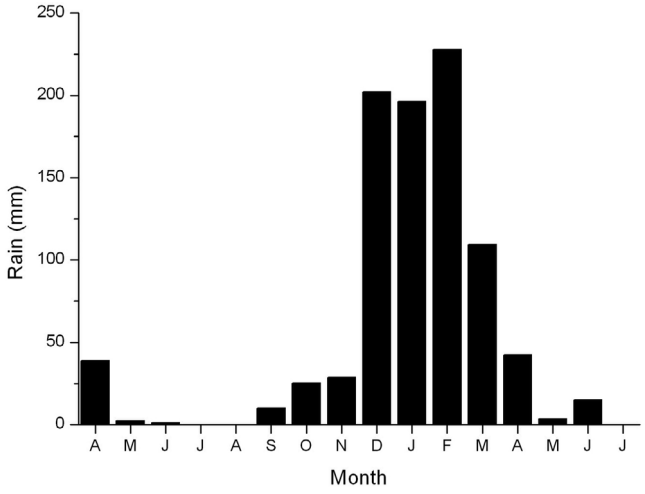

Figure 2. Monthly precipitation in Huelva during the sampling period (April 2009 to July 2010).

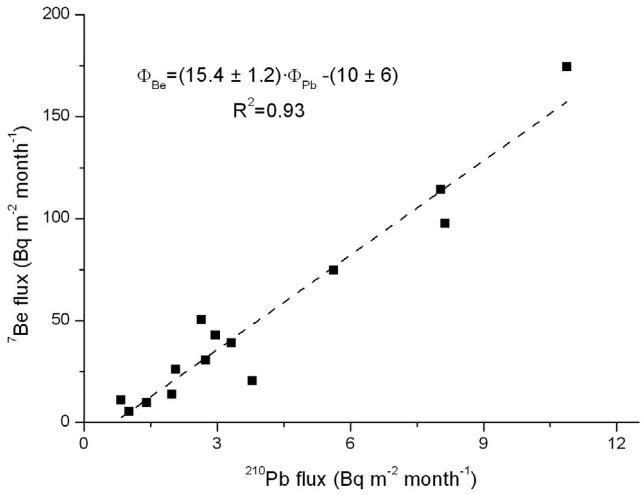

Figure 3. Monthly depositional flux of ^{7}Be versus monthly depositional flux of ^{210}Pb in Huelva, Spain.

much higher specific activity (Bq/gram of resuspended dust) of ^{210}Pb than ^{7}Be, and thus we expect higher dry fallout of ^{210}Pb compared to ^{7}Be.

[17] The lowest deposition was found during the summer months when there is little rain (or there is no precipitation). This is reflected in Figure 3, with a strong correlation between monthly depositional flux of ^{210}Pb and monthly depositional flux of ^{7}Be (r = 0.96). Lead-210 and ^{7}Be in the atmosphere have distinct sources due to different modes of their production. This high correlation between these two radionuclides suggests that both radionuclides cannot be used as independent atmospheric tracers. Even in island locations such as Bermuda, strong correlation between these nuclides was found [*Kim et al.*, 1999] and was attributed to major transport of ^{210}Pb via the upper troposphere from continents. From all the earlier published data before 1993 from different regions around the world, it was shown that there was a strong correlation between the fluxes of ^{7}Be and ^{210}Pb and thus, ^{7}Be and ^{210}Pb could not be used as two – independent atmospheric tracers [*Baskaran et al.*, 1993]. The possibility of fractionation between ^{7}Be and ^{210}Pb scavenging in the atmosphere depending on the intensity of washout with altitude does exist, although it is not proven yet [*Kim et al.*, 2000; *Church and Sarin*, 2008].

[18] The activity ratios of ^{7}Be/^{210}Pb (Table 1) ranged from 5.1 to 23.3, (mean = 11.9 ± 1.3), though a majority of the samples (13 out of 16) remains fairly constant and fall within two ranges, one 5 to 7 and other 11 to 15. It is interesting to note that the ratios tend to decrease in summer months, although there is no clear trend. Due to absence of precipitation during summer months, the fine soil particulate matter containing much higher specific activity of ^{210}Pb compared to ^{7}Be can be easily resuspended and as a consequence may result in lower ^{7}Be/^{210}Pb ratios. This observation is similar to results reported in other studies, although very low summer precipitation is unique in this study [*McNeary and Baskaran*, 2003; *Hirose et al.* 2004; *Dueñas et al.*, 2005].

3.2. Relationship Between Seasonal Variations in the Depositional Fluxes and Amount of Precipitation

[19] In order to quantify the importance of the amount of precipitation on the depositional fluxes of these radionuclides, we have calculated the fractional amounts of precipitation and depositional fluxes of ^{7}Be and ^{210}Pb for the sixteen month sampling period (April 2009 – July 2010). The fractional amount of precipitation and depositional fluxes of ^{7}Be and ^{210}Pb for five seasons from April 2009 until July 2010 are given in Table 2.

[20] From Table 2, it is possible to infer the following: i) The seasonal ^{7}Be flux increased by a factor ~7 from spring 2009 to spring 2010, although the amount of precipitation increased only by a factor ~2.5; ii) lowest depositional fluxes of ^{7}Be and ^{210}Pb were consistently found in the summer months due to very low amount of precipitation; and iii) highest depositional fluxes of both ^{7}Be and ^{210}Pb were found in spring 2010, although the highest rainfall was found during winter 2009/2010. The increase in ^{7}Be is likely due to input from stratosphere-troposphere exchange while the increase in ^{210}Pb could be due to higher release rates of ^{222}Rn from the continents due to warmer temperatures in spring compared to winter and higher inputs of land-derived air masses that are elevated in ^{210}Pb concentrations.

[21] Due to troposphere–stratosphere exchange of air masses in midlatitudes during spring, a certain amount of air is exchanged between the troposphere and stratosphere. In the case of ^{7}Be, the two key factors that control the depositional fluxes of ^{7}Be at any site are: (1) The amount and frequency of precipitation and (2) the amount of ^{7}Be derived from stratosphere due to vertical mixing. During summer months, the atmosphere is quite dynamic and hence large scale atmospheric mixing takes place. During vertical mixing, the ^{210}Pb is mixed upward to the middle and upper troposphere due to convective mixing where precipitation scavenging is much less, leading to a decrease in the depositional flux of ^{210}Pb.

[22] The precipitation-normalized enrichment factor (α) is defined as [*Baskaran*, 1995]

$$\alpha = (F_s/F_t)/(R_s/R_t) \quad (2)$$

Table 2. Seasonal Amount of Precipitation, Depositional Fluxes of ^{7}Be and ^{210}Pb, Normalized Enrichment Factors for ^{7}Be and ^{210}Pb, and ^{7}Be/^{210}Pb Activity Ratios From April 2009 to July 2010

Parameter	Spring 2009	Summer 2009	Autumn 2009	Winter 2009/10	Spring 2010	Summer 2010
Precipitation mm	61.4	1.2	64.1	626.4	155.4	15
^{7}Be Fallout Bq cm^{-2}	0.16	0.087	0.695	0.477	1.198	0.153
^{7}Be (α)	0.87	24.13	3.61	0.25	2.57	3.40
^{210}Pb Fallout Bq cm^{-2}	0.022	0.013	0.050	0.035	0.062	0.005
^{210}Pb (α)	1.79	54.61	3.84	0.28	1.97	1.55
^{7}Be/^{210}Pb	8.2	8.5	15.9	13.7	15.4	5.4

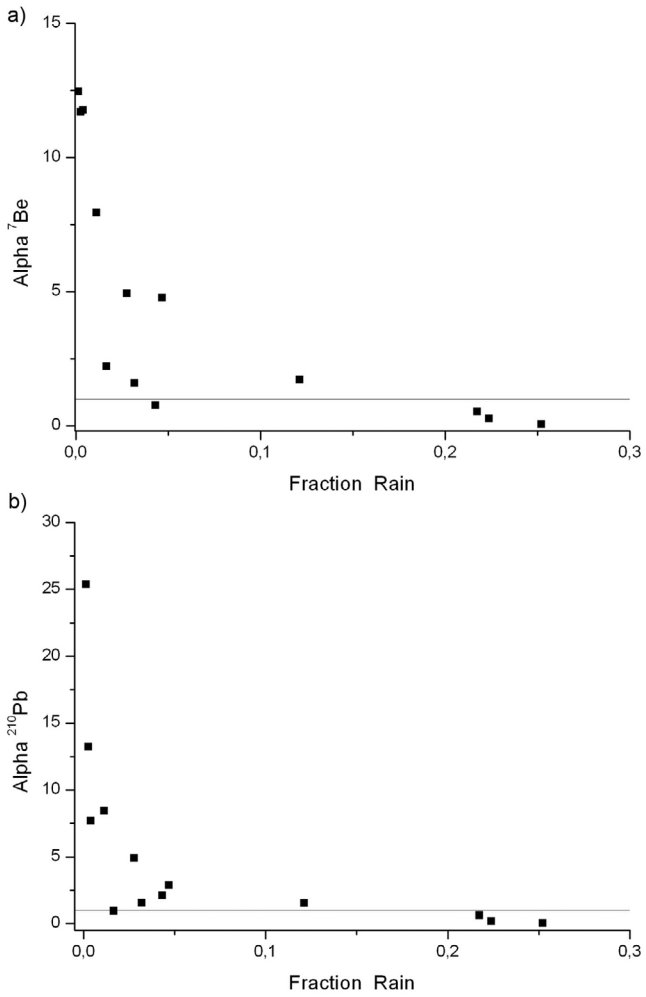

Figure 4. The precipitation-normalized enrichment factor (α, calculated using equation (1)) for monthly (a) ^{7}Be and (b) ^{210}Pb.

where R_s and R_t are the amount of rainfall during a particular season ("s") and in one year ("t" = total) respectively, and F_s and F_t are the corresponding depositional fluxes of ^{7}Be and ^{210}Pb in that particular season and year, respectively. Alpha values greater than 1 indicate that the depositional fluxes are higher than expected from the amount of rainfall, and values less than 1 indicate depletion of radionuclide fluxes.

[23] In Figures 4a and 4b, it is observed that when rainfall is scarce there is enrichment for both ^{7}Be and for ^{210}Pb (higher concentration). This enrichment is observed in summer months, when the precipitation is nearly zero. Using equation (2), the alpha values can be calculated for each month. The range of alpha values for ^{7}Be for each month varied between 0.05 and 12.5, while for ^{210}Pb it varied between 0.06 and 25.4. In both cases the maximum alpha values are observed in June 2009 and the minimum in February 2010. This peak in June 2009 (maximum in summer, Table 2) is likely due to intrusion of air from the stratosphere to troposphere as well as the dominance of dry fallout during summer. The minimum in alpha values occur during February 2010, in which there are more rainy days (21), and amount of precipitation (227 mm) is maximum throughout the sampling period. Similar behavior for ^{7}Be and ^{210}Pb indicates that the main mechanism of deposition is the wet fallout. Furthermore, it can be seen that the ratio of maximum to minimum alpha for ^{210}Pb (195) is about twice the ratio of maximum to minimum alpha for ^{7}Be (95). This fact is consistent with higher dry deposition for ^{210}Pb (24%) compared to ^{7}Be (11%).

3.3. Variations in the Specific Activity of ^{7}Be and ^{210}Pb With Amounts of Rainfall

[24] The variations in the activity concentrations (Bq L^{-1}) of ^{7}Be and ^{210}Pb in the bulk deposition samples may be due to several factors such as cloud height, the amount and duration of rainfall, the time elapsed between successive rain events and the vertical mixing of air masses at the sampling site [*McNeary and Baskaran*, 2003; *Dueñas et al.* 2005]. Results show a range of values for ^{7}Be activity concentrations between 0.03 Bq L^{-1} and 7.42 Bq L^{-1} (Table 1), with a mean value of 2.5 Bq L^{-1}. The corresponding values for ^{210}Pb varied between 0.003 Bq L^{-1} and 1.07 Bq L^{-1}, with mean value of 0.23 Bq L^{-1}. Values of the specific activity concentrations of ^{7}Be and ^{210}Pb are comparable to those reported in other places in the Mediterranean coast in Europe [*Ródenas et al.*, 1997; *Dueñas et al.*, 2005; *García-Orellana et al.*, 2006; *Baskaran*, 2010]. The maximum values for ^{7}Be are reported in 2010 spring (Table 1), which likely correspond to the input of air from the stratosphere to the troposphere. We also observe dilution effect for ^{7}Be in the rainiest months. Moreover, similar behavior was also observed for ^{210}Pb (Table 1), with values higher during the spring months (April, May and June), but the increase in activity may be due to the source of air mass (continent-derived) and/or higher release of ^{222}Rn from the local area due to favorable atmospheric conditions (e.g., pressure, wind velocity, presence of temperature inversion, etc).

3.4. Volume-Weighted Concentrations of ^{7}Be and ^{210}Pb

[25] In this study the volume-weighted concentrations (C) of ^{210}Pb and ^{7}Be have been calculated by the total annual activity (A_t) of ^{210}Pb or ^{7}Be deposited in the bulk collector, divided by the annual precipitation in the collector (R_t) (the period used for estimation of volume-weighted concentrations is from 18 April 2009 to 30 April 2010):

$$C = \frac{A_t}{R_t} \tag{3}$$

[26] The volume-weighted concentration for ^{7}Be is found to be 0.83 Bq L^{-1}, and 0.06 Bq L^{-1} for ^{210}Pb. These values can be compared to the recently summarized values around the globe for ^{7}Be by *Kaste and Baskaran* [2011]: 0.50 to 2.87 Bq L^{-1} and for ^{210}Pb by *Baskaran* [2010]: 0.051 to 0.35 Bq L^{-1}. This is also consistent with environmental concentrations of ^{7}Be in the temperate zones of about 0.7 Bq L^{-1} in rainwater [*U. N. Scientific Committee on the Effects of Atomic Radiation* (*UNSCEAR*), 1982].

3.5. Comparison of Annual Depositional Fluxes of ^{7}Be and ^{210}Pb Along the Mediterranean Coast

[27] It is well known that fluxes of ^{7}Be and ^{210}Pb are controlled by several factors including latitude. Maximum productions in the upper atmosphere along with higher fallout of ^{7}Be and other cosmogenic radionuclides at midlatitudes

Table 3. Average Annual Depositional Fluxes of ^{7}Be and ^{210}Pb in Mediterranean Coast

Location	Latitude-Longitude	^{7}Be Flux (Bq m^{-2} yr^{-1})	^{210}Pb Flux (Bq m^{-2} yr^{-1})	Reference
Málaga, Spain	36°N, 4°W	412		*Dueñas et al.* [2001]
Thessaloniki, Greece	40°N, 23°E	483 to 841		*Papastefanou and Ioannidou* [1991]
Pachino, Italy	36°N, 15°E		56	*García-Orellana et al.* [2006]
Cabo de Gata, Spain	36°N, 2°E		34	*García-Orellana et al.* [2006]
San Felipe, Spain	40°N, 4°E		85	*García-Orellana et al.* [2006]
Ostriconi, Italy	42°N, 9°E		61	*García-Orellana et al.* [2006]
Port Vendres, Spain	42°N, 3°E		61	*García-Orellana et al.* [2006]
Fréjus, France	43°N, 6°E		121	*García-Orellana et al.* [2006]
Huelva, Spain	37°N, 7°W	834	59	Present study

have been reported over 4 decades (summarized by *Kaste and Baskaran* [2011]). Global atmospheric depositional fluxes of ^{210}Pb also indicate higher fallout in tropics and midlatitudes and lowest values at the Polar Regions [*Baskaran*, 2010]. Table 3 presents the results of ^{7}Be and ^{210}Pb fluxes in different sites of the Mediterranean coast. As it was previously mentioned, Huelva is located on the Atlantic coast of the Iberian Peninsula, close to the Strait of Gibraltar and the Mediterranean Sea. The annual flux of ^{7}Be obtained in Huelva is calculated to be 834 Bq m^{-2}, which is similar to those ones from Malaga (Spain) and Thessaloniki (Greece), where values between 412 and 841 Bq m^{-2} have been reported. The ^{210}Pb annual flux in Huelva is 59 Bq m^{-2} which is similar to the annual fluxes of ^{210}Pb reported for other Mediterranean locations (France, Italy and Spain), 34 and 121 Bq m^{-2}. For example, in a continental setting (Geneva, Switzerland, 46°N, 6°E), the reported annual fluxes of 150 Bq m^{-2} for ^{210}Pb, and 2087 Bq m^{-2} for ^{7}Be [*Caillet et al.*, 2001] are significantly higher than that in Huelva. In Santander (43°N, 3°W, Atlantic coast of Spain), annual fluxes for ^{7}Be ranged between 1100 and 2240 Bq m^{-2} [*Ródenas et al.*, 1997]. As can be seen, the ^{7}Be flux values obtained in these zones are higher than those ones obtained in Huelva province. It is worth noting that these studies were carried out at different times, as the values of ^{7}Be annual flux depend on the solar cycle, sunspots, and cosmic ray intensity at the time of sampling [*Papastefanou and Ioannidou*, 2004]. More recent study by *Hirose et al.* [2010] in Far East Asia (no such long-term data exist for the Mediterranean coast) indicates that there is long-term variability in the deposition of ^{210}Pb and is related to climate change and have reported enhanced ^{210}Pb concentration in rainwater during El Niño events.

3.6. Relationship Between ^{7}Be and ^{210}Pb in Bulk Precipitation From Coastal Cities Around the World

[28] To put our data of the bulk depositional fluxes of ^{7}Be and ^{210}Pb in perspective, we have compared our data with those reported for other coastal cities around the world. As seen before, ^{210}Pb fluxes mainly depend on the longitude (whether it is continent or areas influenced by oceanic air mass), while ^{7}Be fluxes essentially depend on latitude and season. For comparison, we have selected coastal cities located at latitudes comparable to Huelva. In monthly precipitation samples collected in Huelva, the specific activity of ^{210}Pb varied between 0.005 and 1.07 Bq L^{-1}, and between 0.03 and 7.42 Bq L^{-1} for ^{7}Be. The ^{7}Be/^{210}Pb activity ratios in bulk deposition obtained in Huelva ranged between 5.14 and 23.3. Table 4 shows results in other coastal locations: In Nagasaki, and Tsukuba (Japan), in a study conducted in 2000–2001, a range of values between 0.04 and 0.52 Bq L^{-1} for ^{210}Pb, and between 0.4 and 2.3 Bq L^{-1} for ^{7}Be have been reported [*Hirose et al.*, 2004]; the ^{7}Be/^{210}Pb activity ratios in bulk deposition varied between 3.9 and 9.8, and 2.8 and 9.7 with a mean value of 6.6 and 6.4, respectively [*Hirose et al.*, 2004]. In the Korean Yellow Sea coastal town, Ansan, the ^{7}Be and ^{210}Pb concentrations varied between 0.6 and 14.1 Bq L^{-1} and 0.01 and 1.89 Bq L^{-1}, during 1992–1993 and the ^{7}Be/^{210}Pb activity ratios varied between 1.3 to 27.7 [*Kim et al.*, 1999]. In Galveston (USA), during years 1988 to 1992, a range of values between 0.03 and 3.6 Bq L^{-1} for ^{210}Pb, and between 0.1 and 21 Bq L^{-1} for the ^{7}Be were obtained; the ^{7}Be/^{210}Pb activity ratios in bulk deposition samples varied between 2.2 and 32.6 [*Baskaran et al.*, 1993]. Also in the United States, Chesapeake Bay, in the period 1995–1996, values between 0.05 and 0.23 Bq L^{-1} for ^{210}Pb, and between 1.2 and 5.0 Bq L^{-1} for ^{7}Be were found, with ^{7}Be/^{210}Pb activity ratios varying between 8.2 and 39.1 [*Kim et al.*, 2000]. In Málaga (Spain) during the period from 1992 to 1999, a range of values between 0.12 and 4.53 Bq L^{-1} for ^{210}Pb, and 0.28 and 6.1 Bq L^{-1} for ^{7}Be was reported; the ^{7}Be/^{210}Pb activity ratios in bulk deposition samples varied between 0.5 and 12.3, with a mean value of 3.0 [*Dueñas et al.*, 2005]. It is thus possible to conclude that the results obtained in our study are similar to those found in other coastal cities.

3.7. Temporal Variations of the Concentrations of ^{7}Be and ^{210}Pb and ^{7}Be/^{210}Pb Activity Ratio in Surface Air

[29] Figure 5 shows the mass concentrations of aerosols retained on the filter for the three different sampling stations. The ranges and mean values of the mass concentrations of the

Table 4. Specific Activities of ^{7}Be and ^{210}Pb in Bulk Precipitation From Coastal Cities Around the World

Collection	Latitude-Longitude	Specific ^{210}Pb Activity (Bq L^{-1})	Specific ^{210}Pb Activity (Bq L^{-1})	^{7}Be/^{210}Pb Ratio	Reference
Galveston, USA 1988–1992	29°N, 94°W	0.03–3.6	0.1–21	2.2–32.6	*Baskaran et al.* [1993]
Chesapeake Bay, USA 1995–1996	37°N, 76°W	0.05–0.23	1.2–5.0	8.2–39.1	*Kim et al.* [2000]
Málaga, Spain 1992–1999	36°N, 4°W	0.12–4.53	0.28–6.1	0.5–12.3	*Dueñas et al.* [2001]
Nagasaki, Japan 2000	36°N, 123°E	0.04–0.52	0.4–2.3	3.9–9.8	*Hirose et al.* [2004]
Tsukuba, Japan 2000–2001	36°N, 140°E	0.08–0.48	0.4–2.2	2.8–9.7	*Hirose et al.* [2004]
Huelva, Spain 2009–2010	37°N, 7°W	0.005–1.07	0.03–7.4	5.14–23.3	Present study

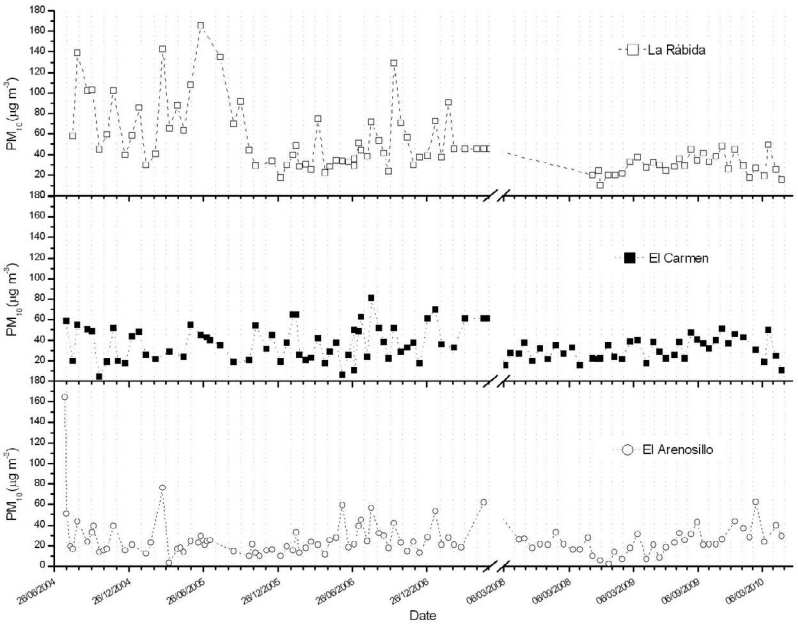

Figure 5. Aerosol mass concentration (PM_{10}) in the sampling stations.

aerosol retained on the filter paper respectively are: 2.0–165.0 μg m^{-3} (mean value: 26.3 μg m^{-3}) in El Arenosillo; 9.9–165.9 μg m^{-3} (mean value: 48.9 μg m^{-3}) in La Rábida and 4.8–80.5 μg m^{-3} (mean value: 34.9 μg m^{-3}) in El Carmen. ANOVA test was conducted over the PM_{10} data taking the sampling site as the factor to analyze. The results indicate that, at 0.05 level, the mean of the PM_{10} concentrations are significantly different in the three sampling sites. The application of the Scheffe test to the data indicates that, at 0.05 level, the mean of PM_{10} concentrations in La Rabida is significantly higher than in El Carmen and that in the last site is higher than in El Arenosillo. This result is a consequence of the fact that El Arenosillo station is the one far from traffic and industrial influence. Also, as it was previously mentioned, La Rábida is located close to an important industrial complex, and higher levels of PM_{10} concentrations reflect the influence of anthropogenic emissions.

[30] Table 5 shows the seasonal averages of the mass concentrations of PM_{10}, ^{210}Pb, ^{7}Be and activity ratios of ^{7}Be/^{210}Pb in atmospheric filters. In El Arenosillo and El Carmen stations, 90% of samples show PM_{10} concentrations in the range 2–60 and 5–80 μg m^{-3} respectively, while in the La Rábida station the PM_{10} concentrations in 90% of samples are in the range 10–110 μg m^{-3}. The distribution of PM_{10} concentrations is more scattered in La Rábida station than the other two stations. Seasonal variations of PM_{10} concentrations are not significantly different at 0.05 level in none of the sampling sites.

[31] Figure 6 shows the concentration of ^{7}Be in surface air of the three sampling stations. The ranges of concentration

Table 5. Seasonal Averages of PM_{10}, ^{210}Pb and ^{7}Be Concentrations and ^{7}Be/^{210}Pb Activity Ratios in Atmospheric Filters in the Different Sampling Stations[a]

		n			MEAN (μg m^{-3})			Minimum to Maximum (μg m^{-3})			P 25% to P 75% (μg m^{-3})		
	Season	EA	LR	EC	EA	LR	EC	EA	LR	EC	EA	LR	EC-EC
PM_{10} (μg m^{-3})	Su	27	19	26	34.0 ± 5.5	56.8 ± 7.7	38.9 ± 3.1	14.8–165.0	28.1–138.7	10.7–80.5	21.0–35.7	35.6–63.8	25.4–49.5
	Au	26	23	25	21.0 ± 2.1	49.5 ± 6.3	31.6 ± 2.8	5.30–43.35	9.9–128.6	4.8–54.0	13.67–25.34	29.4–57.9	20.6–45.1
	Wi	26	26	23	25.1 ± 3.3	41.7 ± 5.6	36.6 ± 3.3	2.0–76.2	17.5–142.4	18.2–69.6	15.9–27.9	25.5–44.3	23.5–43.0
	Sp	25	22	26	25.1 ± 3.1	50.1 ± 7.4	32.4 ± 3.0	3.4–61.5	15.0–165.9	6.3–61.1	17.3–27.6	28.3–59.7	22.7–40.8
^{210}Pb (mBq m^{-3})	Su	27	19	26	0.63 ± 0.08	0.77 ± 0.11	0.69 ± 0.08	0.14–1.70	0.16–1.6	0.09–1.5	0.35–0.84	0.34–1.2	0.41–0.9
	Au	26	23	25	0.52 ± 0.09	0.65 ± 0.13	0.56 ± 0.11	0.06–2.27	0.06–2.8	0.04–2.3	0.22–0.74	0.24–0.9	0.21–0.7
	Wi	25	26	23	0.54 ± 0.08	0.68 ± 0.10	0.66 ± 0.12	0.13–2.1	0.10–2.2	0.07–2.9	0.21–0.8	0.26–1.0	0.32–0.9
	Sp	25	22	26	0.47 ± 0.06	0.45 ± 0.07	0.47 ± 0.05	0.07–1.2	0.09–1.5	0.06–1.0	0.26–0.62	0.23–0.57	0.23–0.60
^{7}Be (mBq m^{-3})	Su	27	19	26	5.5 ± 0.4	6.2 ± 0.5	6.1 ± 0.4	2.0–9.9	2.9–9.6	2.9–9.2	3.6–6.7	4.3–8.2	5.0–7.5
	Au	26	23	25	3.91 ± 0.3	4.3 ± 0.3	3.9 ± 0.4	0.43–7.9	2.22–8.2	0.61–8.4	3.1–4.8	3.2–5.7	2.7–4.4
	Wi	25	26	23	4.8 ± 0.4	4.5 ± 0.4	4.7 ± 0.4	1.1–8.7	1.1–8.5	1.8–8.0	3.6–6.2	2.9–6.0	3.8–6.4
	Sp	25	22	26	5.7 ± 0.5	6.2 ± 0.5	5.7 ± 0.5	0.7–11.9	3.0–11.2	0.6–11.7	4.3–7.4	4.6–7.1	4.4–7.0
^{7}Be/^{210}Pb	Su	27	19	26	11.3 ± 1.4	11.0 ± 1.5	12.3 ± 2.0	4.2–32.1	5.2–24.9	4.3–54.8	6.2–13.9	6.6–14.3	6.6–14.2
	Au	26	23	25	11.7 ± 1.9	11.8 ± 1.9	11.0 ± 1.4	2.6–48.7	2.2–41.6	2.4–28.2	5.5–14.1	5.2–15.1	6.1–13.1
	Wi	25	26	23	12.6 ± 1.7	13.2 ± 2.7	14.7 ± 3.5	2.7–30.0	1.3–44.4	2.2–76.5	4.8–18.3	3.6–16.8	4.2–18.1
	Sp	25	22	26	14.8 ± 1.6	18.5 ± 2.2	14.2 ± 1.1	6.1–38.7	6.4–49.8	5.9–24.6	9.5–19.5	10.3–22.0	10.4–16.8

[a]EA: El Arenosillo; LR: La Rábida; EC: El Carmen.

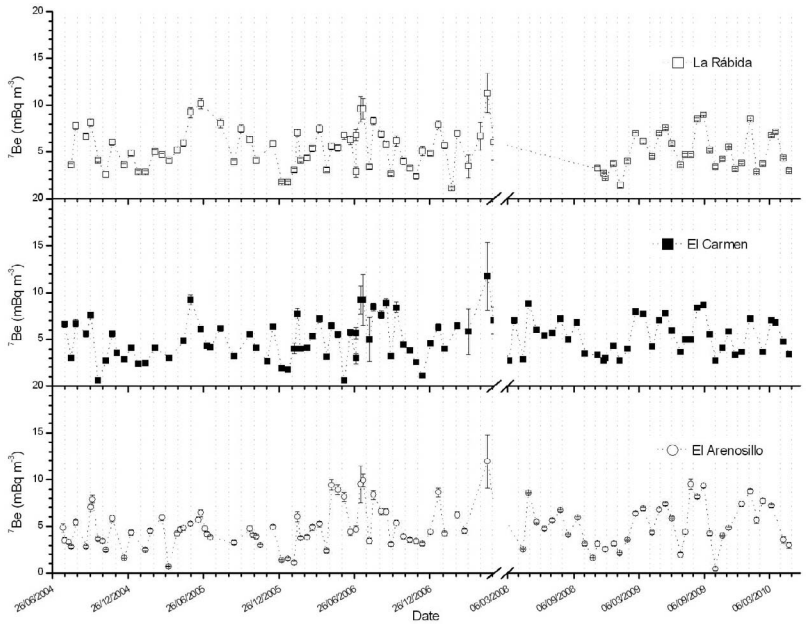

Figure 6. The ^{7}Be activity concentrations (mBq m^{-3}) in the three sampling stations.

of ^{7}Be in surface air are: 0.4–11.9 mBq m^{-3} (mean: 4.9 mBq m^{-3}) in El Arenosillo, 1.1–11.2 mBq m^{-3} (mean: 5.2 mBq m^{-3}) in La Rábida and 0.6–11.7 mBq m^{-3} (mean: 5.1 mBq m^{-3}) in El Carmen. The ANOVA test shows that there are no significant differences between the ^{7}Be concentrations in the three stations, as can be expected from the ^{7}Be origin in surface air. These ranges are comparable to other midlatitude regions such as Detroit [*McNeary and Baskaran*, 2003; *Cannizzaro et al.*, 2004; *Dueñas et al.*, 2004; *Gaffney et al.*, 2004]. The seasonal averages of ^{7}Be in surface air indicate that the concentrations are generally higher during spring and summer months in each of the sampling sites. ANOVA test indicates that ^{7}Be activity concentrations are significantly higher in spring and summer at 0.05 level in the three sampling sites. This observation has been also reported in similar latitudes [*Papastefanou and Ioannidou*, 1991; *Dueñas et al.*, 2004, 2009]. In about 90% of the samples of the three stations, the ^{7}Be concentration varied between 0.5 and 11 mBq m^{-3}. This range is comparable to other midlatitude regions such as Thessaloniki, Greece [*Gerasopoulos et al.*, 2003], Detroit, USA [*McNeary and Baskaran*, 2003], Málaga, Spain [*Dueñas et al.*, 2004].

[32] The concentrations of ^{210}Pb in the atmosphere have been utilized as a tracer of air masses and lithogenic dust (e.g., review paper by *Church and Sarin* [2008]). Figure 7 shows the ^{210}Pb concentrations in surface air from the three sam-

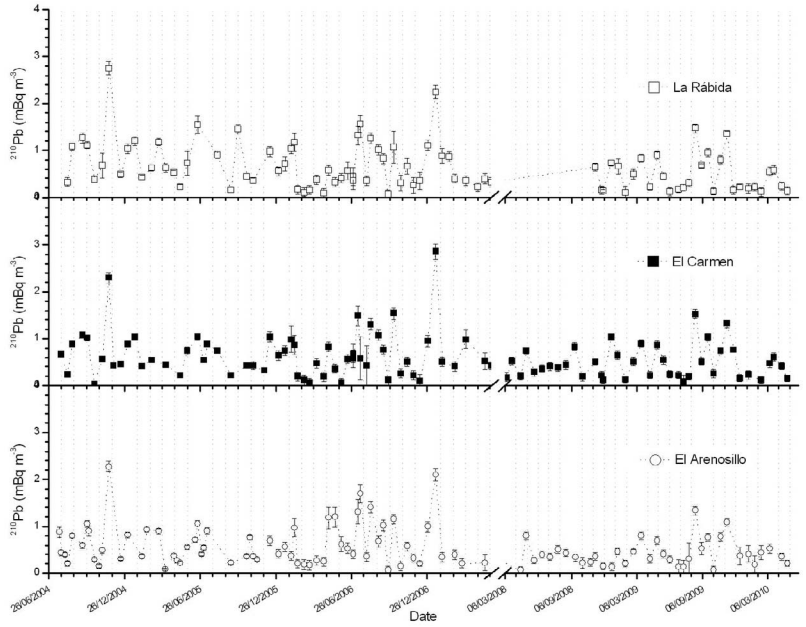

Figure 7. The ^{210}Pb activity concentrations (mBq m^{-3}) in the three sampling stations.

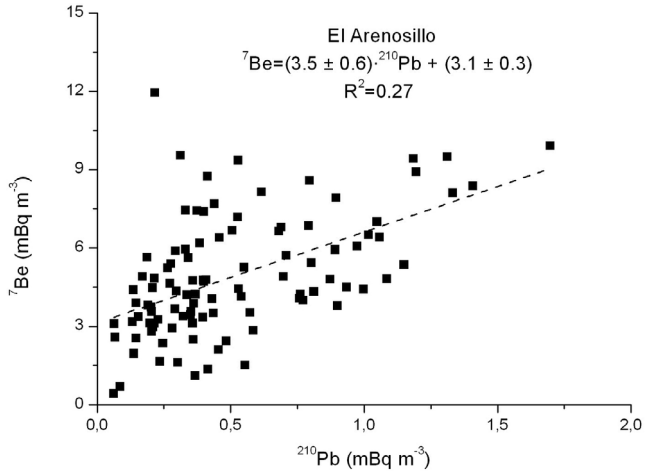

Figure 8. Correlation between specific concentrations of ^{7}Be and ^{210}Pb in aerosols collected from Huelva, Spain.

pling stations. The ranges of the ^{210}Pb concentrations found are: 0.1–2.3 mBq m^{-3} (mean: 0.54 mBq m^{-3}) in El Arenosillo; 0.06–2.8 mBq m^{-3} (mean: 0.63 mBq m^{-3}) in La Rábida; and 0.04–2.9 mBq m^{-3} (mean: 0.59 mBq m^{-3}) in El Carmen. These ranges are comparable to those found in other regions [*Carvalho*, 1995; *Marley et al.*, 2000; *McNeary and Baskaran*, 2003; *Dueñas et al.*, 2004, 2009]. The differences in ^{210}Pb activity concentrations between sampling sites are not significant at 0.05 level. The average values in these three stations are similar to the reference value for ^{210}Pb concentrations in air for northern-hemisphere midlatitude regions, 0.5 mBq m^{-3} [*UNSCEAR*, 2000]. Although ^{210}Pb does not show a marked seasonal variation, the maximum values appear in summer or winter months (Table 5). This is similar to what was observed in the Korean Yellow Sea coast [*Kim et al.*, 1998] and other areas [*Dueñas et al.*, 2004, 2009; *Baskaran*, 2010] and can be attributed to varying fractional inputs of maritime and continental air masses.

[33] In some of the cases, the higher values of ^{210}Pb in autumn/winter season have been attributed to the occurrence of frequent temperature inversion conditions of the surface air layers, resulting in a build-up of radon and its progeny in the ground-level air while the lower values in the spring/summer months correspond to higher air mixing [*Baskaran*, 2010]. The distribution of ^{210}Pb concentration in aerosol shows that the maximum values and the 75% percentile are significantly lower during spring months in all the sampling sites. In Atlantic coastal areas, concentrations of ^{210}Pb in aerosols have been shown to be influenced by the origin of air masses [*Carvalho*, 1995].

[34] The ^{7}Be/^{210}Pb activity ratios in surface air varied between 2.6 and 48.7, with a mean value of 12.6 in El Arenosillo; between 1.3 and 49.8 with a mean of 13.7 in La Rábida and between 2.2 and 76.5 with a mean of 13.0 in El Carmen. Although the mean values of ^{7}Be/^{210}Pb activity ratios are similar to those found for other areas [*Winkler et al.*, 1998; *McNeary and Baskaran*, 2003; *Dueñas et al.*, 2004, 2009], the ranges of variation of these activity ratios are more scattered. This could be due to the influence of air masses of different origin that lead to higher variability in ^{210}Pb concentrations. The maximum values of ^{7}Be/^{210}Pb activity ratios are clearly higher than the rest of values of the distribution indicating that such high value could be due to isolated situations. The 75% percentile value for this activity ratio is about 20, which shows good agreement with data obtained from sites influenced by air masses of oceanic origin [*Turekian and Graustein*, 2003]. These activity ratios do not show seasonal variations and no significant differences are found between the sampling sites. Higher values of ^{7}Be/^{210}Pb activity ratio in surface air have been observed in several areas during late spring and summer months (*Koch et al.* [1996], cited by *McNeary and Baskaran* [2003]) [*Winkler et al.*, 1998; *Dueñas et al.*, 2004, 2009]. In these sampling stations the higher values of ^{7}Be/^{210}Pb are mainly due to diminution in ^{210}Pb activities and higher activities of ^{7}Be during spring months. No strong correlation between ^{7}Be and ^{210}Pb concentrations in aerosols is found (Figure 8, unlike in the precipitation samples (Figure 3)). Although the ^{7}Be concentration in aerosol may be independent of the sources of air masses (maritime versus continental) to the sampling site, the ^{210}Pb concentration will be very sensitive to the sources of air masses [*Carvalho*, 1995; *Hernández et al.*, 2008], and hence if the fractional amount of oceanic air mass changes, the ^{210}Pb concentration in aerosols will also change, while ^{7}Be may not change and hence the linear relationship between ^{210}Pb and ^{7}Be in aerosol samples is expected to be weak. The washout of ^{7}Be and ^{210}Pb during precipitation is from the bottom of the cloud layer to Earth surface and the differences in the sources of air masses for the whole air column will affect ^{210}Pb much less compared to the surface layer (where the aerosols were collected) and thus, there is a stronger correlation between ^{210}Pb and ^{7}Be in precipitation.

[35] In the case of Huelva province, El Arenosillo sampling site is being affected by 7 types of air masses [*Toledano et al.*, 2009]. Although the global air masses arriving to the El Carmen and La Rabida stations can be considered the same, it is likely that the local contribution can be slightly different due to resuspension of fine dust produced by human activities in the neighborhood as it has been shown by the differences in PM_{10} mass concentrations between sampling sites.

[36] Although the variability of the influence of air masses in this type of climate during sampling period (48 h) is very high, a long-term average lead to the distribution of sources of air masses showed in Table 6. From the determination of the ^{210}Pb activity concentrations that can be expected from different source air masses, the sources of air masses can be assessed. The air masses coming from C (Continental), CT (Continental Tropical), L (Local) and Me (Mediterranean) cross continental areas [*Toledano et al.*, 2009] and, as consequence, could transport higher ^{210}Pb activity concentrations than the air masses coming from MT (Maritime Tropical), MP (Maritime Polar) and A (Arctic) that instead travel through Atlantic Ocean mainly. In this way, the origin of air masses arriving to El Arenosillo based on ^{210}Pb activity concentrations could be grouped in two: a group with a maritime origin mainly (MT,MP, A) and a second group with a high continental component (C, CT, L, Me). Table 6 shows the seasonal and annual frequency distribution of these air masses at El Arenosillo sampling site.

[37] *Graustein and Turekian* [1996] using the concentrations of ^{7}Be and ^{210}Pb in aerosols, defined a parameter 'normalized fraction' *f* as an index of the relative influence on an air parcel of two different sources of air masses (upper

Table 6. Frequency of Air Masses (in Percentage) Arriving at El Arenosillo Sampling Site[a]

	Spring	Summer	Autumn	Winter	Annual Average
Maritime polar	36.7	53.2	36.9	38.7	41.4
Maritime tropical	14.9	5.1	13.8	16.2	12.4
Maritime arctic	10.5	6.2	12.2	11.4	10.1
Total maritime	62.1	64.5	62.9	66.3	63.9
Continental	21.1	9.5	13.8	13.8	14.5
Continental tropical	2.4	2.4	6.2	10.0	5.2
Local	4.6	5.7	4.7	3.3	4.6
Mediterranean	9.7	18.0	12.4	6.7	11.8
Total continental	37.8	35.6	37.1	33.8	36.1

[a]Adapted from *Toledano et al.* [2009].

troposphere + lower stratosphere and continental boundary layer). The *f* values depend on the transport history of an air mass and is independent of the effects of precipitation scavenging.

[38] Since the ^{7}Be concentration in aerosol is independent of longitude and both continental and maritime air masses are supposed to have the same concentration for a given latitude and the ^{210}Pb concentration is sensitive to the sources of air masses, in this case, it is preferable to define the parameter f(^{210}Pb,^{7}Be) as the normalized fraction of ^{210}Pb with respect to ^{7}Be of an individual sample as

$$f\left(^{210}Pb,\ ^{7}Be\right) = \frac{^{210}Pb}{^{210}Pb + n^{7}Be} \tag{4}$$

where *n* is the ratio of standard deviation of ^{210}Pb to the standard deviation of ^{7}Be and ^{210}Pb and ^{7}Be represent the activity concentrations of the radionuclides. It is worth noting that f(^{210}Pb, ^{7}Be) and f(^{7}Be, ^{210}Pb) as defined by *Graustein and Turekian* [1996] are related by

$$f\left(^{210}Pb,\ ^{7}Be\right) + f\left(^{7}Be,\ ^{210}Pb\right) = 1 \tag{5}$$

[39] Therefore, although in this case the ^{210}Pb activity concentrations are expected to have a higher variability, the direct relationship between f(^{210}Pb, ^{7}Be) and f(^{7}Be, ^{210}Pb) enables to discuss the results based on the latter.

[40] Values of parameter f(^{7}Be, ^{210}Pb) have been found in the range 0.2–0.9 at Canary Island [*Graustein and Turekian*, 1996], with values close to 0.8 indicating a high proportion of air masses arriving from the upper atmosphere. On the contrary, a value of f(^{7}Be, ^{210}Pb) around 0.2 indicates high proportion of air masses arriving from continental boundary layer. Table 7 shows the ranges, percentiles and mean values of parameter f(^{7}Be, ^{210}Pb) for each season in El Arenosillo. As can be seen from Table 7, the parameter f(^{7}Be, ^{210}Pb) always reaches values above 0.35 and only in 25% of samples this value is below 0.53. This indicates that this sampling site is mainly influenced by air masses with a low component of boundary layer sources, which would lead to f(^{7}Be, ^{210}Pb) of about 0.2. As can be seen from Table 6, in about 60% of the cases the air masses arriving El Arenosillo are from oceanic sources and as a consequence, ^{210}Pb activity concentrations (and f(^{7}Be, ^{210}Pb) parameter) are not expected to be higher. The ANOVA test with the season of the year as factor of variance indicates that at 0.05 level the seasonal variations of parameter f(^{7}Be,^{210}Pb) are not significantly different. This result is in agreement with the frequency distribution of air masses arriving at El Arenosillo. As can be seen from Table 6, in each season the frequency of total maritime component is in the range 62–66% and no significant differences are found between seasons which, as a consequence, do not allow distinguishing significant differences in parameter f(^{7}Be, ^{210}Pb).

3.8. Total Deposition Velocity of Aerosols Using ^{7}Be and ^{210}Pb

[41] Dry and wet deposition scrubs the atmospheric radionuclides and deposits the radionuclides on Earth's surface. Deposition rates are usually characterized by the parameter 'deposition velocity'. The total deposition velocity (V_d) for any nuclide is determined using the following equation [e.g., *McNeary and Baskaran*, 2003]:

$$V_d = F/C_s \tag{6}$$

where F is the total flux of a nuclide to the Earth's surface and C_s is the activity concentration of that nuclide in the surficial air.

[42] The advantages of using ^{7}Be and ^{210}Pb to determine the total deposition velocities are the following: (1) the concentration of ^{7}Be and ^{210}Pb can be easily measured; (2) the production rate of ^{7}Be and ^{210}Pb at any given site remains constant over long periods of time; and (3) the size distributions of ^{7}Be and ^{210}Pb in aerosols are very similar to other particulate contaminants of interest and, therefore, can be used to determine the fluxes of these contaminants to the Earth's surface from a knowledge of the deposition velocities of these nuclides and the concentration of these contaminants in air [*McNeary and Baskaran*, 2003; *Dueñas et al.*, 2004].

[43] The total deposition velocity for ^{7}Be (Table 1) ranges from 0.05 (July 2009) to 1.77 (April 2010) cm s^{-1}, with a mean value of 0.50 ± 0.15 cm s^{-1}. Values for the total deposition velocity for ^{210}Pb vary between 0.06 (August 2009) and 1.33 (January 2010) cm s^{-1}, with a mean value of 0.51 ± 0.12 cm s^{-1}. These data suggest that the ^{7}Be and ^{210}Pb attach onto the aerosols by similar mechanisms [*Winkler et al.*, 1998; *Papastefanou*, 2006], and this fact could explain why deposition velocities obtained using these nuclides are similar. The ^{210}Pb-based deposition velocity can be compared to the range of values, 0.4 to 1.3 cm s^{-1} for the temperate locations and 0.12 cm s^{-1} for the Antarctic summarized by *Church and Sarin* [2008]. The paired t-test analysis indicates that at 0.05 level the deposition velocity for ^{210}Pb and ^{7}Be are not significantly different. Table 8 shows the deposition velocities obtained in different regions of Europe. It can be observed that deposition velocity for ^{7}Be is similar in all locations (0.4–0.5 cm s^{-1}, except in one station), while the one obtained using ^{210}Pb shows a large range, 0.5 and 1.5 cm s^{-1}. Although the deposition velocity of this study

Table 7. Seasonal Averages, Range and Percentiles of Parameter f(^{7}Be, ^{210}Pb) in El Arenosillo Sampling Station

	n	Mean	SD	SEM	Minimum to Maximum	P 25% to P 75%
Su	27	0.63	0.11	0.02	0.43–0.85	0.53–0.75
Au	26	0.70	0.12	0.02	0.41–0.93	0.60–0.79
Wi	25	0.64	0.17	0.03	0.35–0.85	0.48–0.78
Sp	25	0.62	0.11	0.02	0.44–0.88	0.55–0.71

Table 8. Summary of Deposition Velocity of Aerosols Using ^{7}Be and ^{210}Pb in Europe

Collection Time	Latitude and Longitude	^{7}Be (cm s^{-1})	^{210}Pb (cm s^{-1})	Reference
Thessaloniki, Greece 1987–1990	40°N, 23°E	0.4	—	*Papastefanou and Ioannidou* [1991]
Groningen, Netherlands 1990–1993	53°N, 6° E	—	1.0	*Beks et al.* [1998]
Roskilde, Denmark 1990–1993	53°N, 6° E	1.0	—	*Fogh et al.* [1999]
Munich, Germany 1981–1999	48°N, 11°E	—	1.0	*Winkler and Rosner* [2000]
Málaga, Spain 1992–1999	36°N, 4°W	0.4	1.5	*Dueñas et al.* [2005]
Kiruna, Sweden 1975–2000	68°N, 20°E	0.5	—	*Kulan et al.* [2006]
Grindsjön, Sweden 1972–2000	59°N, 18°E	0.5	—	*Kulan et al.* [2006]
Ljungbyhed, Sweden 1975–2000	56°N, 13°E	0.5	—	*Kulan et al.* [2006]
Prague, Czech Republic 1986–2002	50°N, 14°E	0.5	—	*Kulan et al.* [2006]
Dijon, France 1984–2003	47°N, 5°E	0.5	—	*Kulan et al.* [2006]
Palermo, Italy 1982–2002	39°N, 13°E	0.4	—	*Kulan et al.* [2006]
Huelva, Spain 2009–2010	37°N, 7°W	0.5	0.5	Present study

for this area (0.5 cm s^{-1}) is lower than the values reported in other places (1.0 – 1.5 cm s^{-1}), it is consistent with the suggestion that the ^{7}Be and ^{210}Pb attach to particles of similar size, and as a consequence, are affected by similar deposition processes (Winkler *et al.*, 1998).

3.9. Washout Ratio

[44] The washout ratio, W, is a parameter that relates the average concentration of ^{7}Be or ^{210}Pb in surface level precipitation with its average concentration in unwashed surface level air. It is calculated from the following relationship [e.g., *McNeary and Baskaran*, 2003]:

$$W = \rho \frac{C_{rain}}{C_{air}} \tag{7}$$

where ρ is the density of air at standard conditions (1.2 kg m^{-3}, at 20°C and 760 mm Hg) and C_{rain} and C_{air} are the radionuclide (^{7}Be or ^{210}Pb) concentrations in bulk deposition (in Bq kg^{-1}) and surface air (in Bq m^{-3}), respectively. The washout ratio is based on the assumption that the specific ^{210}Pb content of the air in the precipitating cloud is the same as that measured at the surface level in aerosol.

[45] Table 1 shows the washout ratios for the sampling station of Huelva province. As it can be seen from Table 1, the washout ratios for ^{7}Be and ^{210}Pb ranged from 8 to 1604 (average = 496 ± 180) and 27 to 3284 (average = 534 ± 300), respectively. The highest values are obtained for the samples collected in June 2009, September 2009, October 2009 and April 2010, the months with the most significant changes in temperature and precipitation in the Mediterranean climate. On the contrary, the minimum values are obtained in April 2009, December 2009, January 2010, and February 2010, that coincide with the highest rainfall in the period of study.

[46] The washout values for ^{210}Pb are similar to ^{7}Be values, as expected since ^{7}Be and ^{210}Pb attach to aerosols of similar size, and thus rain is equally effective in removing both radionuclides from the atmosphere. The highest values occur in the months with less rain, and the lowest values in the months of more rain. This indicates that the cleaning process of aerosols in the atmosphere is more effective in the first event of rain.

4. Conclusions

[47] The simultaneous measurements of atmospheric bulk depositional fluxes (from April 2009 to July 2010) and ^{7}Be and ^{210}Pb concentrations in aerosols (from July 2004 to April 2010) were conducted at three locations from the Southwest Spain in order to understand the atmospheric behavior of these radionuclides in the border of the Mediterranean Sea and the Atlantic Ocean.

[48] 1. The monthly depositional flux of ^{7}Be and ^{210}Pb during April 2009 to June 2010 did not remain constant but varied between 5.6 and 186 Bq m^{-2} month^{-1} and 0.8 and 8.1 Bq m^{-2} month^{-1}, respectively, depending on the amount of monthly precipitation and the origin of the air masses. The bulk depositional fluxes of ^{7}Be and ^{210}Pb show seasonal trends and the annual depositional fluxes are mainly controlled by the amount of precipitation, although the seasonal factors affect the ^{7}Be and ^{210}Pb differently (^{210}Pb by sources of air masses, continental versus maritime; ^{7}Be by upper atmospheric air).

[49] 2. The maximum annual dry depositional flux is estimated to be ~11% of the total flux for ^{7}Be. However, in the months when there was scanty rain, dry depositional fluxes of ^{7}Be and ^{21O}Pb became a major portion of the bulk depositional fluxes. The fraction of dry depositional flux to total flux appears to be higher for ^{210}Pb (24%) than ^{7}Be. This higher ^{210}Pb dry depositional flux relative to ^{7}Be is attributed to resuspended soil dust that is enriched in ^{210}Pb, but not ^{7}Be.

[50] 3. ^{7}Be and ^{210}Pb depositional fluxes are tightly correlated in our sampling site at the Huelva province, and thus both nuclides cannot be used as two independent atmospheric air mass tracers. Such a correlation has also been found in other continental and coastal stations of the Mediterranean Sea.

[51] 4. The specific activities of ^{7}Be and ^{210}Pb in precipitation varied between 0.03 and 7.42 Bq L^{-1} (mean = 2.5 Bq L^{-1}) and 0.005 and 1.068 Bq L^{-1} (mean = 0.23 Bq L^{-1}), respectively. The annual volume-weighted ^{7}Be concentration was found to be 0.83 Bq L^{-1} similar to the global values reported elsewhere. The annual volume-weighted ^{210}Pb concentration for Huelva province is 0.06 Bq L^{-1} which is smaller than the reported values elsewhere in Europe.

[52] 5. The PM_{10} mass concentrations varied between 2 and 165.9 μg m^{-3}, with the lowest values in the reference station (El Arenosillo), and the highest values in La Rábida and this is attributed to the differences in the industrial activities adjoining these two sites.

[53] 6. The concentrations of ^{7}Be and ^{210}Pb in aerosols varied between 0.4 and 11.9 Bq m^{-3}, and 0.04 and 2.9 Bq m^{-3}, respectively. The spatial variability in the concentrations of these two nuclides in these three stations is negligible. The

concentration of ^{7}Be in air samples showed a seasonal increase during the spring and summer months and no seasonal variation was observed for ^{210}Pb. Lack of seasonal variations is attributed to varying inputs of air masses (oceanic versus continental). There was no significant decrease in the concentration of ^{7}Be in aerosols during months with higher precipitation amounts, suggesting that during these months there was additional input of ^{7}Be from the upper troposphere.

[54] 7. The deposition velocities of aerosols based on ^{7}Be and ^{210}Pb varied between 0.05 –1.77 cm s^{-1} (mean: 0.50 cm s^{-1}), and 0.06 – 1.33 cm s^{-1} (mean: 0.51 cm s^{-1}), respectively. The corresponding washout ratios varied between 8 and 1604 (mean: 496) and 27 – 3284 (mean: 534), respectively.

[55] 8. There is no correlation between the aerosol mass and concentrations of ^{7}Be and ^{210}Pb. There is no significant correlation between the mass of the particulate matter retained on the filter paper and depositional velocities of ^{7}Be and ^{210}Pb in the air masses. This supports earlier hypothesis that only relatively a minor portion of the aerosols actively participate in the removal of these nuclides from the air masses.

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