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A new procedure to validate and optimize ^{210}Po measurements in atmospheric aerosols

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ABSTRACT

The exposure to air fine aerosols can cause health effects due to inhalations of alpha emitters such as ^{222}Rn daughters. Lead-210 and ^{210}Po are mainly associated to aerosols with median aerodynamic diameter lower than 1 μm. The ^{210}Po is characterized by having a high radiotoxicity. The precise measurement of ^{210}Po in surface air aerosols is usually quite complex due to the significant contribution of the ^{210}Pb on their concentrations. Additionally, there is no possible means to manufacture a certified material to validate the measurements of ^{210}Pb and ^{210}Po concentrations in surface air aerosols. For these reasons, this study aims to develop a novel and comprehensive methodology to validate ^{210}Po measurements in surface air aerosols by preparing in our laboratory "standard samples" with known activities of both ^{210}Pb and ^{210}Po. A detailed sensitivity analysis on the precision of ^{210}Po concentration measurements has been carried out as a function of the involved variables such as sampling time, time elapsed between the sampling start and ^{210}Po self-deposition and the ^{210}Po/^{210}Pb activity ratio in surface air aerosols. This study is necessary to find the optimum conditions for a precise measurement of ^{210}Po in surface air aerosols. In addition, this methodology has been applied for the determination of ^{210}Po concentrations in 30 samplings campaigns of atmospheric aerosols carried out at the El Carmen campus (Huelva province) from March 25th to July 15th, 2022. The results obtained for ^{210}Pb and ^{210}Po concentrations and atmospheric aerosol residence times (via ^{210}Po/^{210}Pb activity ratio) were consistent with other previous works.

1. Introduction

The ^{222}Rn (noble gas) is introduced into the atmosphere by its exhalation from the Earth's crust surface. This radionuclide decays to its short-life daughters generating finally ^{210}Pb ($T_{½} = 22.3$ y), this one decays to ^{210}Bi ($T_{½} = 5.01$ d), which produces ^{210}Po ($T_{½} = 138.4$ d) by beta decay, and finally this last radionuclide produces ^{206}Pb (stable) by alpha emission. The radon daughters are produced positively charged and are quickly bound to the surface of atmospheric aerosols particles, being them called clusters or "unattached" radionuclides with diameters from 0.5 to 5 nm.

The exposure to these air fine radioactive aerosols can produce health effects via the inhalation of ultrafine particles and alpha

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emitters radionuclides such as ^{218}Po and ^{214}Po (Hasegawa et al., 2023). In addition, since both ^{210}Pb and ^{210}Po are also associated to atmospheric aerosols with median aerodynamic diameter (AMAD) lower than 1 μm (Paatero et al., 2017), and ^{210}Po is an alpha emitter with high radiotoxicity, its inhalation may lead to undesirable biological effects (Seiler & Wiemels, 2012).

The ^{222}Rn emanation rate for typical soils is about two orders of magnitude higher than the found ones on the ocean (Baskaran, 2011), fact that can be used to distinguish the continental air masses from oceanic ones (Lozano et al., 2012). The levels of ^{210}Pb and ^{210}Po in surface air aerosols are highly variable, ranging between 0.2 and 1.5 Bq m^{-3} and 0.03–0.3 Bq m^{-3}, respectively, depending on the air mass origin being in general the ^{210}Po activity concentrations is air aerosols are one order of magnitude lower than ^{210}Pb ones (Persson & Holm, 2011).

A paradigmatic application of the natural radionuclides is the determination of the mean atmospheric aerosol residence times. Based on both ^{210}Bi/^{210}Pb and ^{210}Po/^{210}Pb activity ratios, mean aerosol residence times from few days to several weeks have been obtained (Baskaran & Shaw, 2001; Paatero et al., 2017). In addition, the assessment of residence time of anthropogenic aerosols is of high importance to evaluate their long-range transport properties and offers a measure of the duration of accidently released radioactivity from nuclear reactor accidents. Furthermore, ^{210}Po and ^{210}Pb in air surficial aerosols are excellent surrogates to study effects of anthropogenic aerosols. There are many human activities that result in the release of radionuclides of ^{238}U- and ^{232}Th-series to the atmosphere, particularly ^{210}Pb and ^{210}Po: oil shale-fired power plants (Vaasma et al., 2017); oil and gas fired power plants (Al-Masri & Haddad, 2012); coal fired power plants (Li et al., 2019); oil refine plants (Behbehani et al., 2021).

Under certain circumstances ^{210}Po level in surface aerosols could be in excess in relation to the unperturbed natural concentration due to different factors such as dust resuspension with ^{210}Pb and ^{210}Po in radioactive equilibrium, industrial emissions, etc. (Aba et al., 2020). In addition, the ^{210}Po concentration in an atmospheric filters increases rapidly because the initial concentration of ^{210}Po is about one order of magnitude lower than that of the ^{210}Pb (Baskaran, 2011; Lozano et al., 2012; Nevissi, 1991), so the measurement of ^{210}Po tends to be overestimated in many works (Lozano et al., 2011a,b). In these cases, the residence time based on ^{210}Po/^{210}Pb activity ratios is longer than that based on ^{210}Bi/^{210}Pb, indicating additional sources of ^{210}Po and, therefore, the determination of aerosols residence times by means of ^{210}Po/^{210}Pb activity ratio is not valid.

The ^{210}Pb activity collected in the atmospheric filter is commonly determined by gamma spectrometry (Barba-Lobo et al., 2024), but in some cases can be applied alpha-particle if more than 5 half-life of ^{210}Po have elapsed from the sampling (Paatero et al., 2017). The ^{210}Po activity concentration in aerosol air is determined through alpha spectrometry by means of the methodology given by (Lozano, Bolívar, et al., 2011). The equations required to obtain ^{210}Pb and ^{210}Po activity concentrations in the aerosol air sampled with filter by considering time decay corrections can be seen elsewhere (Nevissi, 1991). In these general equations several approaches are usually done such as neglecting ^{210}Bi activity concentrations or assuming a certain degree of radioactive equilibrium between ^{210}Pb and ^{210}Bi. For these reasons ^{210}Po must be carefully measured in aerosols for the feasibility of the results and conclusions obtained by using this radionuclide. Despite the large number of articles dealing with determinations of ^{210}Pb and ^{210}Po in aerosol samples, to the best of our knowledge, none have experimentally demonstrated the validity of the equations used to estimate their concentrations. In this paper, this is the first time that an validation procedure of the equations used to determine the couple of radionuclides ^{210}Pb and ^{210}Po in surface air aerosols has been developed. This procedure of validation could be applied by many other research teams worldwide.

Considering the facts previously mentioned, this study aims to develop an experimental validation methodology at laboratory scale to prove experimentally the validity of the equations to determine ^{210}Pb and ^{210}Po in air, addressing different activity ratios between ^{210}Pb and ^{210}Po. In addition, an exhaustive sensitivity analysis of the ^{210}Po concentration precision with several variables such as sampling time, time elapsed between sampling start and ^{210}Po self-deposition, and ^{210}Po/^{210}Pb activity ratio has been carried out. It is worth noting that despite this sensitivity analysis is essential for an optimized measurement of ^{210}Po in air.

2. Materials and methods

2.1. Materials

The methodology developed in this work has been applied in atmospheric samplings carried out at “Campus El Carmen” in Huelva city (Southwestern Spain). The samples were collected in a building roof 6 m above ground.

During the period of study, from March 25th to July 15th, 2022, 30 samplings were carried out with three PM10 samplers under an air flow of 68 m^3 h^{-1} (U.S. EPA, 1999, p. 30), employing fiberglass filters (QF20 Schlicher & Schuell, 25.4 cm × 20.3 cm). These filters were first treated in an oven at 200 °C for 4 h to remove humidity and any volatile compounds. Filters were weighed before and after the sampling to calculate the mass collected during the sampling period. A control filter was used to account to variation in mass due to humidity changes in the lab (Barba-Lobo et al., 2022).

In several of the experiments carried out in this work two certified materials for ^{210}Pb and ^{210}Po (W2) and ^{209}Po (Y1) activities are

Table 1
Characteristics of each liquid standard (codes W2 and Y1) employed in this study.

Code	Medium	^{210}Pb (mBq g^{-1})	^{210}Po (mBq g^{-1})	^{209}Po (mBq g^{-1})	Reference date
W2	2M HNO_3	3600 ± 144	2800 ± 51	N.D.	February, 2015
Y1	2M HCl	N.D.	N.D.	266.0 ± 1.0	February, 2023

N.D.: not detected.

used. In Table 1 are shown the main characteristics (see Table 2).

W2 was used in the validation procedure described in Section 2.4, whereas Y1 is the dissolution containing the tracer (^{209}Po, $T_{1/2}$ = 102 years) used for determining the chemical yield in the radiochemical method for the measurement of ^{210}Po through alpha-particle spectrometry.

For the ^{210}Pb measurement carried out by gamma-ray spectrometry for volumetric samples, a cylindrical plastic geometry was employed with a radius of 17.3 mm and a height of 50.0 mm. The efficiency calibration can be consulted in detail in Barba-Lobo et al. (2021).

2.2. Radiometric techniques for ^{210}Pb and ^{210}Po measurements

Once the filter has been collected is divided in two halves: one for gamma spectrometry, and another one for alpha-particle spectrometry. For this technique, a radiochemical method is applied to the filters. This process involves dissolution of the corresponding section of the filter, isolating the isotopes of Po and depositing them on silver disc for its later alpha measurement. More information about the alpha measurement process and its validations can be found in (Gázquez et al., 2023).

Alpha spectrometry was performed using a ORTEC system with eight integrated Octete PC PLUS chambers (450 mm^2 ion-implanted silicon PIPS detectors). Each chamber was vacuum-sealed and included a vacuum gauge, a variable detector bias supply, a preamplifier, shaping amplifier, a pulse stretcher, a bias amplifier, a test pulse generator, and a leakage current monitor. For each detector the energy resolution was measured, resulting in a maximum full width half maximum (FWHM) of 20 keV for each alpha emission energy of ^{241}Am. The detection efficiency was approximately 25% for distances around 10 mm. The total background counting rate was less than 30 counts per day, being for the ^{210}Po peak about $2{\cdot}10^{-5}$ cps. The "Maestro" software was used to control the spectrometer and analyse and evaluate data.

For gamma measurements, a high-purity coaxial germanium gamma spectrometer (model GX3519) provided by Canberra with an extended range (XtRa) equipped with a carbon fiber and epoxy resin window (0.5 mm thick) has been used. The detector was shielded with three consecutive layers: a thin layer of Cu and then, of Pb and, finally, a 15 cm Fe layer. The detector resolution (FWHM) is 1.74 keV at 1.33 MeV and 0.88 keV at 122 keV, with a relative efficiency of 38.4% at 1332 keV (^{60}Co), relative to a 3" × 3″ NaI(Tl) detector. Genie 2000 software from Canberra was used for data acquisition and analysis of the measurements.

The full energy peak efficiency (*FEPE*) calibration of the gamma spectrometer system to measure the atmospheric filters was done following the guidelines stablished in previous works (Barba-Lobo & Bolívar, 2022, 2023). For this, it was necessary a previous preparation of the atmospheric filters using calibration standards as detailed explained by Barba-Lobo and Bolívar (2023). The *FEPE* at 46 keV (^{210}Pb) was possible to be obtained by simplified version of Eq. (9) since the only needed decay correction for ^{210}Pb was that related to the time elapsed between the reference dates of the calibration standards and the counting of the prepared filters (Barba-Lobo & Bolívar, 2023). Quality control of the measurements, both for alpha-particle and gamma-ray spectrometry, is routinely carried out by intercomparisons exercises organized by the Spanish Nuclear Safety Council.

2.3. Equations for the calculations of concentrations

To calculate ^{210}Po activity concentration in air, it is necessary to consider the evolution of its activity deposited onto the filter since the beginning of sampling until its measurement by alpha-particle spectrometry. An representation of the measurement process time progression is shown in Fig. 1.

The first critical points are the start (t_0) and end (t_1) of the sampling. During this stage the activity of ^{210}Po is collected on the filter during the sampling period, $\Delta t_s = t_1 - t_0$. After the sampling end (t_1), for the determination of ^{210}Po the radiochemical method is applied ending with the self-deposition (t_2), and then ^{210}Po is measured by alpha-particle spectrometry during a specific counting duration, $\Delta t_c = t_4 - t_3$.

To calculate the ^{210}Po concentration, the methodology employed in Barba-Lobo et al. (2023) was followed. In this case we have considered that ^{210}Bi is near to secular equilibrium with ^{210}Pb (Marley et al., 1999). A more detailed explanation of the deduction of the equations is provided in Supplementary Material.

The activities of ^{210}Pb and its daughter, ^{210}Po, in the filter just after sampling can be calculated in function of the respective activity concentrations in the air by using:

$$A^s_{Pb}(t_1) = \phi\, a_{Pb} C^{\Delta t_s}_{Pb} \tag{1}$$

$$A^s_{Po}(t_1) = \phi \left[\frac{a_{Pb}\,\lambda_{Po}}{\lambda_{Po} - \lambda_{Pb}} \left(C^{\Delta t_s}_{Pb} - C^{\Delta t_s}_{Po} \right) + a_{Po} C^{\Delta t_s}_{Po} \right] \tag{2}$$

Table 2
Parameters employed for the sensitivity analysis for each value of Δt_s.

Δt_s				Δt_d				AR										
3	6	10	14	18	22	26	30	0.03	0.06	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
7		10	14	18	22	26	30	0.03	0.06	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

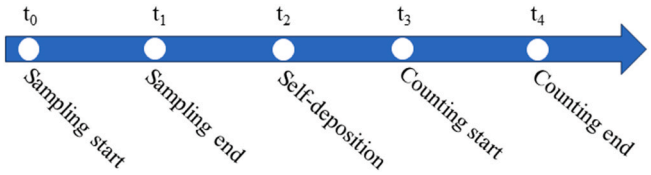

Fig. 1. Idealized timeline of the critical times during the sampling and measurement process for ^{210}Po.

where A^s_{Pb} and A^s_{Po} are the activity (mBq) of ^{210}Pb and ^{210}Po, respectively, deposited onto the filter at the end of the sampling (t_1), ϕ is the air flow ($m^3\,h^{-1}$), a_{Pb} and a_{Po} are the activity concentration in air (mBq m^{-3}) of ^{210}Pb and ^{210}Po, respectively, λ_{Pb} and λ_{Po} are the decay constants (h^{-1}) of ^{210}Pb and ^{210}Po, respectively, and $\Delta t_s = t_1 - t_0$ is the sampling duration (h).

Where the terms $C^{\Delta t_s}_{Pb}$ and $C^{\Delta t_s}_{Pb}$ were used to simplify the equations (Barba-Lobo et al., 2023, 2024):

$$C^{\Delta t_s}_{Pb} = \frac{1 - e^{-\lambda_{Pb}\Delta t_s}}{\lambda_{Pb}} \tag{3}$$

$$C^{\Delta t_s}_{Po} = \frac{1 - e^{-\lambda_{Po}\Delta t_s}}{\lambda_{Po}} \tag{4}$$

The ^{210}Po activity existing in the solution used for the Po self-deposition (t_d) can be calculated using the following equation:

$$A_{Po}(t_d) = \frac{\phi\, a_{Pb}\Delta t_s\, \lambda_{Po}}{\lambda_{Po} - \lambda_{Pb}}\left(1 - e^{-\lambda_{Po}\Delta t_{Po}}\right) + \phi\left[\frac{a_{Pb}\,\lambda_{Po}}{\lambda_{Po} - \lambda_{Pb}}\left(\Delta t_s - C^{\Delta t_s}_{Po}\right) + a_{Po}C^{\Delta t_s}_{Po}\right]e^{-\lambda_{Po}\Delta t_{Po}} \tag{5}$$

where Δt_{Po} is the time elapsed between the sampling end and the Po self-deposition.

And from here an explicit formula for ^{210}Po air activity concentration, a_{Po}, can be obtained in function of the measured Po concentration at the self-deposition time:

$$a_{Po} = \frac{\lambda_{Po}\Delta t_s}{1 - e^{-\lambda_{Po}\Delta t_s}}\left\{a_{Po}(t_d)e^{\lambda_{Po}\Delta t_{Po}} - \frac{a_{Po}}{AR}\left[\frac{\lambda_{Po}e^{\lambda_{Po}\Delta t_{Po}}}{\lambda_{Po} - \lambda_{Pb}} - \frac{1 - e^{-\lambda_{Po}\Delta t_s}}{(\lambda_{Po} - \lambda_{Pb})\Delta t_s}\right]\right\} \tag{6}$$

Where the activity ratio, $AR = \frac{a_{Po}}{a_{Pb}}$, was used to simplify the equation. We can also define a ratio between the ^{210}Po activity concentration at self-deposition and in air as:

$$\frac{a_{Po}(t_d)}{a_{Po}} = \frac{(\lambda_{Po} - \lambda_{Pb})e^{-\lambda_{Po}\Delta t_{Po}}}{\left[\lambda_{Po}e^{\lambda_{Po}\Delta t_{Po}} - \frac{1 - e^{-\lambda_{Po}\Delta t_s}}{\Delta t_s}\right]} + \frac{\lambda_{Po}\Delta t_s e^{-\lambda_{Po}\Delta t_{Po}}}{(1 - e^{-\lambda_{Po}\Delta t_s})}\frac{1}{AR} \tag{7}$$

This equation allows to study the behavior of the ^{210}Po activity concentration ratio between self-deposition and sampling as a function of the activity ratio AR.

Using uncertainty propagation in Eq. (6), the uncertainty of the ^{210}Po concentration in air can be obtained as a function of Δt_{Po}, Δt_s, $\frac{a_{Po}(t_d)}{a_{Po}}$, AR, $\sigma_{ra_{Pb}}$ and $\sigma_{ra_{Po}(t_d)}$:

$$\sigma_{aPo} = \frac{\lambda_{Po}\Delta t_s a_{Po}}{(1 - e^{-\lambda_{Po}\Delta t_s})}\sqrt{e^{2\lambda_{Po}\Delta t_{Po}}\left(\frac{a_{Po}(t_d)}{a_{Po}}\right)^2 \cdot \sigma_r^2 a_{Po}(t_d) + \left[\frac{\lambda_{Po}e^{\lambda_{Po}\Delta t_{Po}}}{\lambda_{Po} - \lambda_{Pb}} - \frac{1 - e^{-\lambda_{Po}\Delta t_s}}{(\lambda_{Po} - \lambda_{Pb})\Delta t_s}\right]^2\left(\frac{1}{AR}\right)^2 \cdot \sigma_r^2 a_{Pb}} \tag{8}$$

where $\sigma_{ra_{Pb}}$ and $\sigma_{ra_{Po}(t_d)}$ are the relative uncertainty of the ^{210}Pb concentration in air and the ^{210}Po concentration at the self-deposition moment, respectively.

The activity concentration of ^{210}Pb in the air can be measured directly by gamma-ray spectrometry using the following relation:

$$a_{Pb} = \frac{N_{Pb}\, e^{\lambda_{Pb}\Delta t_{Pb}}}{P_{\gamma Pb}\,\varepsilon_{Pb}\,\phi\, C^{\Delta t_s}_{Pb}\, C^{\Delta t_c}_{Pb}} \tag{9}$$

where N_{Pb} is the net counts obtained for ^{210}Pb by gamma-ray spectrometry, Δt_{Pb} is the time elapsed between the sampling end and the counting start of ^{210}Pb by gamma-ray spectrometry Δt_c is the counting duration, $C^{\Delta t_c}_{Pb} = \frac{1 - e^{-\lambda_{Pb}\Delta t_s}}{\lambda_{Pb}}$ is the correction applied during the counting duration and $P_{\gamma Pb}$ is the gamma emission probability for ^{210}Pb and ε_{Pb} is the full-energy peak efficiency for ^{210}Pb at 46.5 keV.

2.4. Validation procedure

Since it is not possible to find a certified reference material (CRM) to validate the measurement of ^{210}Po concentration in the atmospheric aerosol, a novel and comprehensive procedure has been developed to carry out the validation at laboratory scale for the methodology used to measure ^{210}Po in air. This validation procedure has been divided into 3 different parts (or experiments) as can be

seen in Fig. 2.

The first experiment consists of validating the measurements of ^{210}Po by alpha-particle spectrometry and ^{210}Pb by gamma spectrometry. The second one is developed to check if there is no ^{210}Pb deposited onto the silver disk during the self-deposition of ^{210}Po. Finally, the third experiment is designed to validate the whole methodology used to determine ^{210}Po and ^{210}Pb in surface air aerosols.

Experiment 1: Validation of alpha-particle and gamma-ray spectrometry

The Experiment 1 consisted of measuring the concentrations of ^{210}Pb and ^{210}Po by using gamma-ray spectrometry and alpha-particle spectrometry, respectively, contained in the liquid CRM W2. Thus, the concentrations measured for ^{210}Pb and ^{210}Po are compared with their reference values. This experiment is made to validate the spectrometric techniques employed for the measurement of ^{210}Pb and ^{210}Po in air. For the validation of ^{210}Pb measurements by gamma-ray spectrometry, a known volume of dissolution W2 was directly poured into the cylindrical container employed for the ^{210}Pb measurements with the XtRa detector, using three replicas with codes 1-γ-A, 1-γ-B and 1-γ-C.

For the ^{210}Po measurements by alpha-particle spectrometry, before the self-deposition of Po isotopes onto silver disks, a known volume of dissolution W2 (in 2M HNO_3 medium) is carried to a medium 2M HCl, which is the appropriate medium for the Po self-deposition (Barba-Lobo et al., 2022; Cuesta et al., 2022). For the assessment of the chemical yield for Po isotopes, ^{209}Po was employed (dissolution Y1). The self-deposition of Po isotopes was carried out onto three silver disks, obtaining three replicas with codes 1-α-A, 1-α-B and 1-α-C. Further information about the radiochemical method for Po isotopes can be seen elsewhere (Barba-Lobo et al., 2022; Cuesta et al., 2022).

Experiment 2: Checking the non-deposition of ^{210}Pb onto silver discs during Po self-deposition.

This part of the validation procedure is focused on checking the possible self-deposition of ^{210}Pb onto the silver disks during the self-deposition of Po isotopes. To the best of our knowledge, all previous works on ^{210}Po measurement in air assumed there is no contribution of ^{210}Pb on the ^{210}Po activity concentration once the self-deposition of Po isotopes has been accomplished. Therefore, checking of this assumption is necessary to assure the correct measurement of ^{210}Po.

For this, the XtRa detector was calibrated in efficiency using the same silver disks and geometry than those employed for the self-deposition of Po isotopes. To do this a known volume of dissolution W2 was added onto the silver disks by using a pipette reproducing the same geometry obtained after the self-deposition of Po isotopes. After adding the W2 dissolution, the silver disks were heated in an oven to make it easier the adsorption of W2 dissolution onto the silver disks. Three silver disks were prepared for this efficiency calibration whose codes are 2-γ-A, 2-γ-B and 2-γ-C. The efficiency obtained for this calibration was used in the measurement by gamma-ray spectrometry of the three silver disks previously employed in Experiment 1 (1-α-A, 1-α-B and 1-α-C). In this way, it is possible to observe whether, ^{210}Pb was also self-deposited onto the silver disks during the self-deposition of Po isotopes.

Experiment 3: Consistency of equations for ^{210}Po determination

The main objective of Experiment 3 is to test the methodology consistency (internal validation) for obtaining ^{210}Po activity concentration in surface air aerosols.

The degree of disequilibrium between ^{210}Pb and ^{210}Po in surface aerosols samples is unknown prior to the measurement of these radionuclides. In this experiment, a set of samples with different degrees of disequilibria between both radionuclides are generated from a certified reference material. Then, the whole procedure to determine ^{210}Po activity concentrations is applied to these samples to

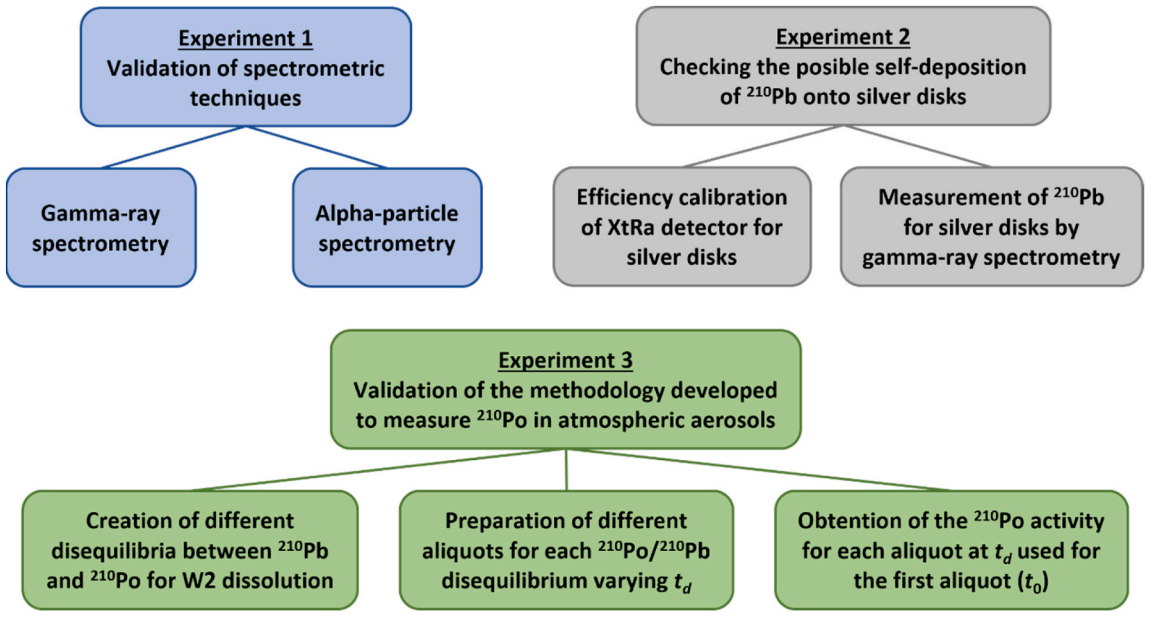

Fig. 2. Scheme of the experiments (Experiments 1, 2 and 3) carried out at the laboratory to validate the methodology developed to determine ^{210}Po in atmospheric aerosols.

compare the results obtained with those expected, allowing us to test the reproducibility of the methodology. In the following paragraphs, the procedure to generate the set of samples with known degrees of disequilibria between ^{210}Pb and ^{210}Po is described in full detail.

Since the self-deposition of Po isotopes onto silver disks was checked to be fully accomplished after at least 4 h of self-deposition duration, if reducing the time of self-deposition to less than 4 h, different degree of disequilibrium in the remaining dissolution can be obtained. In this experiment, three samples with different degree of disequilibrium between ^{210}Pb and ^{210}Po were prepared from W2 dissolution. Three aliquots of solution W2 were self-deposited for time intervals 1.5 h, 2 h and 2.5 h obtaining the remaining solutions M-1.5, M-2 and M-2.5 (M: "dissolution mother"), respectively (see Fig. 3), where the solutions M-1.5, M-2 and M-2.5 are the mother solutions. The volume obtained for each M solution was about 20 mL.

From each of the remaining solutions in the self-deposition (dissolutions M-*i*), 6 aliquots were extracted, obtaining 3 sets of 6 aliquots. After obtaining each aliquot, their volume was increased until about 20 mL adding 2M HCl to proceed with the Po self-deposition (see Fig. 3). It is worth noting that for each set of aliquots, the amounts of the aliquots were carefully taken to assure very similar masses to each other. In this way, the activity concentrations of ^{210}Po are very similar to each other in each of the aliquots (and analogously in the case of ^{210}Pb), i.e., the ^{210}Po activities are similar to each other within each set of samples M-*i* (and analogously occurred for ^{210}Pb). The ^{210}Pb activity concentration was measured by gamma-ray spectrometry in each of aliquots for considering the ^{210}Pb contribution to the ^{210}Po activity concentration. Thus, 18 samples with known ^{210}Pb activities and with similar activities of ^{210}Po (and analogously in the case of ^{210}Pb) within each of the set M-*i* have been generated. For the determination of ^{210}Po in them, each of these aliquots were totally self-deposited (about 4 h) at different moments (t_j), with time intervals (Δt_d) ranging from 0 (t_0) to 20 days (t_5). The 6 aliquots obtained from the dissolution mother M-1.5, were codified as 1.5–0, 1.5–6, 1.5–9, 1.5–13, 1.5–16 and 1.5–20 for $\Delta t_d = t_j - t_0 = 0$, 6, 9, 13, 16 and 20 days, respectively. The dissolutions obtained from dissolution mother M-2 and M-2.5 were codified in a similar way. Thus, a set of 18 samples M-i-j results, where i is the time interval employed for the self-deposition of dissolutions mother (M) and j is the time elapsed from the first self-deposition of sub-samples M-i-j, that is, Δt_d (see Fig. 3). By letting the time pass from the moment of first self-deposition in each set M-*i*, i.e. from $j = 0$, the ^{210}Po activities of each M-*i-j* aliquot must coincide with its corresponding M-*i-0* aliquot when Eq. (6) is applied for considering the proper decay corrections. Since ^{210}Po and ^{210}Pb activities are known in the samples M-*i-j* this procedure can be used to validate the methodology. The M-*i-0* aliquot simulates the filter just after ending the sampling and the consequents M-*i-j* aliquots represent different situations that may occur when measuring that filter sample.

Then, to validate the methodology, the ^{210}Po activity concentrations (a_{Po}) of each M-*i-j* aliquot when decay corrected up to the moment of the Po self-deposition performed for each corresponding M-*i*-0 aliquot (t_0) must coincide with the activity of this last aliquot. Therefore, it was possible to test the reproducibility of the methodology for the ^{210}Po measurement, for each set of aliquots since all the a_{Po} values were obtained at the same moment (t_0) in order to make the comparisons among the a_{Po} obtained values.

3. Results and discussion

3.1. Sensitivity analysis

As previously explained (see Introduction), the precise measurement of ^{210}Po concentration in air can be complicated due to the contribution of ^{210}Pb to the ^{210}Po activity present in the atmospheric filter after starting the sampling of atmospheric aerosols. Therefore, it is really necessary to find the optimal conditions for a precise measurement of ^{210}Po concentration in air. For this, a sensitivity analysis was performed to assess the influence of different variables of interest on the calculation of ^{210}Po activity concentration. Three variables were considered:

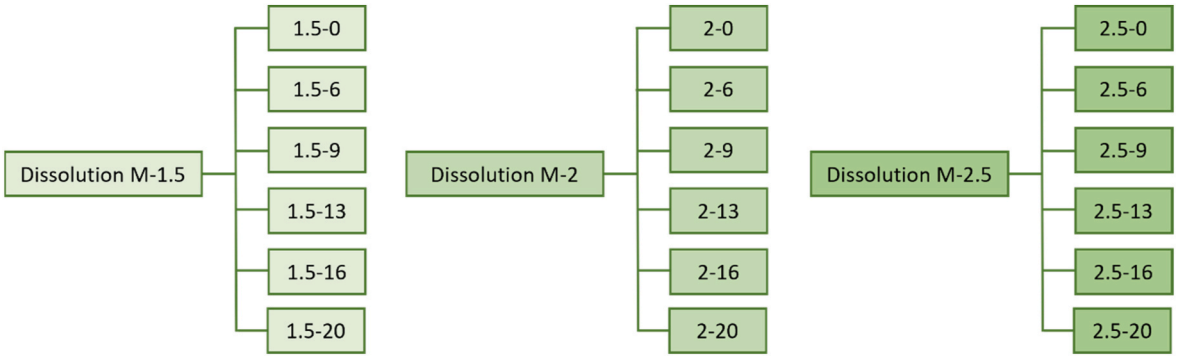

Fig. 3. Aliquots obtained from each dissolution mother (M) prepared using the liquid standard W2. In each dissolution M, a disequilibrium between ^{210}Pb and ^{210}Po was reached by self-depositing it incompletely onto silver disks for 1.5 h, 2 h and 2.5 h, obtaining the dissolutions mother M-1.5, M-2 and M-2.5, respectively. For each dissolution M, six aliquots were obtained varying t_d with respect to the ^{210}Po self-deposition carried out for each first aliquot (t_0), where Δt_d was fixed at 0, 6, 9, 13, 16 and 20 days. Each aliquot was codified as "i-j", where "i" is the ^{210}Po self-deposition duration used to obtain its corresponding M dissolution and "j" is the Δt_d value for which this aliquot was obtained.

- *Sampling time (Δt_s).* Studying this variable allows to estimate an optimal sampling time to collect enough material for the measurements by gamma-ray and alpha-particle spectrometry. In this study we tested 3 and 7 days, the former is a reasonable sampling time period commonly used in the literature and the latter is an extreme long time that could be used to obtain high amounts of particulate matter deposited in the sampling filters.
- *Time elapsed between the sampling start and Po self-deposition (Δt_d).* Due to the decaying nature of ^{210}Pb and ^{210}Po, the self-deposition must be done as soon as possible after the sampling. This variable will help to identify the maximum delays that allow to obtain precise concentrations of ^{210}Po in air.
- *Activity ratio (AR).* As stated previously this parameter defines the relation between the daughter and parent radionuclides, ^{210}Pb and ^{210}Po, respectively. In this study a wide range of values were tested, always considering the limits of what is reasonably found in air.

With the aim of studying the temporal variation of the ^{210}Po activity concentration, the ratio between its activity concentration between the self-deposition and the sampling (air), $\frac{a_{Po}(t_d)}{a_{Po}}$, was used. The importance of this ratio relies on the fact that the higher the activities at the moment of self-deposition, the higher the influence of the ^{210} Pb day on the ^{210}Po activities (see Fig. 4). Thus, as the ^{210}Pb influence on the ^{210}Po activity increases, the precision of the ^{210}Po concentration measurement in air decreases.

In both cases there is an increase of the $\frac{a_{Po}(t_d)}{a_{Po}}$ ratio when the time since sampling to self-deposition increases. This increase is more significant as *AR* is smaller, e.g. 0.03 to 0.2, and is almost negligible for *AR* closed to 1. Additionally, when Δt_d is minimum, the variation in *AR* has a small influence on the $\frac{a_{Po}(t_d)}{a_{Po}}$ ratio in comparison to their effects for larger values of Δt_d. This means that when Δt_d is small, ^{210} Pb decay does not have a significant contribution to the ^{210}Po activity, therefore, $\frac{a_{Po}(t_d)}{a_{Po}}$ ratio is not significantly affected by *AR* variation when Δt_d is small.

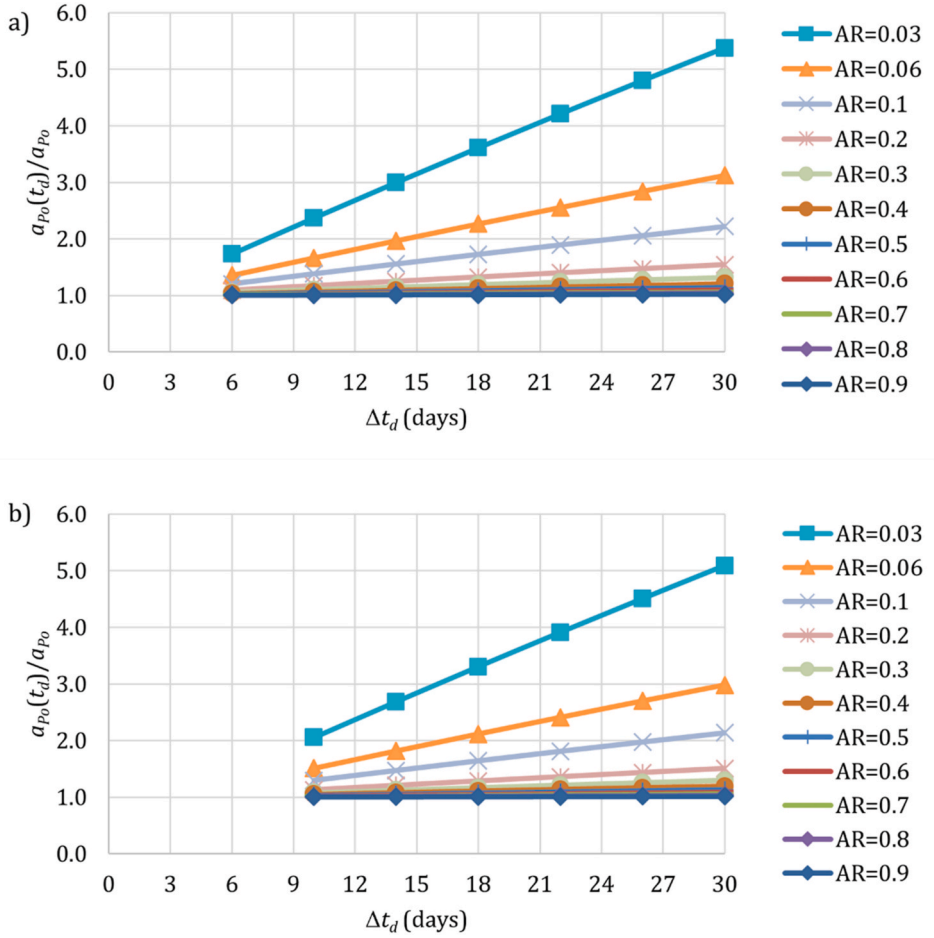

Fig. 4. Behavior of the activity ratio of the ^{210}Po ($A_{Po}(t_d)/A_{Po}$) as function of the time elapsed between the sampling start and the ^{210}Po self-deposition (Δt_d), where $A_{Po}(t_d)$ and A_{Po} are the ^{210}Po total activities existing in the filter at the end of sampling and in the silver disc assuming a 100% of Po recovery, respectively. In addition, the $A_{Po}(t_d)/A_{Po}$ behavior was analyzed for different activity ratios of ^{210}Po/^{210}Pb in air (*AR*), considering different sampling durations: a) $t_s = 3$ days and b) $t_s = 7$ days.

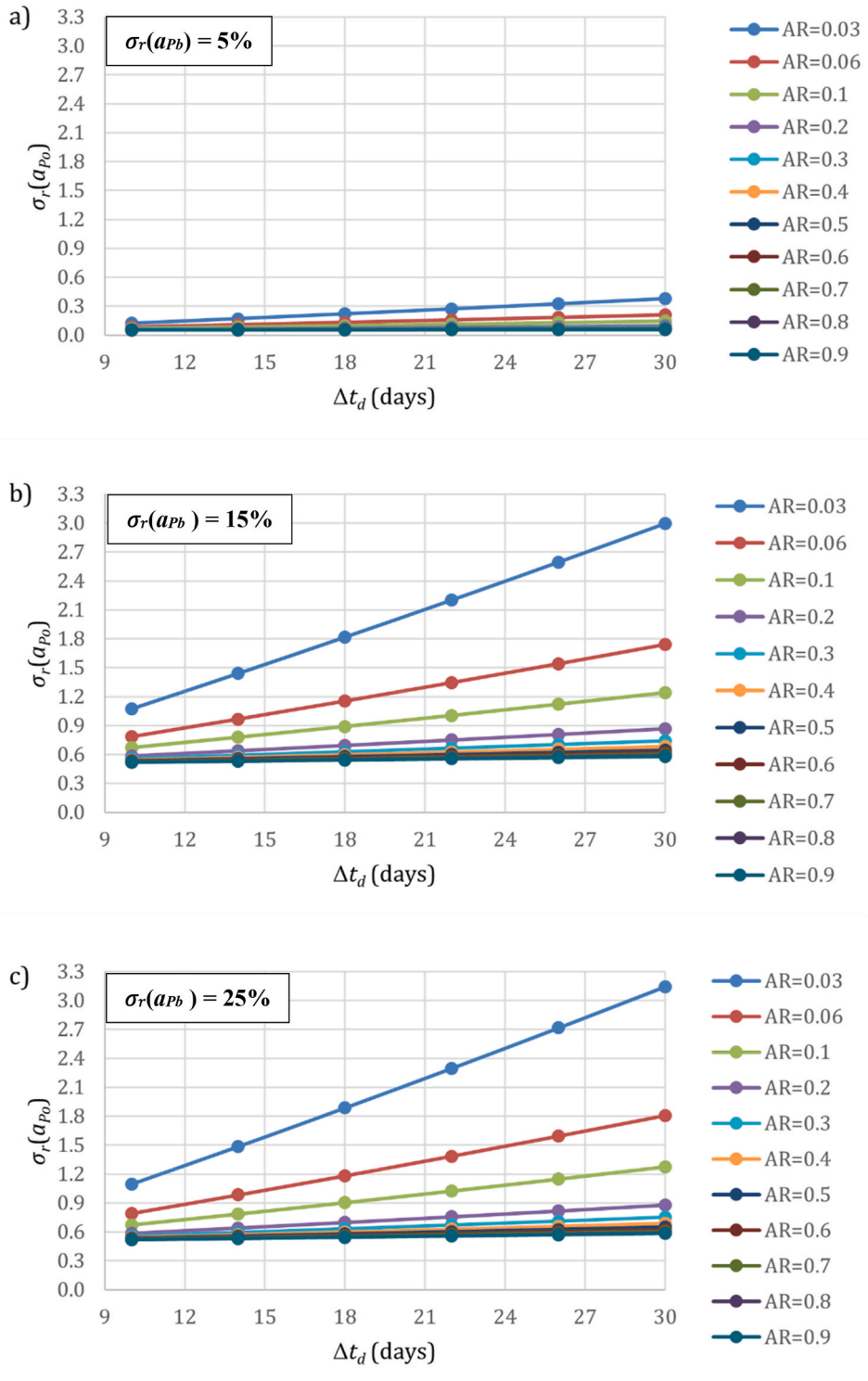

Fig. 5. Behavior of the relative uncertainty of the ^{210}Po concentration in air ($\sigma_r(a_{Po})$) as function of the time elapsed between the sampling start and the ^{210}Po self-deposition (t_d). In addition, the $\sigma_r(a_{Po})$ behavior was analyzed for different activity ratios of ^{210}Po/^{210}Pb in air (AR), fixing sampling duration and the relative uncertainty of the ^{210}Po activity at t_d ($t_s = 7$ days and $\sigma_r(a_{Po}(t_d)) = 5\%$), and varying the relative uncertainty of the ^{210}Pb concentration in air ($\sigma_r(a_{Pb})$): a) 5%, b) 15% and c) 25%.

Additionally, a similar sensitivity analysis was carried out for the uncertainty of the ^{210}Po activity concentration using Eq. (8) and considering a sampling time, Δt_s, of 7 days. The ^{210}Po relative uncertainty at the self-deposition, $\sigma_{ra_{Po}(t_d)}$, was assumed to be constant with a value of 5%, which is an uncertainty often obtained by means of alpha-particle spectrometry in this kind of determinations. On the other hand, for the sensitivity analysis, three different values for the relative uncertainty of ^{210}Pb in aerosols, $\sigma_{ra_{Pb}}$, were considered: a) 5%, b) 15% and c) 25%. The results are shown in Fig. 5.

Like in the previous analysis, the uncertainty increases for higher delays, i.e. higher values of Δt_d, and lower values of *AR*. However, this increase was not constant across the different values tested for $\sigma_{ra_{Pb}}$. An uncertainty of ^{210}Pb concentration of 5% originates significantly lower uncertainties for the ^{210}Po activity in the air when compared to the 15% and 25% cases.

It is noticeable the degree of dependence of the ^{210}Po uncertainty on its parent, ^{210}Pb, uncertainty. Considering the first case, a 5% ^{210}Pb relative uncertainty, the relative uncertainty for ^{210}Po activity concentration would reach up to 38%, obtained for $AR = 0.03$, and $\Delta t_d = 30$ *days*. Even though this is already high, it appears small when compared with the 15% and 25% cases, where values as high as 315% were reached for the same *AR* and Δt_d values. This shows that the ^{210}Pb relative uncertainty during the sampling is a critical factor that needs to be minimized to obtain reliable and accurate measurements of ^{210}Po. As general conclusion, to point out that ^{210}Po concentration increases critically according to the *AR* decreases, fact due to the relative contribution of ^{210}Pb in relation to ^{210}Po coming from the air is higher.

Typical values of *AR* would be between 0.1 and 0.2, as reported in the literature (Lozano et al., 2013). Considering the uncertainty ranges described in Figs. 5a), ^{210}Po relative uncertainties as low as 10% could be achieved for delays between sampling and self-deposition under 18 days, which is reasonable by current standards.

3.2. Validation

In this Section, the results obtained from the different experiments (Experiments 1, 2 and 3) of the validation procedure developed in Section 2.4 are shown.

3.2.1. Experiment 1

Regarding the Experiment 1, in Table 3 are shown the activity concentrations of ^{210}Po and ^{210}Pb obtained by alpha-particle spectrometry and gamma-ray spectrometry, respectively, for the three replicas of the liquid standard W2 (1-α-A, 1-α-B and 1-α-C, and 1-γ-A, 1-γ-B and 1-γ-C, respectively) at the ^{210}Po self-deposition moment (t_d). The reference ^{210}Po and ^{210}Pb activity concentrations at that moment as well as the z_{score} for each case are also shown. As it can be seen from this table, the activity concentrations obtained for ^{210}Pb and ^{210}Po were all of them statistical compatible with the reference concentrations for all the replicas, achieving all z_{score} values less than 2. Therefore, from the results obtained for Experiment 1, a good external validation for both spectrometric techniques (gamma-ray spectrometry and alpha-particle spectrometry) has been proven.

3.2.2. Experiment 2

In the case of the Experiment 2, it was necessary to carry out a previous efficiency calibration in order to be able to quantify the fraction of ^{210}Pb self-deposited onto the silver disks during the Po self-deposition. Thus, in Table A.1 (in Supplementary Material), it is possible to find the full-energy peak efficiencies (*FEPEs*) obtained at 46 keV (^{210}Pb) for the three silver disks (2-γ-A, 2-γ-B and 2-γ-C) prepared for the efficiency calibration by gamma-ray spectrometry, obtaining an average *FEPE* of 0.342 ± 0.007 at 46 keV. This average *FEPE* was applied to the measurement of ^{210}Pb in the three replicas (1-α-A, 1-α-B and 1-α-C) measured by alpha-particle spectrometry in Experiment 1. Thus, for none of these three replicas, the ^{210}Pb concentration reached the minimum detectable activity concentration (*mda*) (see Table A.2 in Supplementary Material). Therefore, the ^{210}Pb self-deposition during the ^{210}Po self-deposition onto the silver disks can be completely neglected (<5% is self-deposited taking the minimum activity detectable).

3.2.3. Experiment 3

Regarding the Experiment 3, to properly test the reproducibility of the methodology employed to measure ^{210}Po in air, the ^{210}Po

Table 3
Experiment 1 of the validation for the methodology developed for the ^{210}Po measurement. Activity concentrations of ^{210}Po and ^{210}Pb obtained by alpha-particle spectrometry and gamma-ray spectrometry, respectively, for three replicas of the liquid standard W2 (codes 1-α-A, 1-α-B and 1-α-C, and 1-γ-A, 1-γ-B and 1-γ-C, respectively) at the ^{210}Po self-deposition moment (t_d). The reference ^{210}Po and ^{210}Pb activity concentrations at that moment were 2800 ± 51 mBq g^{-1} and 3600 ± 144 mBq g^{-1}. The obtained z_{score} was also shown for each case.

^{210}Po	1-α-A	1-α-B	1-α-C
$a_{Po}(t_d)$ (mBq g^{-1})	2904	2883	2957
$\sigma(a_{Po}(t_d))$ (mBq g^{-1})	33	87	82
z_{score}	1.7	0.8	1.6
^{210}Pb	1-γ-A	1-γ-B	1-γ-C
a_{Pb} (mBq g^{-1})	3501	3571	3750
$\sigma(a_{Pb})$ (mBq g^{-1})	223	158	254
z_{score}	−0.4	−0.1	0.5

activity concentration obtained for each aliquot at the moment of its respective Po self-deposition ($a_{Po}(t_d)$) was corrected by using Eq. (6) to be given at the initial moment (simulating the start time of the "sampling filter") of the initial aliquot ($a_{Po}(t_0)$) of each set of aliquots. In order to make easier the comparison among the $a_{Po}(t_0)$ values obtained for the different aliquots for the same set aliquots, the $A_{Po}(t_0)_{i-j}/ < A_{Po}(t_0) >_i$ activity ratios were calculated for each set of aliquots, where $A_{Po}(t_0)_{i-j}$ is the ^{210}Po activity obtained for each specific aliquot with code "i-j" M-*i*-*j* (i: ^{210}Po self-deposition duration used to obtain its corresponding M dissolution and j: Δt_d value for which this aliquot was obtained) (see Fig. 3), and $< A_{Po}(t_0) >_i$ is the average ^{210}Po activity obtained for each set of aliquots M-*i*. The $A_{Po}(t_0)_{i-j}/ < A_{Po}(t_0) >_i$ activity ratios were shown in Fig. 6 for each set of aliquots, that is, for the 6 aliquots obtained from each M dissolution (M-1.5, M-2 and M-2.5).

As can be seen in Fig. 6, the $A_{Po}(t_0)_{i-j}/ < A_{Po}(t_0) >_i$ activity ratios is statistical compatible with 1 in general for the three sets of aliquots, proving the good internal validation (or reproducibility) of the methodology employed to measure ^{210}Po when varying Δt_d from 0 to 20 days. All the $a_{Po}(t_d)$ and $a_{Po}(t_0)$ values obtained for each aliquot and the average $a_{Po}(t_0)$ calculated for each set of aliquots can be found in Table A.2 (in Supplementary Material). In Table A.2, it is possible to observe that the relative standard deviations of the average $a_{Po}(t_0)$ ranges between 1.2% and 2.6% for the three sets of aliquots, which proves the good internal validation of the methodology. Furthermore, as it can also be seen in Table A.2, the average $a_{Po}(t_0)$ values obtained for the first two sets of aliquots (M-1.5 and M-2 dissolutions) were 323 ± 4 mBq g^{-1} and 335 ± 7 mBq g^{-1}, respectively, which are statistical compatible between them. However, in the case of the third set of aliquots (M-2.5 dissolution), the average $a_{Po}(t_0)$ value (224 ± 6 mBq g^{-1}) is significantly lower than the two previously mentioned. This result could be expected because for 2.5 h of Po self-deposition, the fraction of Po isotopes self-deposited is much higher than in the other cases and, therefore, the ^{210}Po activity concentration present in the dissolution mother M-2.5 significantly decreases.

Moreover, the ^{210}Pb activity concentration obtained for each aliquot (a_{Pb}) as well as the average a_{Pb} calculated for each set of aliquots can also be found in Table A.2. Thus, in the case of the a_{Pb}, it is also possible to observe a good reproducibility, obtaining very similar a_{Pb} values within the same set of aliquots and relatively low standard deviations of the average a_{Pb} (less than 1%). In addition, note that the ^{210}Pb activity concentrations obtained for the three sets of aliquots do not show significant differences. This agrees very well with the expected behavior since the ^{210}Pb was not self-deposited onto the silver disks when the three dissolutions mother (M-1.5, M-2 and M-2.5) were obtained. Consequently, the ^{210}Pb activity concentrations must be similar to each other since the ^{210}Pb activity used to prepare the M-1.5, M-2 and M-2.5 dissolutions were also similar to each other.

3.3. Applications

The methodology developed in this work has been applied to the determination of ^{210}Pb and ^{210}Po activity concentrations in air aerosols from the Campus de El Carmen (Huelva) during a 5-month sampling campaign from March to July 2022 by using two air samplers. The activity concentrations of ^{210}Pb and ^{210}Po in surface air aerosols in Fig. 7. In addition, they can also be found in Table A.3 (in Supplementary Material).

The ^{210}Pb activity concentrations in surface air aerosols during sampling campaign range from 0.135 to 0.833 mBq m^{-3} with an average of 0.31 ± 0.04 mBq m^{-3}. Relative standard uncertainties in ^{210}Pb activity concentrations remain below 10% ranging between 5% and 8% (Fig. 7).

From Fig. 7 a significant variation in the activity concentration of ^{210}Pb and ^{210}Po in the surface air aerosols can be observed during the sampling months, with differences up to two or more times the monthly average value. The maximum values for ^{210}Pb activity concentrations in this sampling campaign are observed during July. In the case of ^{210}Po, the higher activities concentrations are obtained during March.

The ^{210}Po activity concentrations range from 1.45·10^{-3} to 0.054 mBq m^{-3} with an average of 0.009 ± 0.002 mBq m^{-3}. As can be seen from Fig. 7, the relative uncertainties of the ^{210}Po activity concentrations were ranged from 6% to 163%. Relative uncertainties of ^{210}Po activity concentrations values exceeding 100% are found in 4 cases; values between 50% and 100% are found in 4 cases and

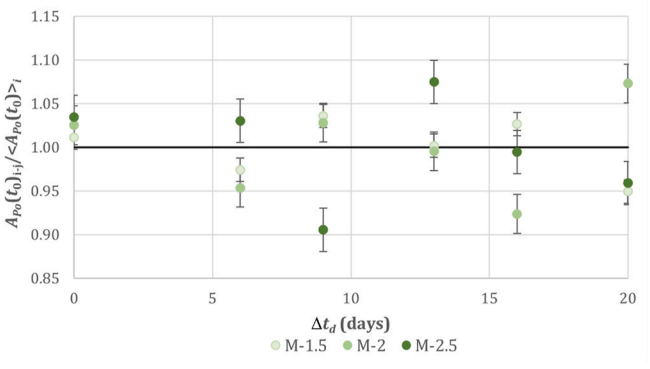

Fig. 6. Activity ratios of the ^{210}Po ($A_{Po}(t_0)_{i-j}/<A_{Po}(t_0)>_i$) obtained for each aliquot by alpha-particle spectrometry at t_0 (time of the ^{210}Po self-deposition for the first aliquot of each set of aliquots).

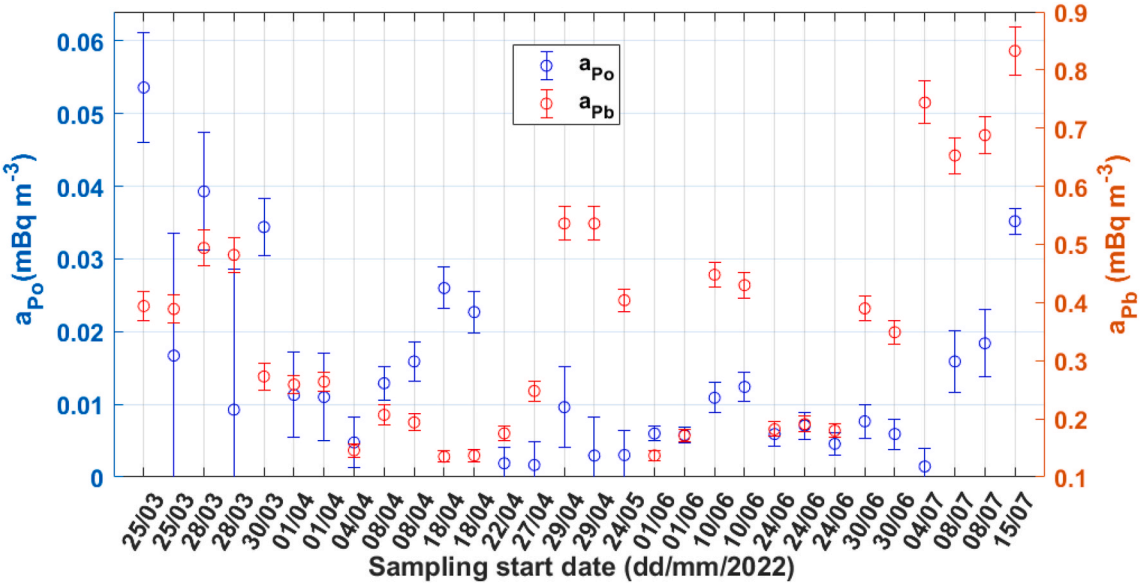

Fig. 7. Lead-210 (a_{Pb}) and ^{210}Po (a_{Po}) activity concentrations in surface air aerosols during sampling campaign. Note that a_{Pb} and a_{Po} are provided in different scales.

values between 20% and 50% in 7 cases. The values of relative uncertainties in ^{210}Po activity concentrations which could be considered as acceptable for experimental determinations, i.e. lower than 10%, are found in only 6 cases out of 30 and ranging between 10% and 15% in 5 cases. On principle, these values of uncertainties so high could be attributed to several factors related to experimental procedure, or environmental conditions during sampling which could lead to low ^{210}Po activity concentrations increasing the lack of precision in the measurement. A possible source of such a high imprecision in the determination of ^{210}Po activity concentrations in surface air aerosols is a delay in the time of ^{210}Po self-deposition as it will be shown further below.

In Table 4, average ^{210}Pb (a_{Pb}) and ^{210}Po (a_{Po}) activity concentrations in atmospheric aerosols obtained in different sites worldwide are shown just to compare with the values obtained in this work. Mean atmospheric aerosol residence time (T_r) was also included in

Table 4
Comparison between the average ^{210}Pb and ^{210}Po activity concentrations in atmospheric aerosols (a_1 and a_3, respectively) obtained in this work and other previous studies. In addition, the atmospheric aerosol residence time (T_r) was also included in this comparison. N.M.: not measured.

Reference	a_{Pb} (mBq m^{-3})	a_{Po} (mBq m^{-3})	T_r (days)	Ubication
Arimoto et al. (2004)	0.2	0.0220 ± 0.0011	N.M.	South Pole
Baskaran and Shaw (2001)	0.22–1.02	0.0–0.152	12–32	Alaska
Dlugosz et al. (2010)	0.516 ± 0.115	0.057 ± 0.011	N.M.	Lodz, Poland
Dueñas et al. (2004)	0.51	0.045–0.070	N.M.	Málaga, Spain
Gavini et al. (1974)	N.M.	N.M.	2-320 (average: 40)	Arkansas, USA
Sarin (2012)	0.5–4.8	0.002–0.28	2-68 (average: 29)	Kampur, India
Lehmann and Sittkus (1959)	N.M.	N.M.	20	Freiburg, Germany
Lozano et al. (2013)	0.53 ± 0.07	N.M.	N.M.	Huelva, Spain
Marley et al. (1999)	N.M.	N.M.	33–66	Illinois, USA
McNeary and Baskaran (2007)	1.07	0.072	6-61 (average: 21)	Michigan, USA
Peirson et al. (1966)	N.M.	N.M.	40	Milford Haven, Wales
Persson and Holm (2011)	0.26	0.007	N.M.	Antarctica, Arctic Ocean, and coastline of Siberia
Poet et al. (1972)	0.15–0.78	0.002–0.052	11-77 (average: 24)	Colorado, USA
Yi et al. (2007)	N.M.	0.03–0.21 (average: 0.11)	N.M.	Xiamen, China
This work	0.135–0.833 (average: 0.31 ± 0.04)	0.001–0.054 (average: 0.009 ± 0.002)	2-55 (average: 11 ± 2)	Huelva, Spain

this table.

As it can be seen from Table 4, the ^{210}Pb activity concentrations obtained in this work are within the range provided for other authors in different sites. On the other hand, ^{210}Po activity concentrations determined in different sites show a high range of variability being the minimum 0.007 mBq m^{-3} those obtained in Antarctica, Arctic Ocean, and coastline of Siberia by Persson and Holm (2014) and several values obtained in Alaska by Baskaran and Shaw (2001). As it was the case of ^{210}Pb, the ^{210}Po activity concentrations obtained in surface air aerosols in this work are within the range provided for other authors in different sites.

The value reported by Lozano et al. (2013) for the site analyzed in this study is compatible with our result at 95% confidence level. The average value obtained by Lozano et al. (2013) for ^{210}Pb activity concentrations higher than that obtained in this work can be explained due to the short-term variability in ^{210}Pb activity concentrations depending on the provenance of the air masses of different origin arriving at this area. It has been shown that the low values of ^{210}Pb are strongly linked to air masses from the Atlantic Ocean, whereas air masses that have a clear continental influence, such as the Iberian Peninsula and north of Africa, are associated with the highest values of ^{210}Pb activity concentrations (Lozano et al., 2011, 2013). Additionally, high levels of ^{210}Pb during summer and low levels in winter were generally found in this sampling site (San Miguel et al., 2019), likely reflecting the differing rates of ^{222}Rn emanation from soil during winter (wet soil conditions) and summer (dry soil conditions) (Ioannidou et al., 2005).

Fig. 8 shows the ^{210}Po/^{210}Pb activity ratio (*AR*) in surface air aerosols determined during the sampling campaign, which can also be found in Table A.3 (in Supplementary Material).

The ^{210}Po/^{210}Pb activity ratio ranges between $1.95{\cdot}10^{-3}$ and 0.19 with an average value of $3.0{\cdot}10^{-2}$. As it can be seen from this figure, the maximum of ^{210}Po/^{210}Pb activity ratio is obtained on April 18th whereas the minimum is registered on July 4th. The range of ^{210}Po/^{210}Pb activity ratio is in good agreement with those reported in the literature (Arimoto et al., 2004; Baskaran & Shaw, 2001; Dueñas et al., 2004; Kirpa Ram & Sarin, 2012; McNeary & Baskaran, 2007). The relative uncertainties in ^{210}Po/^{210}Pb activity ratios are mainly due to the contribution of ^{210}Po. The lower the values for ^{210}Po/^{210}Pb activity ratios, the higher the uncertainties for this activity ratio are obtained. Furthermore, these values are obtained for those cases in which relative uncertainties in ^{210}Po activity concentrations are higher than 100%.

Fig. 9 shows the relative uncertainty of the ^{210}Po concentration in surface air aerosols determined in this sampling campaign, $\sigma_r(a_{Po})$, as a function of the time elapsed between the sampling start and the ^{210}Po self-deposition, Δt_d.

As can be seen from Fig. 9, the relative uncertainties of ^{210}Po exceed 50% when Δt_d is longer than 20 days. The maximum values of ^{210}Po relative uncertainties are about 200%. Such high values in the relative uncertainties of ^{210}Po activity concentrations do not guarantee acceptable accuracy of the measurements. These maxima are obtained when elapsed time between sampling and self-deposition of ^{210}Po exceeds 20 days, whereas the minimum value of ^{210}Po relative uncertainty, around 11%, is obtained when that time interval is 12 days.

According to the previous sensitivity analysis and considering that for this sampling the average *AR* (^{210}Po/^{210}Pb) is 0.03 and ^{210}Pb relative uncertainties are 6%, to keep relative uncertainties in ^{210}Po activity concentrations in surface air aerosols below 25% is recommended working with a maximum time span between sampling and self-deposition of 20 days.

In Fig. 10, the mean atmospheric aerosol residence time (T_r) obtained in the sampling campaign carried out from March 2022 to July 2022 is depicted. In addition, they can also be found in Table A.3 (in Supplementary Material).

As it can be seen from Fig. 10, the mean atmospheric residence time is lower as the climate in the area becomes warmer. As it was

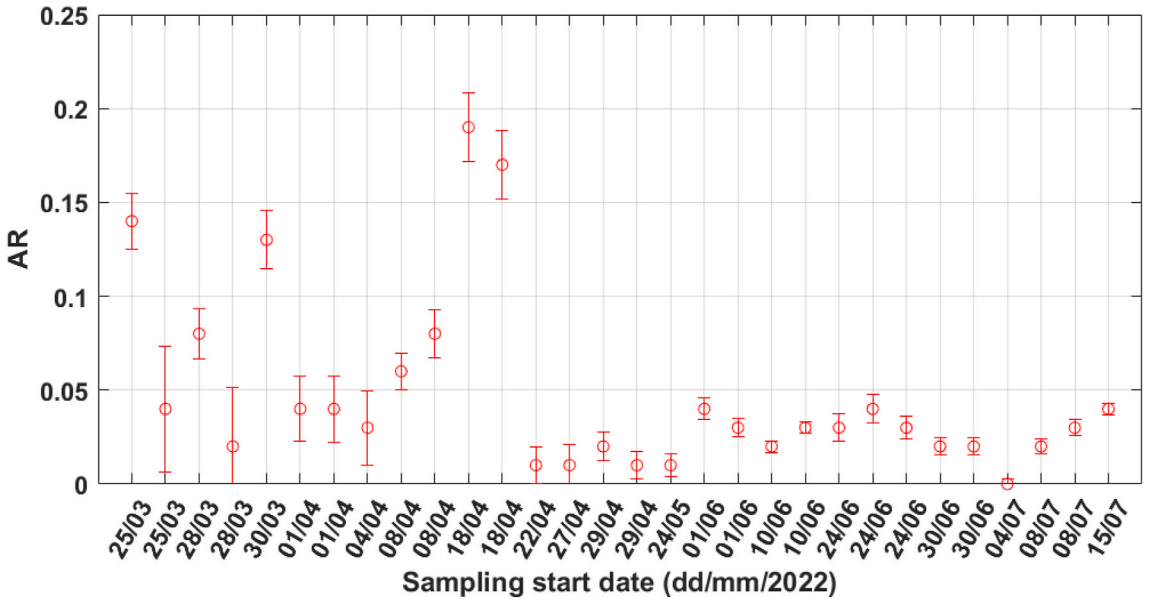

Fig. 8. Activity ratio (*AR*) of ^{210}Po/^{210}Pb in surface air aerosols from March 2022 to July 2022.

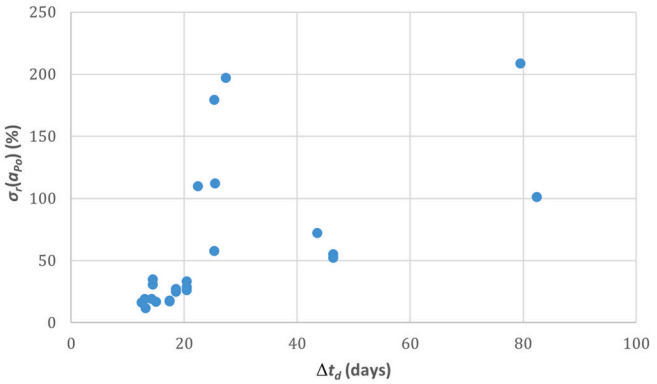

Fig. 9. Relative uncertainty of the ^{210}Po concentration in air, $\sigma_r(a_{Po})$, as a function of the time elapsed between the sampling start and the ^{210}Po self-deposition, Δt_d, where the sampling duration, Δt_s was ranged from 3 days to 5 days.

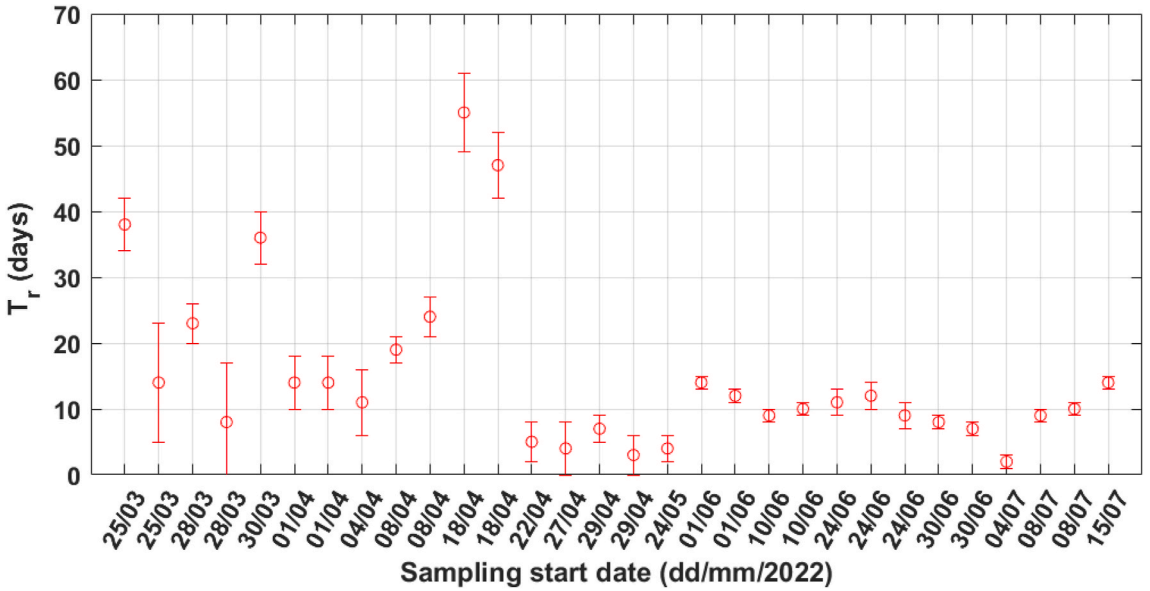

Fig. 10. Mean atmospheric aerosol residence time (T_r) obtained during sampling campaign in this work.

previously commented there are several factors that may influence the ^{210}Pb and ^{210}Po activity concentrations in surface air aerosols of this area and consequently, the mean atmospheric residence time calculated from this pair of radionuclides.

4. Conclusions

In this study, a novel and comprehensive methodology was developed to validate the ^{210}Po measurements in air aerosols by alpha-particle spectrometry. The main conclusions of this study were:

1. From the sensitivity analysis of the relative uncertainty of ^{210}Po concentration in air, $\sigma_r(a_{Po})$, the time elapsed between the sampling start and ^{210}Po self-deposition, Δt_d, was found to be $\leq$ 18 days to achieve $\sigma_r(a_{Po})$ about 10%.
2. With respect to the validation procedure, both spectrometric techniques (alpha-particle spectrometry and gamma-ray spectrometry) were externally validated by using a liquid certified reference material. Moreover, it was proved that the ^{210}Pb is not self-deposited onto the silver disks during the ^{210}Po self-deposition. In addition, the consistency (internal validation) of the methodology employed for the ^{210}Po measurement was comprehensively tested varying Δt_d for several aliquots taken from dissolutions where different secular disequilibria between ^{210}Pb and ^{210}Po.
3. The methodology for the ^{210}Pb and ^{210}Po measurement was applied to 30 atmospheric aerosols filters, obtaining ^{210}Pb and ^{210}Po concentrations in air (averages: 0.31 $\pm$ 0.04 mBq m^{-3} and 0.009 $\pm$ 0.002 mBq m^{-3}, respectively) and atmospheric aerosol residence times (average: 11 $\pm$ 2 d) that agreed with other previous works. Moreover, for the obtention of a relatively good precision

for the measurement of ^{210}Po in air ($\sigma_r(a_{Po}) \leq 25\%$), the Δt_d needed to be less than about 21 days, which is very consistent with the results obtained in the sensitivity analysis carried out for the ^{210}Po concentration precision.

CRediT authorship contribution statement

A. Barba-Lobo: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **E.G. San Miguel:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **J.P. Bolívar:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jaerosci.2024.106469.

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