



A simple and precise methodology to determine particulate matter mass in atmospheric filters; validation and application cases

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ABSTRACT

In the past decades, particulate matter (PM) measurements have been used extensively in atmospheric sciences, as it allows studying the evolution of tracers for different atmospheric processes and the effects of atmospheric pollution on human health. However, measuring PM mass requires a constant control of the laboratory conditions due to its capacity to absorb humidity. For this reason, this study was focused on developing a novel, simple and precise methodology to determine the corrections of the filter mass due to humidity changes. The control and corrections are possible using a “control filter”, which is always adapted to the environmental conditions of the laboratory. To check the consistency of this method, it was proved that the mass of any problem filter and that of the control filter behave in a very similar way. This allows quantifying the mass changes of any problem filter by using the control filter, where the problem filters and the control filter must have the same chemical composition and dimensions. To validate this methodology, a comparison was made between the methodology proposed in this study (Method-1) and the one proposed by the EPA (Method-2), which is generally applied. The particulate matter mass (m) was obtained for a problem filter for different weights, achieving similar values using both methods. However, Method-1 still provided reliable mass measurements for relative humidities very different from 50%, even as low as 18%. It was also proved that the adsorption or loss of water by the particulate matter can be neglected, since m is much smaller than the blank filter mass. Method-1 was also employed in several samplings carried out using three PM₁₀ samplers to determine contaminants, such as ⁷Be and ²¹⁰Pb, obtaining a good agreement between all particulate masses and activities measured by the three samplers for all samplings.

1. Introduction

Over the years, particulate matter has proved to be very useful to understand atmospheric pollution and its effects on air quality and global climate (Davidson et al., 2005; Fuzzi et al., 2015; Lu et al., 2016; Ouyang, 2013). Fine particulate matter pollution can generate human health problems, especially those related to the cardiorespiratory system (Dominici et al., 2006; Pope et al., 2009). In addition, the assessment of particulate matter concentrations can be very valuable to research the evolution of certain infectious diseases, such as the clear and recent example of the SARS-CoV-2 virus (Mehmood et al., 2021-a; Mehmood et al., 2021-b; Paez-Osuna et al., 2022). Particulate matter is also helpful to quantify trace metals (e.g., As, Cu, Fe, etc.) associated with

atmospheric pollution (Penezic et al., 2021; Sharma et al., 2020; Wadinga et al., 2020). Furthermore, the most relevant contaminants related to particulate matter include both natural and anthropogenic radionuclides, which can be used as tracers of atmospheric processes or in environmental radiological control (He and Gao, 2021; Hong et al., 2011; Hu et al., 2010; Sykora and Froehlich, 2009).

There are two main magnitudes related to the determination of contaminants: the contaminant concentration given per volume unit and that given per mass unit (a_v and a_m , respectively). The former can be employed to assess the exposure to the contaminants of interest. However, a_v cannot provide information about the origin of the contaminant source. Therefore, the second concentration type (a_m) is useful, as it allows determining the origin of the contaminant source (Cesari et al.,

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2017). Consequently, a precise determination of the particulate matter mass is needed in order to correctly study the contaminants present in the environment.

Regarding the atmospheric natural radionuclides, it is necessary to highlight two of them which are of great interest: ^7Be and ^{210}Pb . ^7Be (half-life = 53.1 days) is generated in the stratosphere and thus has been widely used to determine residence times (T_r) of atmospheric processes in the order of 0.3–3 years (Bondietti et al., 1988; Ceballos et al., 2016; Lujanienė et al., 1997; Papastefanou and Ioannidou, 1996; Yu and Lee, 2002). ^{210}Pb (half-life = 22.3 years) is supplied into the atmosphere by the ^{222}Rn decay contained in the atmospheric air (Poet et al., 1972; Tokieda et al., 1996), after ^{222}Rn exhalation from surface soils. Due to its short half-life (3.82 days), most of the ^{222}Rn only reaches the tropopause. Its T_r in the troposphere is relatively short (several weeks), making it useful as a tracer for air masses that move regionally.

Considering the abovementioned facts, the accurate determination of the particulate matter mass is essential in the study of atmospheric processes, for which atmospheric filters are used. Therefore, the mass deposited on the filter should be measured with as low uncertainty as possible. The main aim of this study was to develop a novel, simple and precise methodology to determine the particulate matter mass deposited on atmospheric filters, avoiding the corrections due to humidity changes, as well as the usage of equipment to control and measure the humidity (Düsing et al., 2019; Lozano et al., 2011; Montgomery et al., 2015). The new methodology is based on the use of a “control filter” to correct the mass variation of the problem filter due to the different humidity values recorded during its mass measurement before and after the sampling. This method was validated by comparing it with that proposed by the EPA (Environmental Protection Agency), which is applied in most studies.

2. Materials and methods

2.1. Materials

The aerosol samplings in “El Carmen” (Huelva, Spain) were carried out using three PM_{10} high-volume samplers: two samplers provided by MCV (PM10-1 and PM10-2), and an Andersen sampler (Andersen). All three samplers operated at a flow of $68 \text{ m}^3 \text{ h}^{-1}$, following the US EPA Compendium Method IO-2.1 (EPA, 1999-a). Quartz fiber filters (QF20 Schleicher and Schuell, $25.4 \text{ cm} \times 20.3 \text{ cm}$) were used. Furthermore, the following experimental equipment was employed to measure and control the relative humidity (RH) of the filters: a sensor provided by Lascar Electronics (model EASYLOG USB, version 7.5.00) and a dehumidifier to measure and control RH , respectively.

^7Be and ^{210}Pb were determined employing a gamma-ray spectrometry system with an extended range high purity germanium detector “XtRa” (model GX3519 provided by Canberra). The XtRa detector has a relative efficiency of 38.4% at 1332 keV (^{60}Co) in relation to a $3'' \times 3''$ NaI (Tl) detector, a full width at half maximum (FWHM) of 1.74 keV and 0.88 keV at 1332 keV and 122 keV, respectively, and a peak-to-Compton ratio of 67.5:1. Moreover, the XtRa detector is connected to a conventional electronic chain to obtain the gamma spectra using the Genie 2000 software.

Then, the calibration in efficiency of the XtRa detector was performed using a certified reference material (CRM) provided by the IAEA (International Atomic Energy Agency). This CRM standard was RGU-1, which only contains natural radionuclides belonging to the ^{238}U -series, with all these radionuclides being in secular equilibrium, where the reference activity concentration was $4940 \pm 15 \text{ Bq kg}^{-1}$ with the uncertainty given at 1 sigma level (IAEA, 1987).

2.2. Methods

2.2.1. EPA methodology

Firstly, in order to remove the impurities contained in the filters, they were heated in a drying oven at $200 \text{ }^\circ\text{C}$ for 4 h. Then, when applying the EPA methodology, it is previously necessary to ensure that the RH and temperature of the laboratory where the filters are handled are $50 \pm 5\%$ and $25 \pm 10 \text{ }^\circ\text{C}$, respectively, according to the instructions provided by EPA, 1999-b.

2.2.2. Methodology developed in this study

Then, a new, simple, and precise methodology was developed in this study to determine the filter mass and the particulate matter mass deposited on the filters during the samplings. This methodology consists in selecting a clean filter, called “control filter” (c), with similar chemical composition and dimensions as those used for measuring, called “problem filters” (p). The control filter is kept inside the laboratory at all times and weighted alongside the problem filters. Consequently, the control filter is always completely adapted to the environmental conditions of the laboratory, and its mass variations due to the relative humidity are similar to those of the problem filters; therefore, with this methodology, it is not necessary to maintain a constant relative humidity in the laboratory (EPA, 1999-b) or to apply corrections based on RH (Lozano et al., 2011). Thus, once a filter is placed inside the laboratory, the estimated time for its complete adaptation to the environmental conditions of the laboratory is approximately 48 h. Moreover, it is necessary to clarify that, in order to apply this methodology, the same heating process for filters previously explained in Section 2.2.1 was followed. The equations, which are employed when applying this methodology, are discussed in Section 3.1.1.

2.2.3. Methodology for XtRa detector efficiency calibration

To carry out the efficiency calibration of the XtRa detector, RGU-1 standard was added to the filters. Then, after measuring the filters by the XtRa, the experimental efficiencies were calculated. To this end, the full-energy peak efficiency (FEPE) was calculated for each gamma emission energy (E_γ) of interest, which are 46.54 keV and 477.60 keV to determine ^{210}Pb and ^7Be , respectively. Thus, the efficiencies obtained at these two energies were 0.156(5) and 0.042(2), respectively.

3. Results and discussion

3.1. Methodologies used to determine the particulate matter mass

In this Section, the equations involved in the particulate matter mass determination are explained for both methodologies analyzed in this work: the methodology developed in this study and the one proposed by the EPA. Let us call them Method-1 and Method-2, respectively.

Thus, in order to obtain m , it is necessary to calculate the uncertainties related to the filter mass before and after carrying out the samplings, that is, for blank and loaded filters, respectively. For this, it was necessary to weigh a blank filter several times (twenty times). Then, an average mass was obtained, which was used to determine the standard deviation. Thus, in Table S1 (in Supplementary Data), it is possible to find the uncertainty corresponding to the blank filter mass, σ_B , which was 0.7 mg. On the other hand, in the case of the uncertainty related to the mass of the loaded filters, σ_{m_T} , it was assumed that it was the same as that obtained for the blank filters, that is, 0.7 mg.

3.1.1. Methodology developed in this study (Method-1)

To apply this methodology, a “control filter” was employed to determine the mass changes, with these changes being quantified by a variable denoted as δ . As was explained in Section 2.2.2, the variations related to the masses of the control and problem filters are expected to be the same, that is, δ has the same value for both cases. Thus, the equation that allows us to determine m when using Method-1 can be

written as follows:

$$m = m_T - m_B - \delta \tag{1}$$

where m_T and m_B are the total masses of the loaded and blank filters, respectively. In addition, δ is the mass change of the control filter due to the RH, which is given by the following equation:

$$\delta = m_c^f - m_c^0 \tag{2}$$

where m_c^0 and m_c^f are the control filter masses when the problem filter is weighted before and after carrying out the sampling, respectively.

Considering that $\sigma_{m_T} \sim \sigma_B$ and taking Eqs. (1) and (2), it is possible to know the uncertainty associated with m when this methodology is applied:

$$\sigma_m^2 = \sigma_{m_T}^2 + \sigma_B^2 + \sigma_\delta^2 = 2 \sigma_B^2 + \sigma_{m_c^f}^2 + \sigma_{m_c^0}^2 = 4 \sigma_B^2 \tag{3}$$

where σ_{m_T} and σ_B are the uncertainties corresponding to the total masses of the loaded and blank filters, respectively, and σ_δ is the uncertainty related to Eq. (2), thus making it possible to write $\sigma_\delta^2 = \sigma_{m_c^f}^2 + \sigma_{m_c^0}^2$. Consequently, given that $\sigma_{m_c^f} = \sigma_{m_c^0} = \sigma_B$, it is possible to know σ_m when employing Method-1, where its value was found to be 1.4 mg.

In order to apply this methodology, it is required to neglect the adsorption or loss of water by the particulate matter that is deposited onto the filter, due to the relative humidity changes. This is possible given that m is usually at least one order of magnitude less than m_T for all samplings carried out (see Section 3.2.2). Furthermore, another requirement to be considered when applying this methodology is the need for reaching a sampled air volume below the value by which the clogging of the filters takes place.

3.1.2. Methodology proposed by the EPA (Method-2)

When applying Method-2, the uncertainty of the particulate matter mass deposited on the filters, σ_m , can be determined by the following equation:

$$\sigma_m^2 = \sigma_{m_T}^2 + \sigma_B^2 \tag{4}$$

where σ_{m_T} and σ_B are the uncertainties at 1 sigma level for the total mass of the loaded and blank filters, respectively.

To obtain Eq. (4), it was necessary to consider the following equation for m :

$$m = m_T - m_B \tag{5}$$

where m_T and m_B are the total masses of the loaded and blank filters, respectively.

Therefore, considering that $\sigma_{m_T} \sim \sigma_B$, Eq. (4) can be rewritten in the following way:

$$\sigma_m = \sqrt{2} \sigma_B \tag{6}$$

where σ_m and σ_B were previously defined in Eq. (4). Therefore, the σ_m value can be completely determined, which was 1.0 mg in the case of utilizing Method-2.

3.2. Testing the consistency of the methodologies; determination of the particulate matter mass

3.2.1. Comparing both methodologies

In order to verify the consistency of the proposed methodology, a problem filter was weighted before and after the sampling using a PM10 sampler. Let us call this specific problem filter F_p . Thus, in Fig. 1a, the total mass of the problem filter (m_T) and of the control filter (m_c) were determined ten times (one weight for each day). Then, in Fig. 1b, the differences between the total mass obtained for a weight n , $m_T^{(n)}$, and the one related to the weight previous to n , that is, $n - 1$, $m_T^{(n-1)}$, were compared for both filter types. Therefore, it is easy to realize that the behaviors of $m_T^{(n)} - m_T^{(n-1)}$ were very similar for the control and F_p filters. In addition to this good similarity in the qualitative behaviors of both filter types, it is possible to clearly observe that $m_T^{(n)} - m_T^{(n-1)}$ values were also very similar for the same weight in the case of the control and F_p filters. Furthermore, it is necessary to clarify that, when plotting $m_T^{(n)} - m_T^{(n-1)}$, the experimental uncertainties related to this magnitude (2 mg at 2 sigma level) were not shown, in order to make it easier to observe the good similarity between the $m_T^{(n)} - m_T^{(n-1)}$ values obtained for both filter types for each weight. Thus, all the obtained results are very consistent, as the mass behaviors of the control and problem filters must be analogous, since both filters are subjected to the same environmental conditions in the laboratory. Moreover, the results obtained for $m_T^{(n)} - m_T^{(n-1)}$ must be very similar, since the RH changes, which occurred between weights, are the same for both filter types. This must occur in this way, since δ is the only main factor that contributes to the changes of the total masses for both the control and problem filters.

To further corroborate the consistency of the proposed methodology, the sample mass deposited on the F_p filter, m , was calculated for each weight. The results obtained using the method developed in this study,

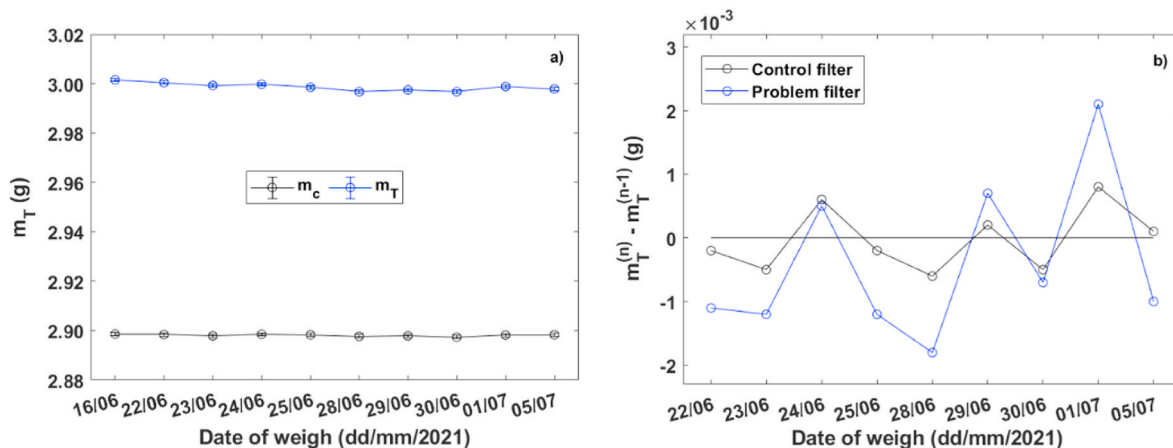


Fig. 1. Verification of the consistency of the methodology proposed to obtain the sample mass deposited on the filters after sampling, m . Ten weightings on ten days (one weighting for each day) were carried out for the control and problem filters. Let us call this specific problem filter F_p . a) The total mass of the control and F_p filters, m_c and m_T , respectively, are shown; b) the differences between the total mass obtained for a weight n and that related to the weight previous to n , that is, $n - 1$, were compared for both filter types.

Method-1, were compared with those obtained employing the method proposed by the EPA, Method-2.

Thus, as can be seen in Fig. 2a, all m values were very close to the average value obtained for this problem filter, $\langle m \rangle$, after applying Method-1, where $\langle m \rangle$ was 156.4(4) mg. Then, a very good agreement was also obtained when employing Method-2, where all m values were also very close to the average value, which was 155.6(3) mg. This is very consistent, since m must be constant if no sample loss occurs. Moreover, another reason why m is also considered almost constant is because m is generally much smaller than m_T . Consequently, the m variations due to the RH changes can be completely neglected when compared to variations in m_T .

In order to show more clearly that the variations related to the calculated sample mass can be completely neglected, the relative differences between m and $\langle m \rangle$, Δ_m (%), are displayed in Fig. 2b. Thus, as can be seen, all Δ_m values were below 2% for Method-1 and Method-2, where their average Δ_m values were 0.7(3)% and 0.8(2)%, respectively, proving the consistency and similarity of both methodologies. Furthermore, in Fig. 2b, note that all Δ_m values are compatible with 0% when considering m uncertainties at 2 sigma level. However, it is necessary to clarify that RH was quite constant for all weights shown in Fig. 2a, where all RH values were found to be about 50%. Consequently, it is consistent that Method-2 provides good results to determine the particulate matter mass, since according to EPA, 1999-b, RH must be about 50% in order to employ Method-2.

Nevertheless, it is necessary to clarify that RH has to be very different from 50% in order to properly verify which method provides results that are more consistent with those obtained in the previous comparison. To this end, RH was varied by using a dehumidifier, covering a wide interval that ranged from 18% to 62%. Thus, as can be seen in Fig. 3a, for each RH value, the control and F_p filters were weighted to observe the dependence of the masses of the control and F_p filters on RH , as well as to compare the results provided by Method-1 and Method-2 when RH reaches values very different from 50%.

Thus, the total masses of both control and F_p filters, m_c and m_T , respectively, are plotted in Fig. 3a for each RH value reached. This allows observing a clear dependence of the total filter mass for both the control and F_p filters, finding that, as RH increases, the total mass increases for both filter types. Then, in Fig. 3b, m_T was plotted versus m_c for each RH value, proving the similarity of the mass variations for both filter types. Furthermore, the experimental values that resulted from plotting m_T versus m_c were fitted, achieving a linear relation whose slope and ordinate at the origin were 0.98(7) and 0.2(2) g, respectively. This is very consistent, since, in Eqs. (1) and (2), considering that δ is the same for both the control and problem filters, m_T can be written as $m_T =$

$b + m_c$. Therefore, when fitting m_T versus m_c , the slope of the linear fit must be very close to 1, where b is the ordinate at the origin. This is in strong agreement with Lozano et al. (2011), where a linear dependence was obtained for a function used in order to correct m_T due to the RH variations.

Furthermore, the particulate matter mass, m , was calculated using Method-1 and Method-2 for each selected RH value. Thus, as can be seen in Fig. 3c, all m values were much closer to the average value, $\langle m \rangle$, when employing Method-1 with respect to the ones obtained using Method-2, where the relative differences, Δ_m , were 0.1(4)% and 0.9(3)%, respectively (see Fig. 3d). In addition, it is worth mentioning that, in the case of Method-2, Δ_m increased as RH became more different from 50%, while for Method-1, all m values were similar. This is very consistent, since the methodology proposed by the EPA can be applied only if the conditions required are fulfilled, while the methodology developed in this study can be employed for any RH value, which makes Method-1 a more general and simple methodology to determine the particulate matter mass.

The $\langle m \rangle$ value achieved when applying Method-2 was 154.8(3) mg; therefore, considering uncertainties at 1 sigma level, this $\langle m \rangle$ is incompatible with the one obtained from the calculations when RH was about 50% (see Fig. 2a). However, in the case of Method-1, the $\langle m \rangle$ value obtained from varying RH was 156.0(4) mg, which is very consistent with the one achieved previously in the cases for which RH was about 50%. This further corroborates the generality character of Method-1, as well as the fact that the results provided by this method are clearly better than those ones obtained with Method-2 when considering RH values very different from 50%. Furthermore, the fact that $\langle m \rangle$ is almost the same value when applying Method-1 means that $\langle m \rangle$ can be considered as a constant, which is very reasonable, since, given that $\langle m \rangle$ is much smaller than m_T , the dependence of $\langle m \rangle$ on RH can be completely neglected.

3.2.2. m determination for samplings carried out in “El Carmen” (Huelva, Spain)

Once the methodology proposed to determine the sample mass collected on the problem filters, m , was described and its consistency was fully proved in Section 3.2.1, the results related to the “El Carmen” campaign are shown in this Section, for which the methodology was applied to determine mass concentration, μ , which can be determined by the following equation:

$$\mu = m/V \quad (7)$$

where m is the particulate matter mass deposited on the filters during the samplings and V is the sampled volume.

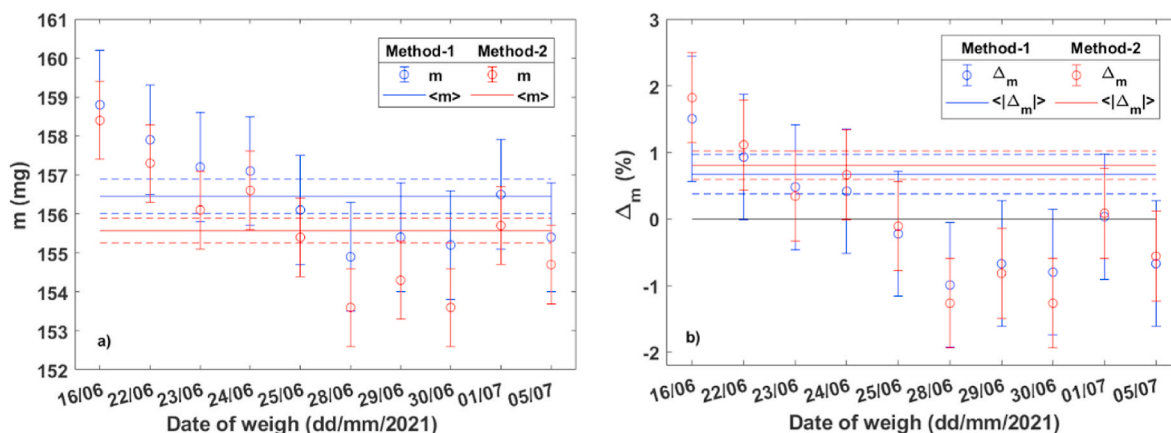


Fig. 2. Values of the particulate matter mass deposited on the F_p filter after sampling, a), and its relative differences, b), m and Δ_m , respectively, for each date of weight. Δ_m values were calculated comparing m with its average value, $\langle m \rangle$, also showing the average value for Δ_m , $\langle |\Delta_m| \rangle$. m and Δ_m values were calculated for the F_p filter using both methods: the one developed in this study (Method-1) and that proposed by the EPA (Method-2).

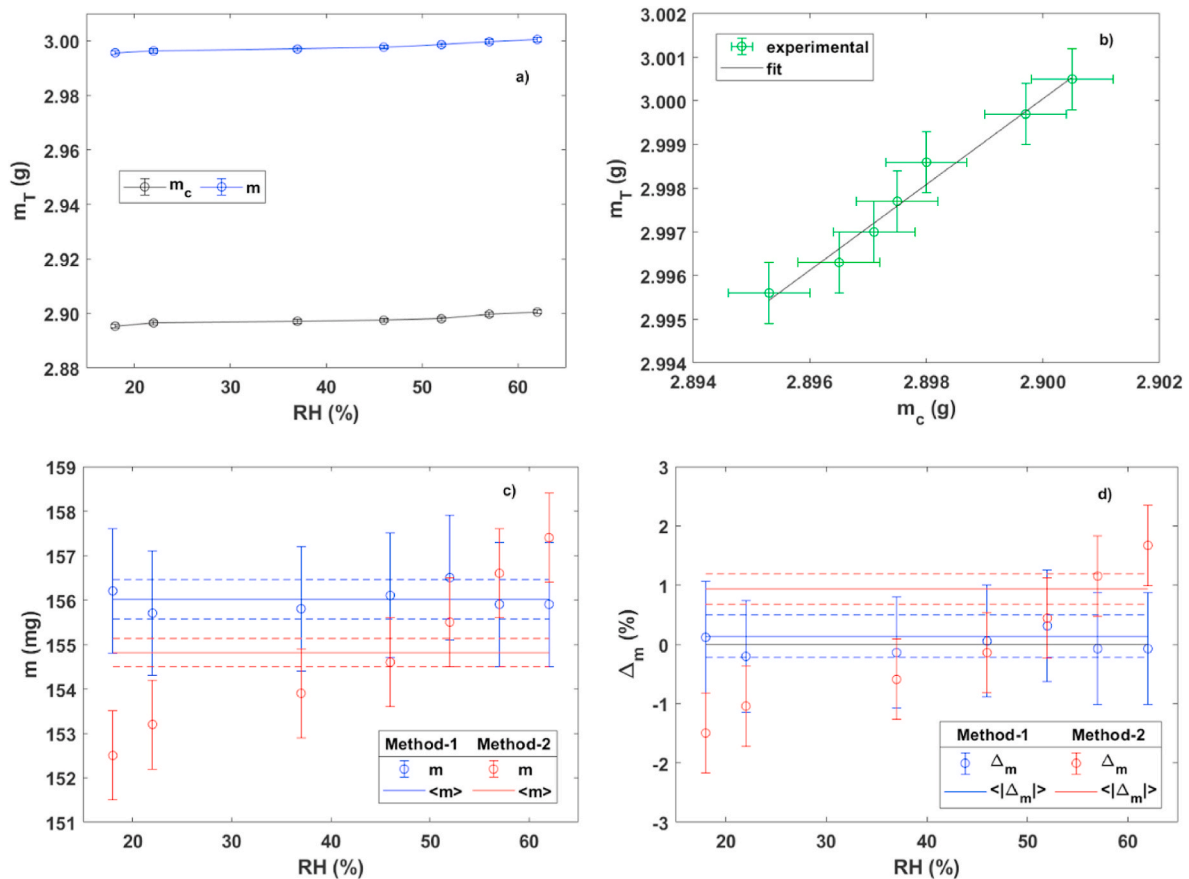


Fig. 3. a) Dependence of the total masses of the control and problem filters, m_c and m_T , respectively, on the relative humidity, RH (%); b) m_T was plotted versus m_c to compare their variations; c) m and d) Δ_m were calculated for the F_p filter after varying RH from 18% to 62%. For these calculations, both methods (Method-1 and Method-2) were employed.

Six samplings were carried out during the “El Carmen” campaign (samplings from I to VI), which took place during the year 2021, using three PM10 samplers (PM10-1, PM10-2 and Andersen). Furthermore, two magnitudes were mainly analyzed to verify the validity of the proposed methodology: m and Δ_m .

Fig. 4 shows the relative differences, Δ_m (%) (Fig. 4a) and Δ_μ (%) (Fig. 4b), that resulted from the comparisons between the m and values, respectively, which were obtained using the three samplers, and their respective average values. Therefore, in the case of the Δ_m and Δ_μ

values, it is possible to observe that both had almost identical behaviors and values, which is very consistent, since both are related to the sample mass, m . Furthermore, very good Δ_m and Δ_μ values were obtained for the six samplings, where their absolute values ranged from 0.0(0.8)% to 5.3 (1.8)% (with both cases corresponding to the Andersen sampler), and from 0.1(0.8)% to 5.0(1.8)% (also with both cases corresponding to the Andersen sampler), respectively, with their average values, $\langle|\Delta_m|\rangle$ and $\langle|\Delta_\mu|\rangle$, being 2.1(3)% and 1.9(3)%, respectively. Furthermore, Table S2 (see Supplementary Data) shows the values corresponding to m

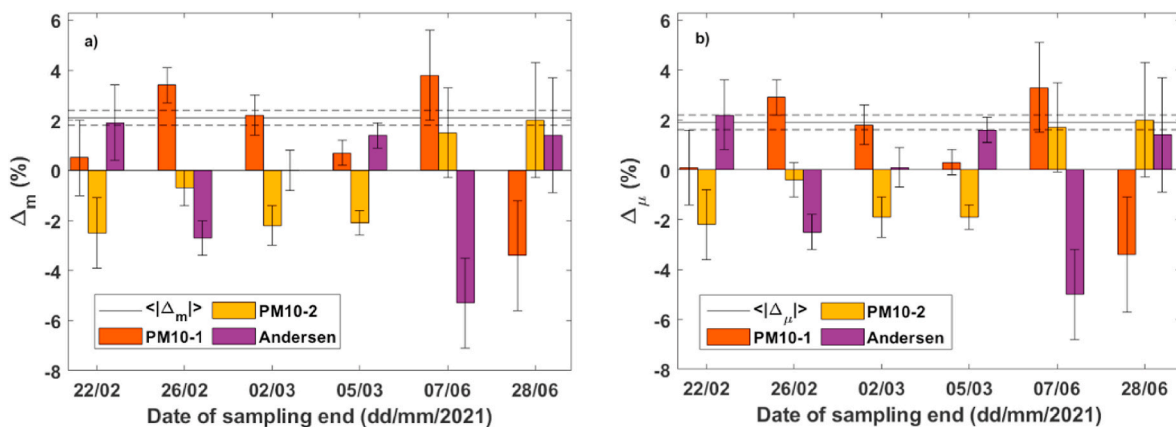


Fig. 4. Application of the methodology proposed in this work to obtain the sample mass deposited on the filters, m . The samplings were carried out using three samplers (PM10-1, PM10-2 and Andersen). Δ_m , a), and Δ_μ , b), are the relative differences between the values obtained for m and the sample mass concentration, respectively, with respect to their average values corresponding to each sampling, with $\langle|\Delta_m|\rangle$ and $\langle|\Delta_\mu|\rangle$ being the relative average differences obtained for Δ_m and Δ_μ , respectively, considering all samplings carried out.

(mg) and ($\mu\text{g m}^{-3}$) obtained for each sampler during each sampling, as well as their average values, $\langle m \rangle$ and $\langle \mu \rangle$, respectively.

3.3. Application to the determination of radionuclides (^7Be and ^{210}Pb)

Fig. 5 shows the Δa_V and Δa_m values corresponding to ^7Be and ^{210}Pb using each sampler, where the Δa_V and Δa_m definitions are analogous to those given for Δ_m and Δ_μ (see Fig. 4), although, in this case, they were applied to the activity concentration obtained in Bq g^{-1} and mBq m^{-3} , respectively. Thus, in the case of ^7Be (Fig. 5a and b), very good $|\Delta a_V|$ and $|\Delta a_m|$ values were obtained, which ranged from 0(3)% (case corresponding to PM10-2) to 9(3)% (PM10-1), and from 0(3)% (PM10-2) to 9(2)% (PM10-2), respectively, where their average values, $\langle |\Delta a_V| \rangle$ and $\langle |\Delta a_m| \rangle$, were 3.7(7)% and 3.3(6)%, respectively. Then, regarding the cases related to ^{210}Pb (Fig. 5c and d), there was also a good agreement between the results obtained using the three samplers, where $|\Delta a_V|$ and $|\Delta a_m|$ values ranged from 1(4)% (cases corresponding to PM10-1 and Andersen) to 11(5)% (Andersen), and from 1(5)% (Andersen) to 10(5)% (Andersen), respectively, with average values of 4.5(1.0)% and 3.6(1.0)% for $|\Delta a_V|$ and $|\Delta a_m|$, respectively.

In Tables S3 and S4 (see Supplementary Data), the values corresponding to a_V and a_m obtained for each sampler during each sampling, as well as their average values, $\langle a_V \rangle$ and $\langle a_m \rangle$, respectively, can be consulted both for ^7Be and ^{210}Pb , respectively. In addition to that, it is worth mentioning that the a_V values that resulted from ^7Be and ^{210}Pb determinations (see Tables S3 and S4, respectively, in Supplementary Data) were very similar to those obtained in other studies performed in Huelva (where the ^7Be and ^{210}Pb a_V values were 5.1(4) mBq m^{-3} in Lozano et al. (2013) and 0.57(4) mBq m^{-3} Lozano et al. (2012),

respectively, and 5.2(5) mBq m^{-3} and 0.50(10) mBq m^{-3} , respectively, in Ordúz, 2012, in Málaga (Spain) (where the ^7Be and ^{210}Pb a_V values were 4.8(1.6) mBq m^{-3} and 0.6(2) mBq m^{-3} , respectively, in Dueñas et al. (2009)), and in Mallorca Island (Spain) (where the mean ^7Be and ^{210}Pb a_V values were 6.5(3) mBq m^{-3} and 0.70(7) mBq m^{-3} , respectively, in Ceballos et al. (2016)). This demonstrates the good validity of the methodology developed to obtain m , as well as the efficiency calibration conducted in this study.

Then, to further verify the validity of the methodology proposed in this study in order to determine m , the z_{score} values corresponding to m , a_V and a_m are shown in Table 1 for the samplings I – VI, where the reference value taken for each z_{score} type was the average value obtained for each magnitude type, that is, analogously to the cases related to the relative differences, which were previously analyzed. Thus, as can be seen in Table 1, the $|z_{\text{score}}|$ values obtained in the case of m ranged from 0.1 to 4.7, obtaining an average z_{score} of 1.96. Regarding the $|z_{\text{score}}|$, in the case of the ^7Be obtained for a_V and a_m , it ranged from 0.1 to 3.3 and from 0.2 to 4.0, respectively, with average values of 1.4 and 1.2, respectively; in the case of the ^{210}Pb , the $|z_{\text{score}}|$ obtained for a_V and a_m ranged from 0.4 to 2.2 and from 0.1 to 2.0, respectively, with average values of 1.0 and 0.8, respectively. Consequently, the great validity of the methodology developed to determine m was fully demonstrated. Moreover, using this methodology, it is possible to assess the uncertainties related to the masses of the particulate matter that deposited on the filters during the samplings. This is essential in order to test the compatibilities of the results obtained using different samplers (PM10 samplers in our case), and thus verify the correct operation of the selected samplers.

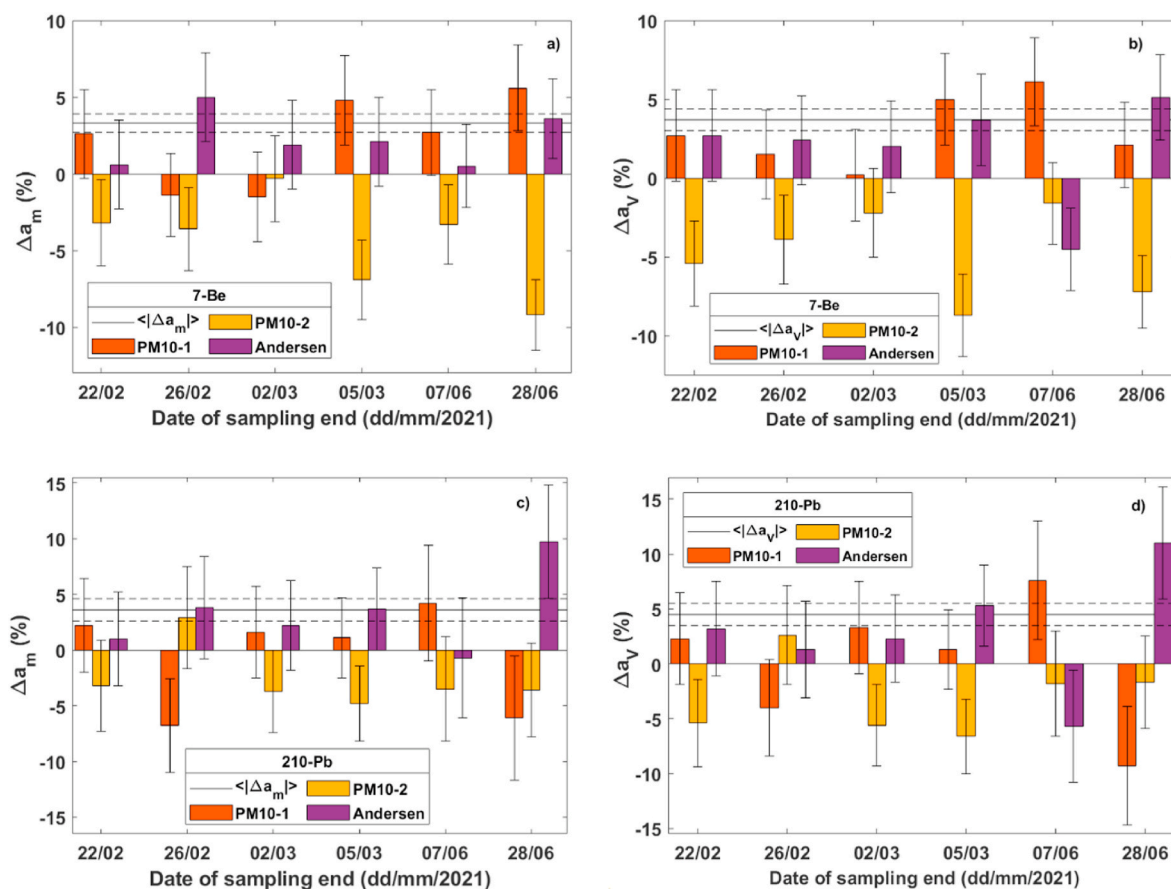


Fig. 5. Application of the methodology proposed in this work to determine ^7Be , a) and b), and ^{210}Pb , c) and d), contained in the sample deposited on the filters. The samplings were carried out using three samplers (PM10-1, PM10-2 and Andersen). Thus, the definitions of Δa_m and Δa_V are analogous to those given for Δ_m and Δ_μ (see Fig. 4), although, in this case, they were applied to the activity concentration obtained in Bq g^{-1} and mBq m^{-3} , respectively, where $\langle |\Delta a_m| \rangle$ and $\langle |\Delta a_V| \rangle$ are relative differences that resulted from averaging all Δa_m and Δa_V values, respectively, obtained for all samplings.

Table 1

values obtained for the sample mass deposited on the filters, m , and the activity concentrations in Bq g^{-1} and in mBq m^{-3} , that is, a_m and a_V , respectively, resulted from applying the methodology proposed in this study to the ^{210}Pb and ^7Be determination. Furthermore, the resulted average values of z_{score} for m , a_m and a_V have also been given for ^{210}Pb and ^7Be . In order to perform the samplings, three samplers were employed (PM10-1, PM10-2 and Andersen).

Sampling	Date of sampling end/duration	Samplers	m	^{210}Pb		^7Be	
			z_{score}	$z_{\text{score}}(a_m)$	$z_{\text{score}}(a_V)$	$z_{\text{score}}(a_m)$	$z_{\text{score}}(a_V)$
I	22/02/2021 / 66.3 h	PM10-1	0.4	0.5	0.5	0.9	0.9
		PM10-2	-1.7	-0.8	-1.3	-1.1	-2.0
		Andersen	1.3	0.2	0.7	0.2	0.9
II	26/02/2021 / 100.7 h	PM10-1	4.7	-1.6	-0.9	-0.5	0.5
		PM10-2	-1.0	0.6	0.6	-1.3	-1.5
		Andersen	-3.7	0.9	0.3	1.7	0.9
III	02/03/2021 / 91.0 h	PM10-1	2.8	0.4	0.8	-0.5	0.1
		PM10-2	-2.8	-1.0	-1.5	-0.1	-0.8
		Andersen	-0.1	0.5	0.6	0.6	0.7
IV	05/03/2021 / 76.3 h	PM10-1	1.3	0.3	0.4	1.7	1.8
		PM10-2	-4.0	-1.4	-1.9	-2.6	-3.3
		Andersen	2.6	1.0	1.4	0.7	1.3
V	07/06/2021 / 64.7 h	PM10-1	2.1	0.8	1.4	1.0	2.2
		PM10-2	0.8	-0.7	-0.4	-1.3	-0.6
		Andersen	-2.9	-0.1	-1.1	0.2	-1.7
VI	28/06/2021 / 66.0 h	PM10-1	-1.5	-1.1	-1.7	2.0	0.8
		PM10-2	0.9	-0.9	-0.4	-4.0	-3.1
		Andersen	0.6	2.0	2.2	1.4	2.0
Average z_{score}			1.96	0.8	1.0	1.2	1.4

4. Conclusions

In the present work, a new and simple methodology was developed to accurately determine the mass of the particulate matter, m , deposited onto sampled atmospheric filters. To this end, a filter known as “control filter” was employed, which is always exposed to the environmental conditions present in the laboratory, where the weights of the filters are measured.

Then, the methodology proposed in this work to determine m was tested to prove its consistency, which required the use of a problem filter: F_p filter. Thus, the total mass of the F_p filter, m_T , showed the same behavior as that of the control filter mass. Moreover, the differences between the total mass obtained for a weight n and that related to the previous weight, $n - 1$, were compared for both filter types, obtaining very similar differences in the cases of the F_p and control filters between any weights n and $n - 1$. This is very consistent, since the problem and control filters are subjected to the same environmental conditions in the laboratory, with the filter mass changes being caused mainly by the relative humidity changes and, therefore, the differences related to the total masses of the control and problem filters can be quantified by a variable that was denoted as δ , where $\delta = m_c^f - m_c^o$, with m_c^o and m_c^f being the control filter masses when the problem filter is weighted before and after carrying out the sampling, respectively.

Furthermore, the method developed in this study to determine m (Method-1) was compared with the methodology proposed by the EPA (Method-2), for which the relative humidity, RH , must be about 50%, specifically $50 \pm 5\%$. In order to make this comparison, the problem filter previously mentioned (F_p) was selected. Thus, the m value of the F_p filter was determined after carrying out ten weights (a daily weight) using Method-1 and Method-2 when RH was about 50%, achieving relatively small differences, Δ_m , as well as very similar values when using both methods. Another comparison was made between Method-1 and Method-2, where RH was varied from 18% to 62%. In this case, the Δ_m that resulted from using Method-1 was relatively smaller than that obtained by Method-2. Furthermore, the $\langle m \rangle$ value that resulted from Method-1 when varying RH was very similar to that obtained when RH is very close to 50%, while in the case of employing Method-2, clear differences were found considering $\langle m \rangle$ uncertainties at 1 sigma level. This is very consistent, since Method-1 is a general methodology to determine m . Then, using Method-1, $\langle m \rangle$ can be considered as a constant, which is very consistent, since $\langle m \rangle$ is much smaller than m_T and,

therefore, the dependence of $\langle m \rangle$ on RH can be completely neglected.

Once the consistency of the methodology proposed in this study to quantify m was proved, this methodology was applied to the samplings carried out in “El Carmen” in order to determine contaminants, specifically ^7Be and ^{210}Pb radionuclides. To this end, a previous efficiency calibration of the Xtra detector was conducted for the filter type selected in this study.

To proceed with the samplings, three PM_{10} samplers were selected to achieve a more complete validation for Method-1, as well as for the efficiency calibration employed in this study. For this validation, several magnitudes were considered, such as the activity concentrations of ^7Be and ^{210}Pb per mass and volume units, that is, a_m and a_V , respectively, as well as the particulate mass and its concentration, m and μ , respectively. Thus, the a_V calculated for ^7Be and ^{210}Pb after carrying out the samplings were very similar to those obtained in other works, and very good agreement was found between the a_V values that resulted from using the three samplers. Furthermore, in the cases related to m , μ and a_m values obtained for each sampling using Method-1, very good similarity was found between all values that resulted from using the three samplers, with this similarity being very good for each of these magnitudes. Consequently, the great consistency, simplicity and validity of Method-1 to calculate m was fully proved, making it unnecessary to employ any humidity management system in order to measure and control the relative humidity in the laboratory. Moreover, this methodology allows calculating the uncertainties related to the masses of the particulate matter. This is very important to check the compatibilities of the results obtained using different samplers, which allows verifying the correct operation of the selected samplers.

Credit author statement

A. Barba-Lobo: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **I. Gutiérrez-Álvarez:** Conceptualization, Writing – original draft, Writing – review & editing. **J.A. Adame:** Conceptualization, Writing – original draft, Writing – review & editing. **J.P. Bolívar:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2022.113817>.

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