Positive bias caused by residual water in reference PM$_{10}$ measurements

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Abstract—Dry aerosol mass concentrations (PM$_{10}$, PM$_{2.5}$) are determined after conditioning of the filter at t=20±1 °C and RH=50±5% for 48 hours according to the standard protocol EN 12341. The main result of this work is that applying the standard pre-conditioning step, complete removal of adsorbed water cannot be attained. In our experiment, aerosol samples collected in Budapest between November 2008 and March 2010 using a CEN (European Committee for Standardization) gravimetric sampler (Digitel, DHA-80) were studied. Following PM$_{10}$ mass concentration measurements according to the EN 12341 protocol, we repeated the gravimetric aerosol mass measurements in the laboratory using a glove box after in-situ pre-conditioning for 48 h at t=20±1 °C and RH<30%. We assumed that at this low relative humidity all the adsorbed residual water was removed, and the absolute dry mass concentrations of PM$_{10}$ could be determined (referred in the following as dry PM$_{10}$ concentration). The mass concentration of adsorbed residual water, defined as the difference between the results of the standard and dry PM$_{10}$ measurements, varied greatly in the range of 0.05–16.9 µg m^{-3}. Expressed relative to the absolute dry PM$_{10}$ mass concentrations, the residual water content in the standard measurement procedure amounted to 4.2±1.5% and 7.9±0.8% in summer and winter, respectively. In winter, relative contributions of adsorbed water as high as 33.2 m/m% was found. The significant seasonal differences as well as the large variations between individual samples may depend on various factors such as the chemical composition of the samples, particle load, and the RH history of the particles before and after sample collection. This last factor is expected to exert rather significant influence on the amount of adsorbed residual water, yet it is impossible to reconstruct. These findings have severe implications on reported dry PM$_{10}$ mass concentrations using the EN 12341 protocol, especially in the winter period when most limit exceedances occur.

Key-words: urban PM$_{10}$, standard protocol, adsorbed residual water, dry mass concentration, low relative humidity

1. Introduction

Liquid water is a highly variable, but very often overlooked constituent of atmospheric particulate matter (PM_{10} or $PM_{2.5}$). The interaction between ambient aerosol particles and water vapor plays a crucial role in many fundamental atmospheric processes. Adsorbed water may significantly increase the size of the particles, which, in turn, enhances the extinction (mainly scattering) of visible light in the atmosphere. This is manifested in strongly reduced standard visibility at high relative humidity (RH) (*Cheng et al.,* 2011, *Deng et al.,* 2011). Liquid water on aerosol particles can serve as a medium for multiphase reactions (e.g., sulfur conversion in sea-salt aerosol particles, *Sievering et al.* (1991)), or secondary organic aerosol formation *Strollo* and *Ziemann* (2013); *Ervens* and *Volkamer* (2010). In supersaturated air, particles called cloud condensation nuclei can grow into cloud or fog droplets. The interaction between particles and water vapor depends on the relative humidity as well as the size, chemical composition, and wettability of the particles. Based on differences in their chemical compositions, particles of various origins can behave quite differently with changing humidity, from being purely hydrophobic to strongly hygroscopic. Hygroscopic particles take up water continuously with increasing RH, whereas deliquescent particles do not adsorb water up to a certain RH limit called the deliquescence point (DRH). At this point, however, a sudden phase change occurs with a steep increase in the mass of the particles. Increasing the RH further above the DRH, the liquid particle will continue to grow. However, once such a particle is turned into liquid, decreasing the RH will not make the particle recrystallize at the DRH. Below the DRH, the liquid particle becomes supersaturated resulting in a metastable state until the RH decreases below a critical value at which recrystallization occurs (*Hansson et al.,* 1998). This RH is called efflorescence relative humidity (ERH). For example, aqueous ammonium sulfate is saturated with respect to its crystalline phase at 82.6% RH at 260 K (*Clegg et al.,* 1998; *Onasch et al.,* 1999; *Cziczo* and *Abbatt,* 1999), whereas laboratory studies show that homogeneous crystallization of droplets does not occur before RH drops to 32.7% (*Onasch et al.,* 1999). Conversely, solid ammonium sulfate does not deliquesce at RH lower than 82.6%. Therefore, in the range 32.7% < RH < 82.6% the physical state of such a particle in the atmosphere depends on its RH history (*Colberg et al.,* 2003), the particles exist as a metastable droplet when the particles had not been exposed to relative humidity greater than their deliquescence RH.

There is often a discrepancy in chemical mass closures of atmospheric aerosol samples when they are normalized to gravimetrically measured mass of particulates. In other words, after all identified components are quantified, a part of PM mass remains unidentified. One possible source for the observed discrepancy between gravimetric PM mass and the total mass of all identified

components is particle-bound water. The amount of water in PM samples varies for different samples and measurement sites, depending on the particle composition and the ambient relative humidity and temperature (e.g., *Warneck,* 2000). According to *Kajino et al.* (2006), in winter when the relative humidity is high and the concentration of hygroscopic compounds is also high, approximately 70% of unidentified non-carbonaceous fraction of urban $PM_{2.5}$ (or about 10% of $PM_{2.5}$ mass) was assumed to be water. The authors also found that the aerosol water content in winter was 6–7 times higher in winter than in summer.

In spite the fact that *Saxena et al.* (1995) pointed out the importance of atmospheric water-soluble organic carbon (WSOC) for the observed hygroscopic behavior of atmospheric aerosols, the water uptake of aerosol particles has been largely associated with their inorganic constituents. Depending on the ambient conditions during and prior to sampling, particles can either adsorb or lose water under post-equilibration (*Tsyro,* 2005). The relationship among particle mass and composition and particle water content is rather complicated due to hysteresis in the behavior of particle-bound water. In many cases the atmospheric aerosol particles show strong RH-hysteresis behavior and retain substantial particle-bound water (*Santarpia et al.,* 2004; *Randriamiarisoa et al.,* 2006). This means that potentially a significant fraction of strongly hygroscopic particles exist as supersaturated droplets even at RH as low as 50%. One possible explanation for the significant amount of retained water is the acidity of the particles. This was observed in several places, e.g., in Pittsburgh, USA (*Khlystov et al.,* 2005) and in Switzerland (*Fisseha et al.,* 2006). According to *Tsyro* (2005), pure ammonium sulfate particles can still retain as much as 30% (m/m) of water at 50% relative humidity. *Ansari* and *Pandis* (1999) investigated the hysteresis of equimolar model aerosol mixtures (Na_2SO_4-NaCl and Na_2SO_4-NaCl-$NaNO_3$) and found that the residual mass of retained water at RH=50% was 83% and 71%, respectively. On the other hand, beside particle acidity, a number of organic components are shown to inhibit the aerosol deliquescence and efflorescence behavior (*Marcolli* and *Krieger,* 2006). *Zardini et al.* (2008) showed that the retained mass of water in the case of ammonium sulfate: adipic acid (2:1.1) model mixture was 30% at RH=50% following equilibrium dehumidification.

In recognition of the water-retaining characteristics of atmospheric particulate matter, standard off-line gravimetric measurement protocols all require the relative humidity to be set at a relatively low value and the filter samples be equilibrated before weighing. In Europe, the reference method developed by the European Committee for Standardization (CEN) prescribes that the filters should be equilibrated for 48 h prior to weighting at RH=50±5% and t=20±2 °C before and after sampling. This standard reference method is used to validate the readings of automatic beta-gauge

monitors (FH 62-IN, Thermo Andersen) that are in use in hourly PM concentration measurements.

Several studies indicated that there were deviations between automatic and standard off-line PM mass concentration measurements (*Shin et al.,* 2011, *Takahashi et al.,* 2008, *Salminen* and *Karlsson,* 2003), with higher differences at high ambient RHs (*Chang* and *Tsai,* 2003). These results also imply the significance of retained water of particles under the standard reference methods.

The objective of this study is to determine the residual water content of PM filter samples collected in winter and summer in the city of Budapest, Hungary, which are equilibrated according to the standard analysis protocol. This is done to determine the potential bias of standard gravimetric measurements due to the incomplete removal of particle-bound water upon equilibration.

2. Methodology

2.1. Aerosol sampling

The aerosol sampling was carried out in Budapest (Marczell György Observatory, Hungarian Meteorological Service) at a suburban sampling site. The aerosol sampling were carried out in 57 consecutive days in winter of 2008–2009, 22 days in summer of 2009, and further 75 days in winter of 2009–2010.

PM_{10} aerosol samples were collected on glass fiber filters (Munktell MG 160, d=150 mm) at a flow rate of $30 \, m^3 \, h^{-1}$ by using a Digitel-DH 80 reference sampler (CEN, 1998) at a height of 2 m.

2.2. Gravimetric measurements

Before and after the sampling, glass fiber filters were placed for 48 hours into an isolated chamber at a temperature of 20 ± 1 °C and RH of $50 \pm 5\%$, as required by the EN 12341 standard protocol (CEN, 1998). Then PM_{10} mass was determined by weighing with an electrical micro-balance (Sartorius, BP 211 D) of 10 μg accuracy.

Filter blanks were treated in the same way. The relative humidity was measured by a hygrograph, which was calibrated in the climate chamber of the Hungarian Meteorological Service. The detailed measurement conditions can be found in *Imre* and *Molnár* (2008). In order to determine the residual water content of aerosol mass measured according to the EN 12341 protocol, the filter sample was equilibrated for another 48 h at t=20 ± 1 °C and RH<20% prior to the following gravimetric measurement. The relative humidity in the measurement chamber was set by DRIERIT (calcium sulfate, W.A. Hammond Drierite Co. Ltd.) heated at 230 °C for 2 hours.

3. Results and discussions

The PM_{10} dry mass concentrations measured from the collected filter samples according to EN 12341 standard protocol are shown *Fig. 1*. The 24-hour health threshold limit for PM_{10} concentration in Hungary (and EU) is 50 µg m^{-3}, while the air quality public warning "Information" and "Alert" threshold limits are 75 and 100 µ gm^{-3}, respectively, as regulated by the Ministry of Rural Development (4/2011) are also indicated in the figure.
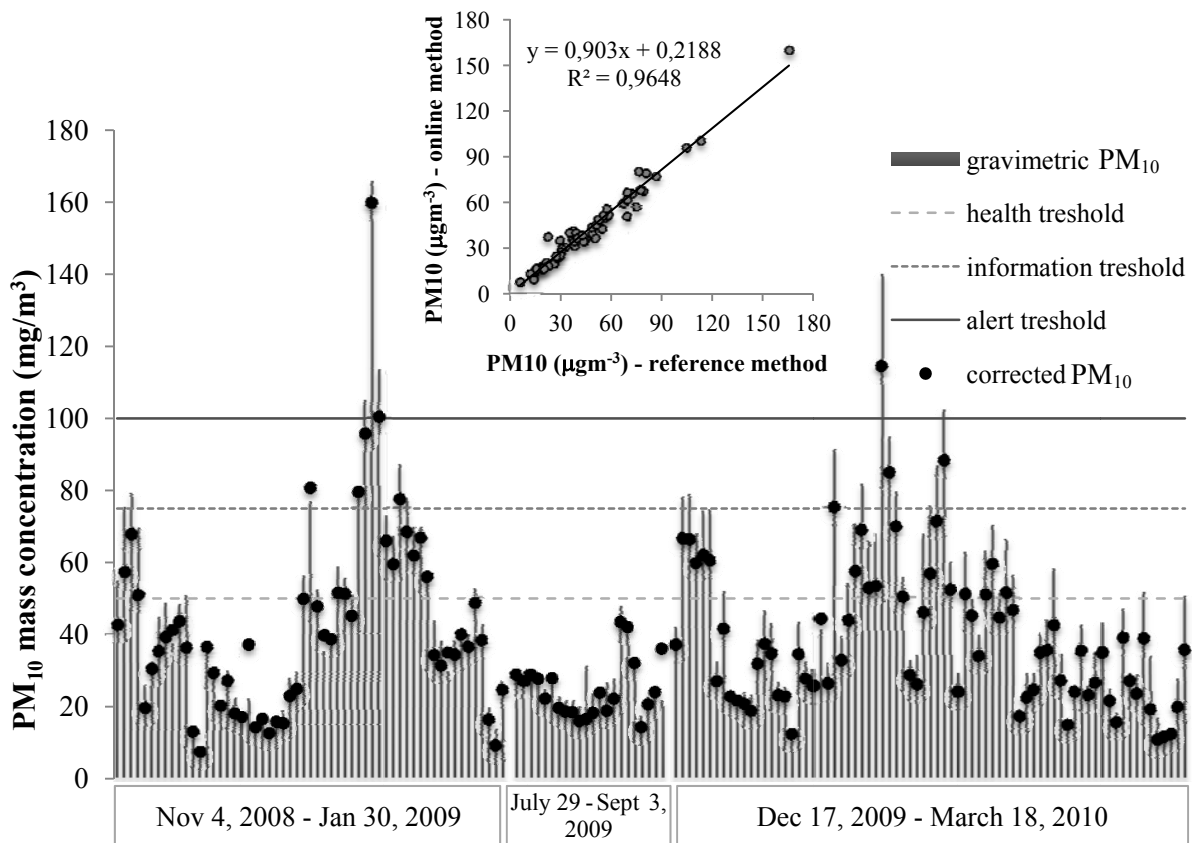

Fig. 1. Gravimetrically determined dry mass concentration at 50% RH according to EN 12341 (CEN 1998) and the relationship between the online and gravimetric PM_{10} concentrations (inserted picture).

According to the regulations, the evaluation of the limit exceedances should be based on the 24 h PM_{10} mass concentrations measured by an automatic beta-gauge monitor FH 62-IN (Thermo Andersen) and not on those measured by the reference method. For this reason these data are also shown in *Fig. 1*. (It should be noted that this instrument was located adjacent to the Digitel-DH 80 reference sampler and the data of beta-gauge monitor are averaged for the time period of sample collection.) Adding this constraint (to the

calculation) the measured PM_{10} reference dry mass concentrations exceeded the alert threshold for 34 days, for additional 14 days the information, threshold and for another 5 days the health limits.

In the following we considered that under the equilibrium conditions required by the reference method ($20\pm1°C$ and RH of $50\pm5\%$ for 48 h), residual water was retained in the particles. In order to determine the residual water content of the aerosol, further gravimetric measurements were necessary that is specified by equilibration at $t=20\pm1$ °C and RH<30% lasting for 48 h. The mass concentration of water retained under the conditions of the standard protocol was determined as a difference between the mass concentrations measured according the EN 12341 protocol and the dry mass concentration specified above. The mass fraction of residual water expressed in percentage of the PM_{10} mass concentrations measured by the reference method is shown in *Fig. 2*. It is interesting to note, that despite the fact, that the aerosol water content was higher in winter than in summer, no significant relationship between the ambient RH (during the sampling) and the measured water content was found.
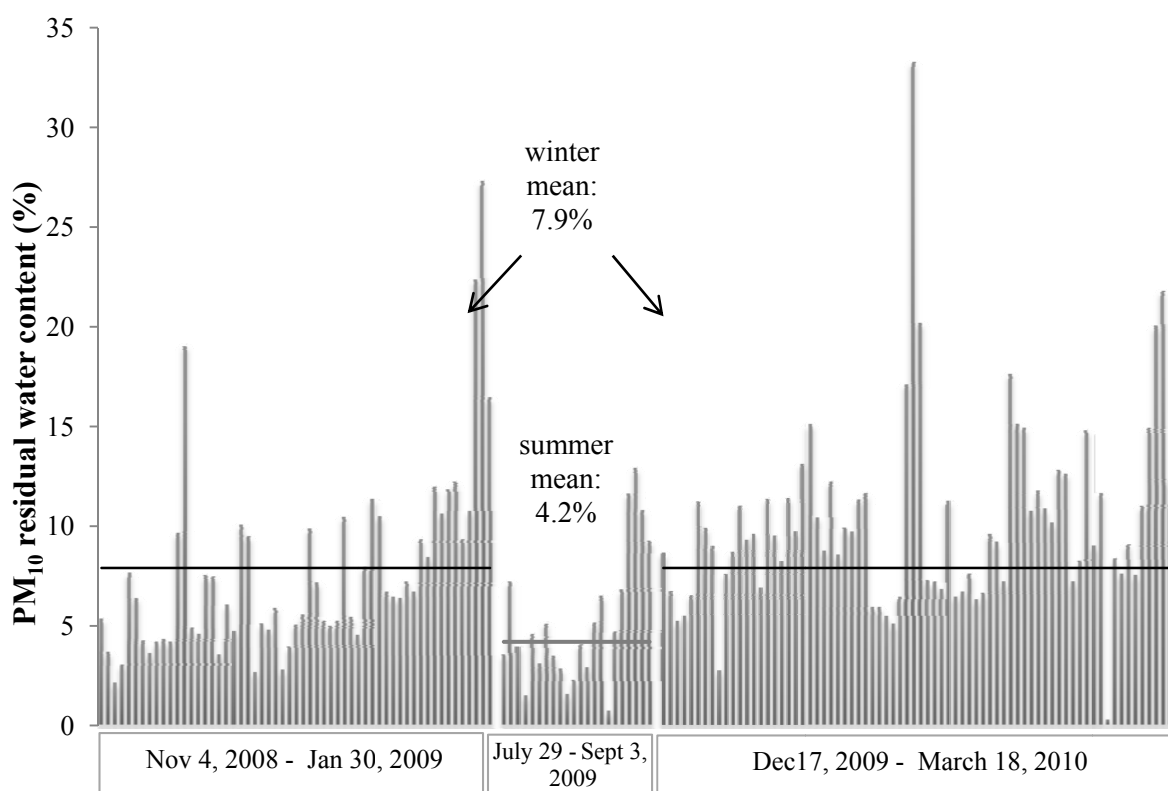

Fig. 2. Experimentally determined residual water content of PM_{10} under the conditions on EN 12341 protocol.

It follows that the mass fraction of residual water quantity reflects the share of particle-bound water to the mass of particles measured at 30% RH. The mass concentrations of residual water varied between 0.05 and 16.9 $\mu g\ m^{-3}$. The histograms of the relative contributions of residual water are depicted in *Fig. 3* both for summer and winter.
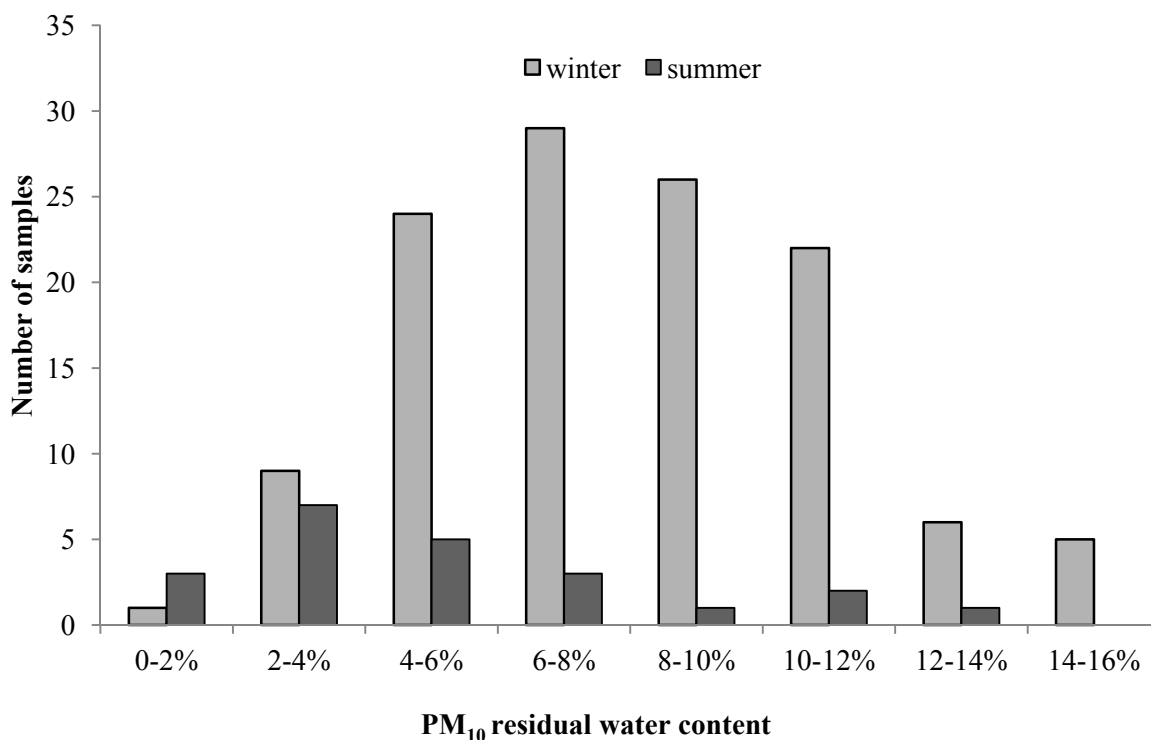

Fig. 3. Frequency distributions of residual water content of PM_{10} mass measured according to EN 12341 protocol.

The frequency of the contribution of residual water can be well described by a log-normal distribution in both seasons. In summer the mean water content is 4.2±1.5% (p=95% (Student-probe), while in winter the peaks are significantly shifted towards higher values (mean: 7.9±0.8%, p=95%) indicating that in winter the aerosol has lower DRH values and more hygroscopic than in summer.

After determination of the water content of the aerosol particles, the PM_{10} mass concentrations were corrected with these water content values. An important consequence of replacing the measured PM_{10} reference with the absolute dry mass concentrations is that the number of total exceedances of the health, information, and alert limits could be reduced by 9 (26%), 7 (50%), and 2 (40%) days, respectively (*Fig. 4*).
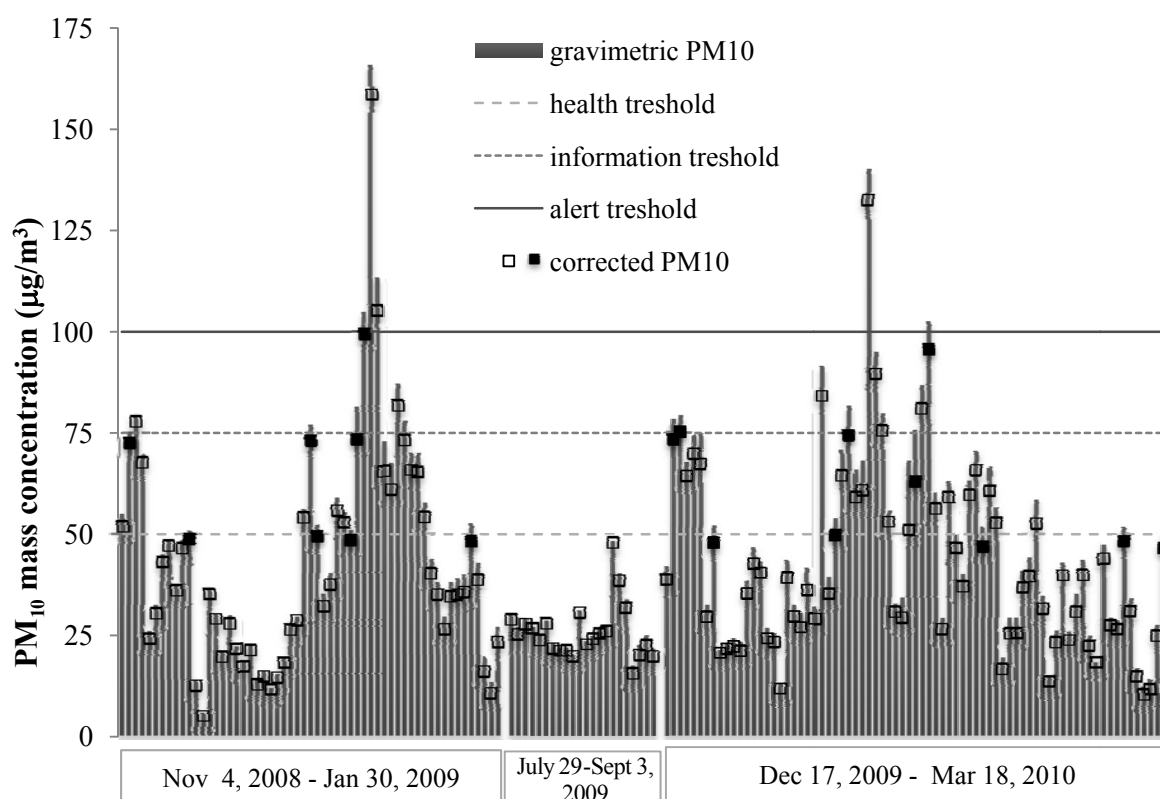
Fig. 4. Gravimetrically determined and calculated dry mass concentrations.
(Full squares indicate when the corrected PM_{10} concentration falls below the threshold limits.)

The results of our experiments suggest that PM_{10} filters measured gravimetrically according to the EN 12341 protocol do retain variable but sometimes significant amount of residual water at RH of 50±5% and at temperature of 20±1 °C after equilibration for 48 h. This finding questions that the reference measurements yield dry PM_{10} mass concentrations as intended to be according to the EN 12341 protocol. These results are not necessarily surprising based on previous laboratory and theoretical studies that showed that many abundant aerosol constituents exhibit hysteresis in their hygroscopic behavior and retain water down to their efflorescence RH well below 50% (*Weingartner et al.,* 1995; *Zhou et al.,* 2000; *Gao et al.,* 2008). Since adsorbed water does not pose any health risk but contributes quite significantly to measured PM_{10} mass concentration, the justification of environmental legislation based on EN 12341 protocol is questionable. Given the complexity of the issue and for lack of feasible methodological solutions, we suggest that the uncertainties of measured PM_{10} concentration values should be extended with a statistically derived seasonal factor that may account for the residual water content that causes positive bias in the reference measurements. Since the scope of our study is limited, extension of this research to biases caused by residual water in the readings of automatic beta-gauge monitors is clearly warranted.

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