Effect of aerosol water content on mass concentration

1. Background and objectives

Air pollution has a considerable impact on the quality of life and it is a permanent problem in cities leading to considerable health risk. The respirable fraction of atmospheric aerosol (particulate matter <10μm, PM10) belongs to the most dangerous group of air pollutants. Epidemiological studies have shown that these atmospheric particles, particularly those of very small size (ultrafine particles), endanger human health by causing respiratory and cardiovascular illnesses (Natusch and Wallace, 1974; Donaldson et al., 2002; Hoek et al., 2013). Beyond health effects the concentration of the particles has an influence on visibility, which is an important issue for road and air transport in addition to its significance in tourism and landscape protection.

According to the regulations of the European Commission operative at present the daily average concentration of PM10 should not exceed 50 μg m^{-3}, while the upper limit for the yearly average is 40 μg m^{-3}. The number of transgressions of the daily limit should not exceed 35 days/year. Furthermore, in case of reaching the alert threshold (100 μg m^{-3}) there is need for restrictions, which affect the way of life of the population as well as the economy. Hence knowledge on the reliability and environmental sensitivity of the method used for the measurement of the PM10 mass concentration is of great importance from health, air quality control and economic point of view.

As discussed above the mass concentration of aerosol particles serves as a base for air quality control. However, the uncertainty of the mass concentration measurement, especially its sensitivity to environmental conditions are not clarified, thus PM10 aerosol is the most problematic component of air quality control. Water vapour is the most significant condensable species in the atmosphere that may considerably distort standard PM measurements. Adsorbed water may be partly retained on the filter and particulates even at low relative humidities (called hysteresis) introducing a bias into the PM mass concentration values.

Although regulation is based on daily and annual average PM values, there is often need for PM data with higher temporal resolution, e.g. during air pollution episodes with high PM mass concentrations. For this reason, particulate monitors, such as the tapered element oscillating microbalance (TEOM; Patashnick and Rupprecht, 1980; Allen et al., 1997), or instruments working on the beta-attenuation principle (BAM; Macias and Husar, 1976) were developed for the continuous measurement of atmospheric particulate mass. Today these monitors have been standardized and recommended by several organizations (e.g. EPA, EMEP) and used worldwide. In many countries hourly PM data and air quality indices (AQI) are also publicly available (Air Pollution in World; Air Quality in Europe). These instruments also use filters for particle collection and are therefore subject to the same artefacts as other filter-based methods such as positive artefacts from adsorption of gaseous components on deposited particles and/or the filter media (Solomon and Sioutas, 2008). Obviously, the particulate mass collected in 1 h is small thus the bias caused by water may be excessive. Furthermore, the sensitivity of the particulate monitors may also limit the reliability of hourly PM data especially in less polluted environments.

In addition to the gravimetric reference method the daily average PM10 mass concentration can be determined with a PM monitor working on the beta attenuation principle as well. The advantage of this latter method is the unnecessity of weighing and time-consuming conditioning of the filter before and after sampling. Consequently, daily average PM10 concentrations can be obtained automatically and without any delay as opposite to the gravimetric method. It is worth mentioning that because of the ease of automation and less labour intensive nature daily

PM10 average concentrations are reported on the basis of beta attenuation measurements in many countries (also in Hungary). Therefore, positive errors arising from particle-bound water may contribute to the number of exceedances of the daily health limit value (50 ug m^{-3}) and may even lead to legal consequences (e.g. infringement procedure).
In the light of the abovementioned issues we had the following objectives in the project:

1. Quantification of the extent of the error in the beta attenuation method (BAM) and the gravimetric measurements of PM10 mass concentration caused by the water content of the aerosol particles with particular regards to special atmospheric conditions (fog and smog events, days with high relative humidity).

2. Construction of a sampling and measurement system suitable for the online determination of PM10 mass concentration without the interference of retained water.

3. Defining of conditioning circumstances suitable for the gravimetric determination of PM10 mass concentration without the interference of retained water.

4. A further objective of the project is to find a relationship among the meteorological conditions, the water content and the chemical composition of the aerosol particles.

5. The seasonal variation of the hygroscopic growth factor of the aerosol particles will be examined as well as the possibility to take it into account for the correction of the BAM data.

2. Main results of the project

2.1 Quantification of the extent of the error in the beta attenuation method (BAM) caused by water vapour

In order to determine the error in the BAM measurement of the mass concentration of atmospheric aerosol (PM10) caused by water vapour we intended to compare the data of two PM monitor operated simultaneously using the β-ray attenuation method. Either instrument (a Thermo FH62C14) was equipped with a dryer inserted into the inlet flow before entering the monitor while the other instrument (Environnement SA) measured PM10 concentration without dryer. The Thermo instrument was tested both with and without inlet heating (at 40 ^{0}C) while the Environnement SA monitor (run by the Hungarian Air Quality Network (HAQN)) was used with automatic inlet heating (at 40 ^{0}C) when the ambient RH exceeded 60%. The former setup was intended to measure dry PM10 concentration while the other to record PM10 concentration influenced by water vapour. The investigations were carried out in a temperature controlled (at 20 ^{0}C) air monitoring container located at the Marczell György Observatory of the Hungarian Meteorological Service.

First, hourly and daily PM10 concentrations measured without dryer were compared to check the equivalency of the instruments in different periods from June to December in 2015. Very good correlation of daily average PM10 concentrations was found between the two instruments although the hourly results occasionally differed considerably (Fig.1). PM10 concentrations measured with the Thermo monitor were almost identical to those recorded with the BAM monitor of the HAQN.

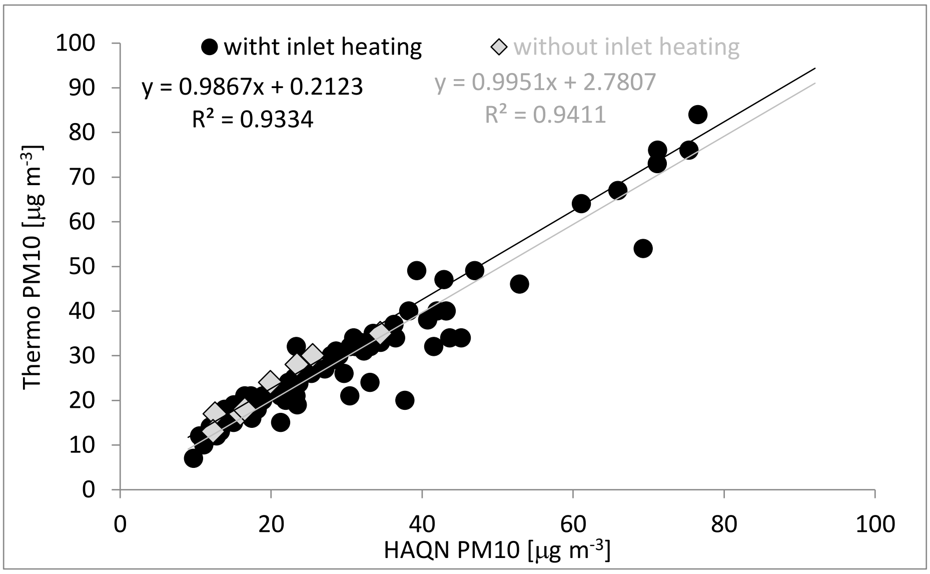
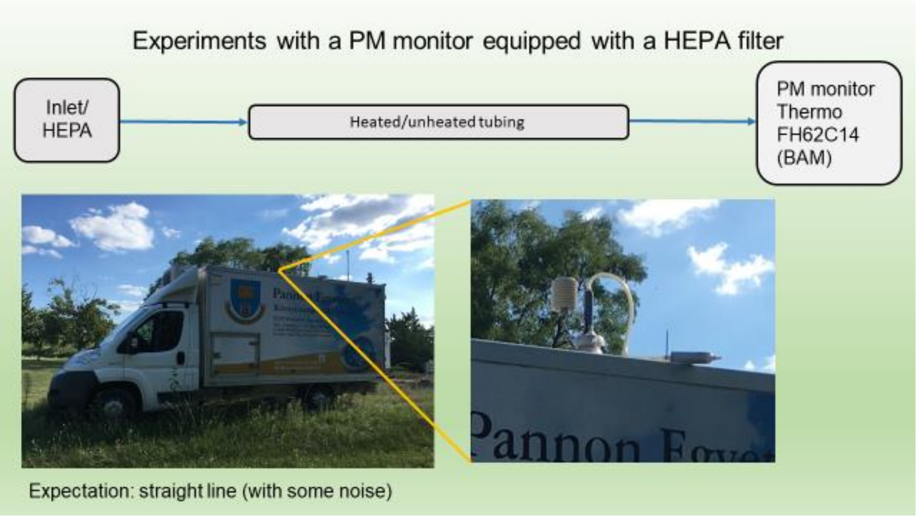


Figure 1: Equivalency test of the daily PM10 data measured with two different beta attenuation monitor

Next, the baseline signal of the Thermo instrument was checked in a sampling campaign in July 2015. In this study aerosol particles were removed from the ambient air by a HEPA filter (Fig.2).



Experiments with a PM monitor equipped with a HEPA filter

Inlet/ HEPA

Heated/unheated tubing

PM monitor Thermo FH62C14 (BAM)

Expectation: straight line (with some noise)

Figure 2 Scheme of the sampling line for the study of instrument baseline performed in the mobile air pollution lab of University of Pannonia

Between 9 and 15 July the sampling system was operated without heating, while from 15 to 19 July inlet heating was set to 40°C. The temporal variation of the apparent PM mass concentrations (measured as PM mass concentrations by the monitor on an empty GF filter) showed considerable fluctuation in the hourly average values (Fig. 3) since the incremental mass change was obviously close to the lower limit of concentration determination of the monitor. The term ‘the apparent PM’ is used here because zero mass concentration would have been expected since particle-free air was sampled.

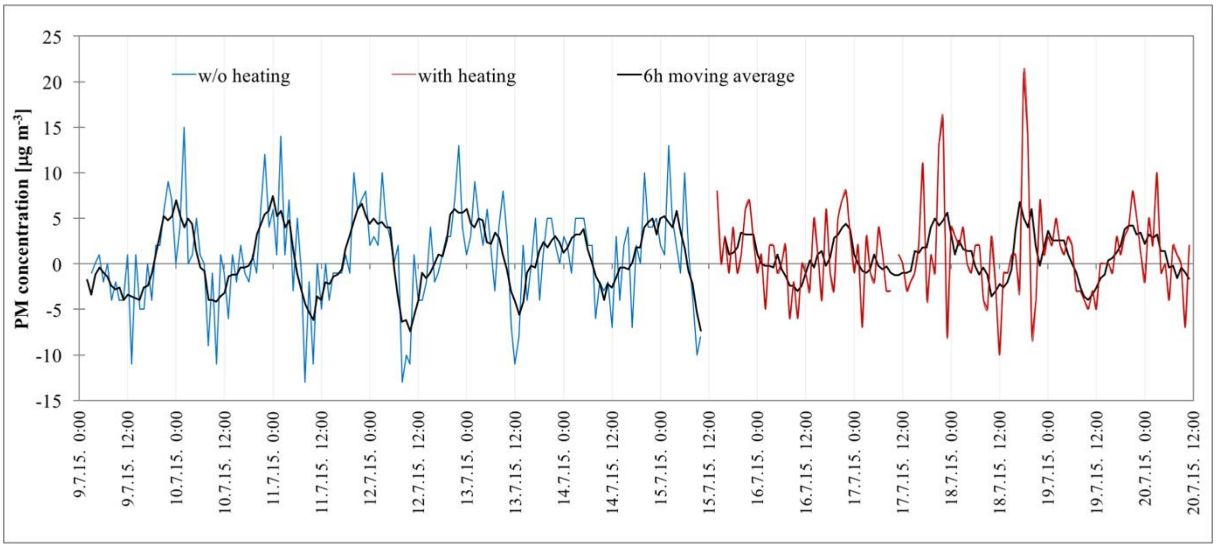


Figure 3: Temporal variation in the apparent PM mass concentration measured with particle-free air on an empty GF filter under ambient conditions in July 2015 with heated (red) and non-heated (blue) sampling inlet on an empty GF filter.

Despite this fluctuation apparent PM mass concentrations showed a periodic diurnal variation which was even more pronounced in the 6-hour moving averages: positive bias in the evening and at night while negative bias during daytime was observed irrespectively whether the inlet heating was on or off. The magnitude of the apparent hourly average PM concentration ranged from −13 to +21 µg m^{-3} and even the 6-hour moving average concentration values varied between −7 and +7 µg m^{-3} (average: 0.7 µg m^{-3}; SD: 3.6 µg m^{-3}). In the case of a heated sampling inlet the measured 6 h moving average apparent PM mass concentrations were generally smaller (−4 and +6 µg m^{-3}; average: 0.7 µg m^{-3}; SD: 2.2 µg m^{-3}) than when a non-heated inlet was applied. This clearly indicates that a heated inlet (at 40 ^{0}C) can lower this fluctuation to some extent although the temperature should be kept as low as possible in order to avoid losses of semivolatile compounds (e.g. ammonium nitrate evaporates in 5 s at 42 ^{0}C). Thus in summertime, especially at high ambient RH, heating of the inlet is not an efficient solution.

As shown above the adsorption and desorption of atmospheric water vapour may increase and decrease, respectively, the mass of the filter, thus leading to erroneous readings of 1-hour PM concentrations. Our experiments with particle-free air in July 2015 were run simultaneously at the same site with the monitoring of ambient PM10 concentrations by using another BAM monitor as part of the Hungarian Air Quality Network. In the first half of the July sampling period the standard PM10 concentrations ranged from 7 to 31 µg m^{-3} with higher values measured during the night, at dawn or in the morning. In the second half of the period elevated PM concentrations (up to 50 µg m^{-3}) were recorded reaching the maximum on 17th July. In these days, the highest values were obtained during the night.

Large relative errors - both positive and negative - were revealed when the ratio of apparent PM and ambient PM10 concentrations was calculated as shown in Fig. 4. Each day of the campaign the magnitude of the relative error exceeded 38% during late evening/night when the inlet heating was switched off. In four out of the six days the relative error approached or exceeded 50% in this period of the day and the two highest values were 64% and 67%. The reasons for such high relative errors are the relatively high apparent PM concentration resulting from the condensation of water vapour and the low ambient PM10 concentrations at this time of the day (often between 9 and 15 µg m^{-3}). Heating of the inlet tube to 40 ^{0}C decreased the magnitude of the error but still relative errors exceeding 35% were observed occasionally. It should also be noted that the decrease of relative error experienced with a heated sampling inlet can be attributed partly to higher ambient PM10 concentrations that occurred during the second half of the campaign.

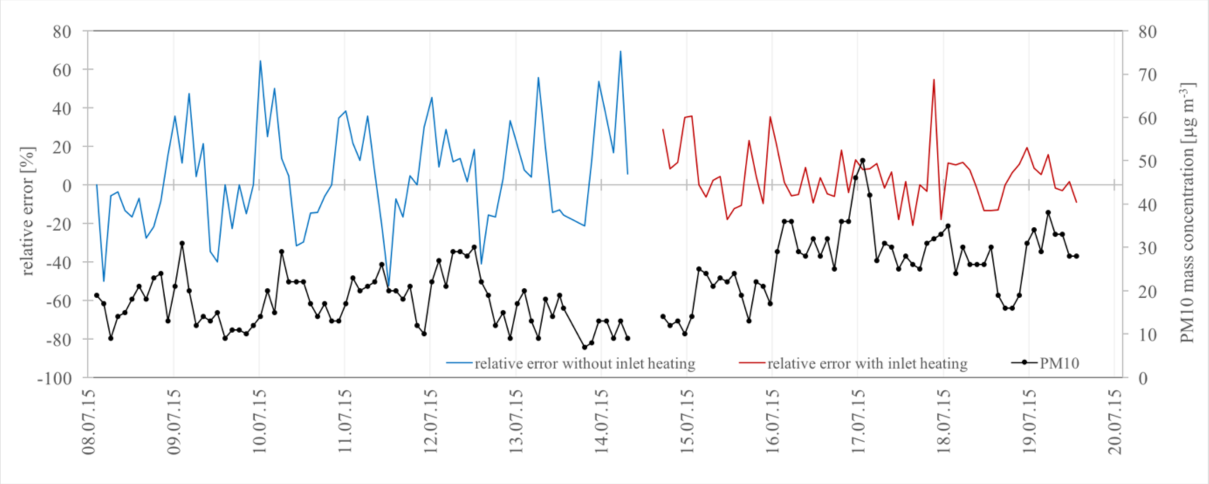


Figure 4: Relative errors in ambient hourly PM10 measurements due to the condensation and evaporation of water onto the glass fibre filter of the monitor. The hourly PM10 concentrations shown in this figure are the official values reported by the Hungarian Air Quality Network and measured also by a BAM monitor.

This experiment was repeated with a preloaded filter in August, 2017 (Fig. 5). Similar results were obtained to those with empty GF filter. The apparent 30 min average PM10 concentrations varied from ca. -10 µg m^{-3} to +15 µg m^{-3} and even the 4h moving averages ranged from ca. -5 µg m^{-3} to +10 µg m^{-3}. The maxima and minima in the apparent PM10 concentration were observed at 5-8 pm and 6-10 am, respectively. These peaks corresponded to the fastest increase and decrease of RH during the day in this campaign.

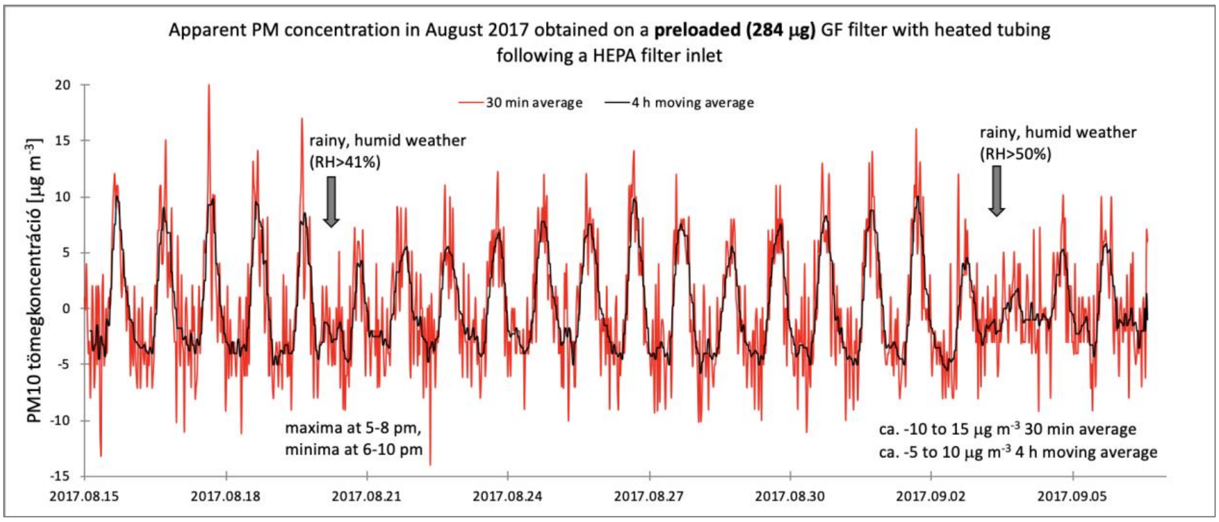


Figure 5: Temporal variation in the apparent PM mass concentration measured with particle-free air on a preloaded filter under ambient conditions in August and September 2017 with heated sampling inlet.

These findings clearly indicate that atmospheric water vapour can significantly distort high time resolution (hour scale) PM10 measurements carried out with beta attenuation monitors.

2.2 Construction of a sampling and measurement system suitable for the determination of PM10 mass concentration without the interference of retained water.

In order to eliminate the bias in the PM measurements by BAM, water vapour has to be removed from the sample flow. Thus a Dekati DD-600 diffusion dryer was inserted into the sampling line of the Thermo monitor. Then PM10 concentrations measured with the dryer were compared to PM10 data obtained with the BAM monitor of the Hungarian Air Quality Network running concurrently. The measurement system was built in the air pollution mobile lab of University of Pannonia. Since in aerosol measurement technique (e.g. in measuring aerosol optical properties) RH=40% is more and more often used instead of 50% (considered earlier as adequately dry to eliminate the effect of water) our primary goal was to reduce the RH of the ambient air to ca. 40% before entering the monitor. The efficiency of the dryer was checked by monitoring RH in the air stream outflowing from the dryer as well as recording PM concentrations with the monitor using a HEPA filter instead of the PM10 inlet. Since the HEPA filter removes particles from the air flow and the concentration of water vapour in ambient air is orders of magnitudes higher than that of other condensable gases, any mass change recorded by the monitor indicates the presence of water on the sampling filter. It was observed that the efficiency of the dryer strongly depended on the operation of the air conditioning system in the mobile lab. When the air conditioner switched on, the dryer cooled down and consequently the RH inside the dryer increased. Thus, the arrangement was modified accordingly. Potential particle loss in the dryer was studied in the following manner: a.) Our Thermo PM10 monitor equipped with the diffusion dryer ran simultaneously with the instrument of the Hungarian Air Quality Network and the daily PM10 concentrations were compared. The slope of the regression line (0.48) and the correlation coefficient (r^2=0.34) highlighted that our setup equipped with the dryer measured ca. half of the PM10 concentrations recorded with the other monitor (Fig. 6) and the former very good correlation between the two instruments (shown in Fig.1) decreased drastically.

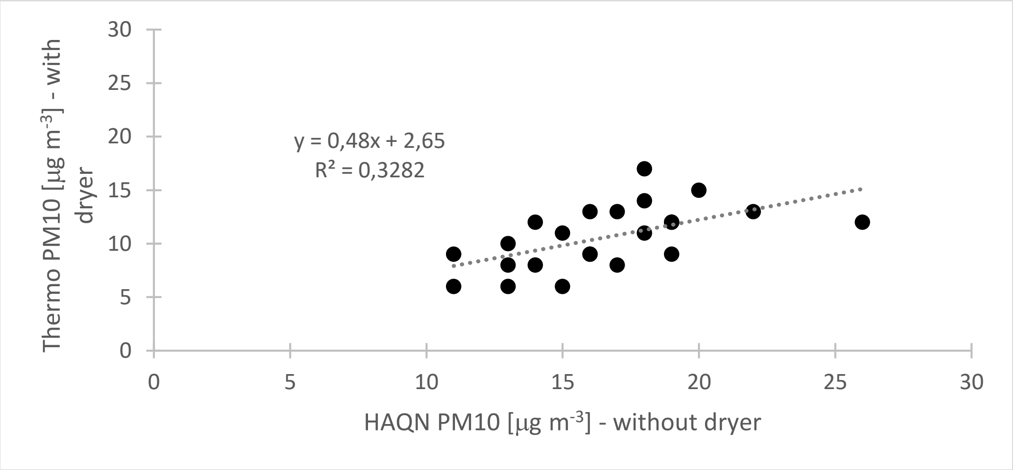


Figure 6: Comparison of daily PM10 data obtained with two beta attenuation monitor: one equipped with a diffusion dryer and the other without dryer

This considerable difference between the results may arise partly from the water content of the aerosol and partly due to particle loss caused by the dryer. Particle loss may occur due to the inertia of coarse particles but evaporation losses cannot be excluded either since there is low pressure (10 kPa) in the dryer. b) In order to quantitate these effects our PM10 monitor equipped with the diffusion dryer was operated simultaneously with the instrument of the Hungarian Air Quality Network but in this case the vacuum pump of the dryer was switched off. Thus the difference between the PM10 concentrations should derive from inertial particle loss caused by the dryer. The slope of the regression line (0.76) and the correlation coefficient (r^2=0.60) indicated that inertial particle loss of the dryer caused ca. half of the deviation (Fig. 7).

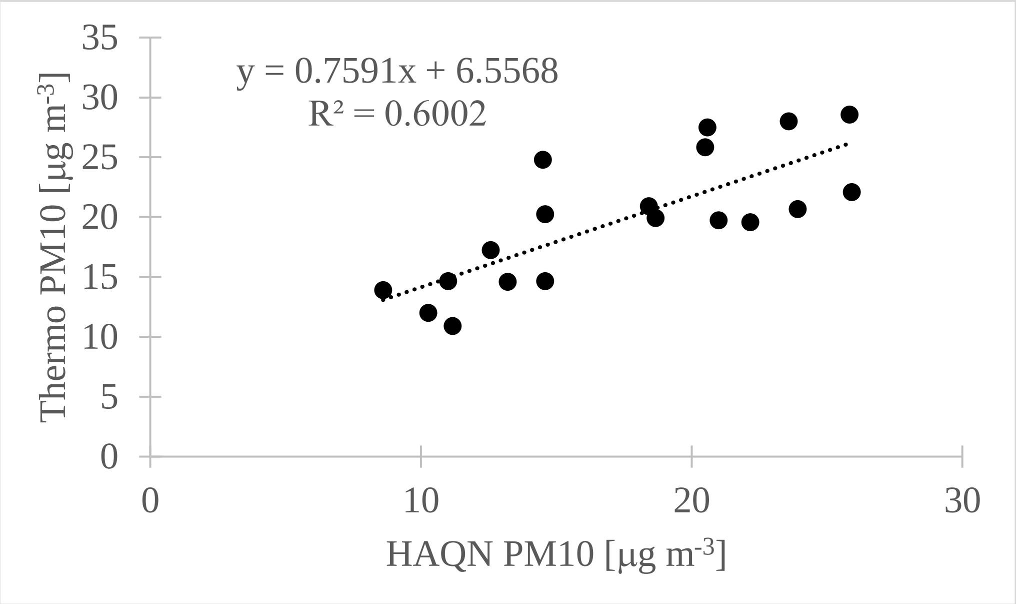


Figure 7: Comparison of daily PM10 data obtained with two beta attenuation monitor: one equipped with a diffusion dryer and the other without dryer. The vacuum pump of the dryer was switched off thus the drying function did not work in this case.

From these results it can be concluded that evaporation loss and the removal of water content led to 25-30% difference in PM10 measurements. Since the removal of water solely cannot explain this difference (see in section 2.4) it can be stated that the vacuum applied within the dryer resulted in evaporation of volatile aerosol components in addition to impaction losses of particles leading to underestimation of PM10 concentrations. Therefore, experiments with the dryer were terminated at this point. The bias in PM10 concentrations caused by water in beta attenuation monitors was studied in a different way.

2.3 Quantification of the extent of the error in the gravimetric measurements of PM10 mass concentration caused by the water content of the aerosol particles

In Europe, for the gravimetric determination of PM10 the filters have to be equilibrated for 48 h prior to weighing at RH=50 ± 5% and t=20 ± 2 °C before and after sampling according to the reference method developed by the European Committee for Standardization (CEN). A number of studies concluded that particle-bound water may be present under these conditions. Therefore, the PM10 mass concentration was determined at a lower RH value as well (RH≈20%, hereinafter referred to as dry PM10 concentration) and it was compared to the PM10 mass concentration measured according to the gravimetric reference method (at RH between 45% and 55%). The difference is caused by the water content of the aerosol particles that is still retained at RH≈50%. Particle-bound water does not pose any health effect, however it increases the apparent PM10 mass concentration leading to a measurement error. This error of the reference method as a function of dry PM10 mass concentration is shown in Fig. 8 for eight sampling campaigns implemented in different seasons from 2016 to 2018. Seasonal variation was observed in the measurement error: in the samples collected in May and July the average of the measurement error ranged from 1.9% to 4.3% while it raised to 6.0%-8.5% in the samples collected in April, autumn and winter. It is noteworthy, however, that the overestimation of the PM10 mass concentration in individual samples occasionally exceeded 10%. In absolute terms the average error introduced by the water content was found in the 0.30-0.75 ug m^{-3} and 1.24-3.25 ug m^{-3} range in the abovementioned periods. The seasonal variation can be explained with the difference in the meteorological conditions (relative humidity primarily) and chemical compositions of the aerosol particles as discussed later. It is interesting to remark that despite the fact that more pronounced overestimation of PM10 was observed in the campaigns with higher RH (typical from autumn to spring in Hungary) there was no correlation found between the ambient RH and the error of gravimetric measurements at RH=50% within the same campaign. This finding indicates that in addition to RH there must be at least one more variable that influences the reliability of the gravimetric measurements.

In the samples collected in December 2016 and April 2017 the PM10 mass concentration was determined at lower (35-40%) RH as well. It was found that the overestimation of PM10 concentration decreased from 6.6% to 2.9% and from 6.5% to 4.2% in December and April, respectively.

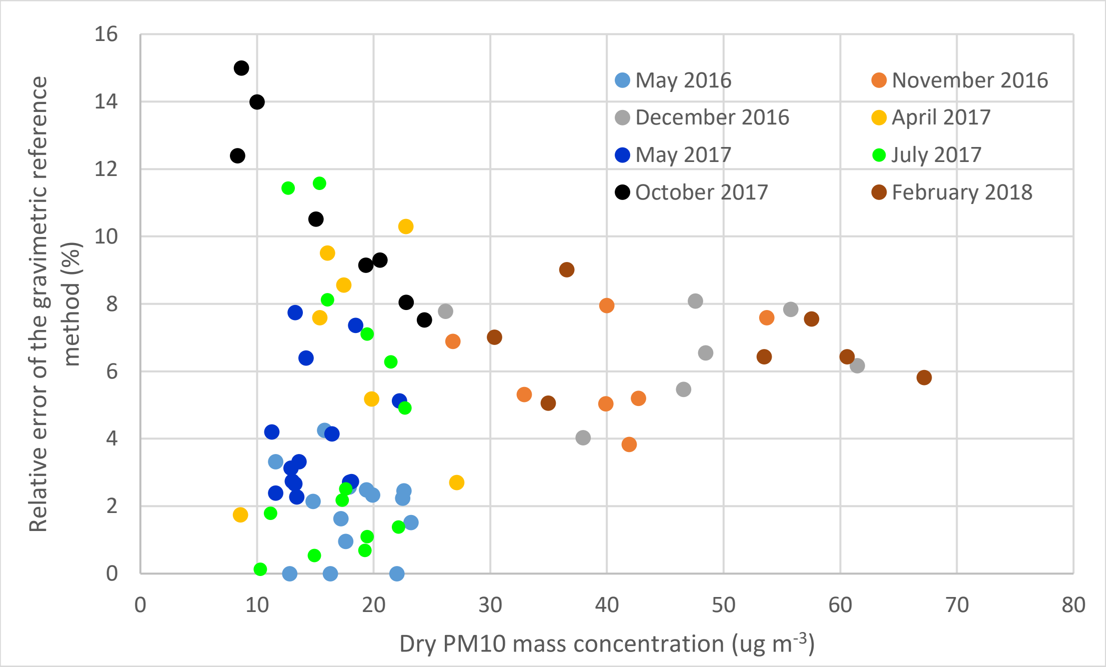


Figure 8: Relative error in the determination of daily PM10 mass concentration according to the gravimetric reference method as a consequence of particle-bound water.

Gravimetric results on the water content of PM10 aerosol at different RH values are hardly available in the literature probably because of the time-consuming nature of the measurement. Instead, the particle-bound water in ambient aerosol is estimated as the water content of the main inorganic aerosol constituents using the models such as E-AIM, AIOMFAC, ISORROPIA or the ZSR mixing rule. The advantage of this approach is that the water content can be calculated at any RH for those compounds that the model can handle. However, the number of such inorganic and especially organic components is limited while in the aerosol hundreds or even thousands of organic compounds may be present with unknown properties and effect on the water uptake of other aerosol constituents. Another method for the estimation of the aerosol water content at different RH values is the measurement of the growth factor by using hygroscopicity tandem differential mobility analyzers (HTDMA). This technique can be applied to individual compounds, mixtures of known components, group of compounds isolated from ambient aerosol or ambient aerosol itself. With the help of such approaches it was concluded that depending on the geographical position and the RH conditions PM10 aerosol may contain substantial (10-40%) residual water at 50% RH (Tsyro et al. 2005, Engelhart et al. 2011).

Numerous phenomena may give rise to particle-bound water at RH=50% such as a.) hysteresis in the deliquescence and crystallization of inorganic salts, b.) modification of deliquescence and crystallization RH of inorganic salts caused by organic aerosol components, c.) high RH conditions during sampling.

a.) Most of atmospherically relevant inorganic salts (such as ammonium-sulfate, sodium chloride, etc.) exhibit considerable hysteresis in water content, i.e. their efflorescence RH is significantly lower than the deliquescene RH. The efflorescence RH for some relevant inorganic salts such as ammonium sulfate and sodium chloride is smaller than 50% (Jacobson 2005). If during sampling an aerosol particle experienced RH>DRH and the ERH of its main inorganic constituent(s) is smaller than 50% then the particle will contain residual water during weighing at RH=50%. The situation becomes even more complex by the fact that mixtures of salts behave differently from the individual components.

The hysteresis in the water content (deliquescence/crystallization) of the samples was studied in a subset of samples by weighing the filters following 48 hours equilibration at different RH values. The average hysteresis in different seasons is shown in Fig.9. It can be concluded from the figures that the samples may retain considerable (on average 8-14%) amount of water at RH=50% once they have been equilibrated in humid (RH=76-81%) conditions. The shape of the hysteresis curves and the extent of water content were similar in spring, summer and autumn but the winter samples took up significantly more water under the highest RH conditions examined. However, the water release was also more pronounced in the winter samples with decreasing RH resulting in similar residual water content at RH=50% on the descending branch of the hysteresis curve. The deviation in hysteresis can be explained with the seasonal difference in the chemical composition of the samples as detailed in section 2.5.

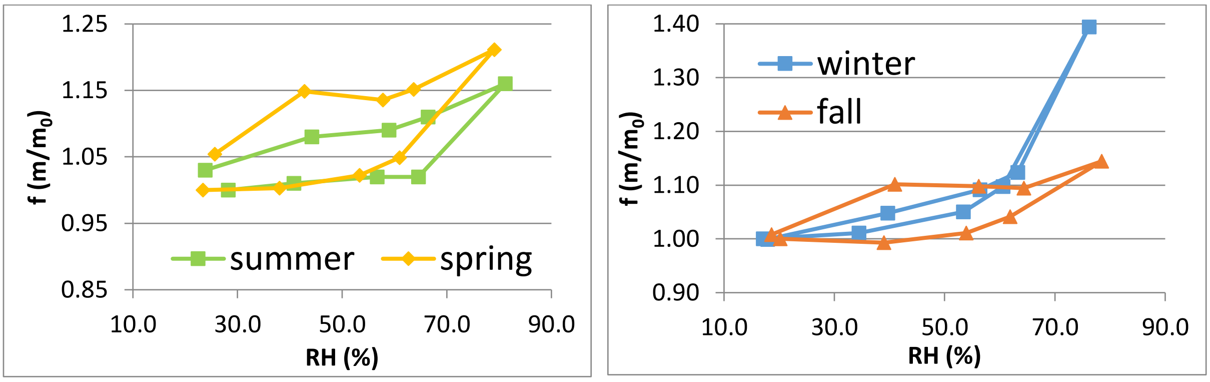


Figure 9. Average hysteresis in the water content of the aerosol samples in different seasons as determined by gravimetry under different RH conditions. (Data points are connected to guide the eyes, the continuous lines have no physical meaning.)

b.) In addition to inorganic salts aerosol particles contain a variety of organic compounds as well that may influence both deliquescence and efflorescence of the inorganic components (Lightstone et al., 2000; Gysel et al., 2004; Wang et al., 2016). In the presence of organic compounds the efflorescence of ammonium sulfate may be shifted to higher or lower RH depending on the type and relative amount of the organic component or it may even be suppressed completely (Ling and Chan, 2008; Lei et al. 2018). Suppressed efflorescence or decreased ERH of inorganic aerosol constituents may also lead to residual water content at 50% RH.

c.) The RH conditions during sampling may also influence the amount of particle-bound water. If the RH exceeds the DRH of the dominant inorganic components and its (modified) ERH is lower than 50% then the aerosol mass will be overestimated at RH=50% as a consequence of residual water content. Since 24-hour sampling in our experiments was carried out from 0-24 h aerosol collection was finished in a usually humid period of the day (at midnight). If the RH was high in the last hours of sampling then inorganic aerosol components were dissolved. In addition to this, particles that had been collected during the day (even under lower RH conditions) faced a humid air stream of 500 l min^{-1} on the filter and may have taken up some water, too. This phenomenon may contribute to the higher overestimation of PM10 mass concentration in humid periods of the year.

As mentioned above the dry PM10 concentration was derived from weighing the filters at RH≈20%. Hygroscopicity studies carried out with individual organic and inorganic compounds, mixtures of purely organics and organics mixed with inorganic salts as well as water-soluble components of atmospheric aerosol samples showed that the water content of these individual compounds and mixtures was generally negligible at RH≈20% although for some model mixtures it accounted for a couple of percents of the dry mass measured at RH=0% (Gysel et al., 2004; Wang et al., 2016). If the aerosol samples studied in this work contained e.g. 3% water at RH≈20% then the error made in the determination of PM10 mass concentration by applying the gravimetric reference method at RH=50% would be even bigger: 5-7.7% instead of 2-4.7% in May and July and 9-11.5% instead of 6-8.5% in April, autumn and winter.

Our findings clearly show that gravimetric measurements carried out according to the EN 12341 protocol overestimates PM10 mass concentration. The reliability of the gravimetric reference method (GRM) could be increased by performing weighing of the filters at RH of 35% but even at this low relative humidity some water remains adsorbed on the particles. It is recommended to carry out gravimetric measurements at RH of ca. 20% because this condition ensures more reliable results on the dry aerosol mass.

2.4 Comparison of PM10 concentrations determined by the beta attenuation method and gravimetry at low RH

The dry PM10 mass concentrations determined by gravimetry at RH≈20% (as detailed in the previous section) were compared to the PM10 concentrations measured by a beta attenuation monitor of the Hungarian Air Quality Network at the same site. The results obtained for different seasons in 2016 and 2017 are summarized in Figure 10.

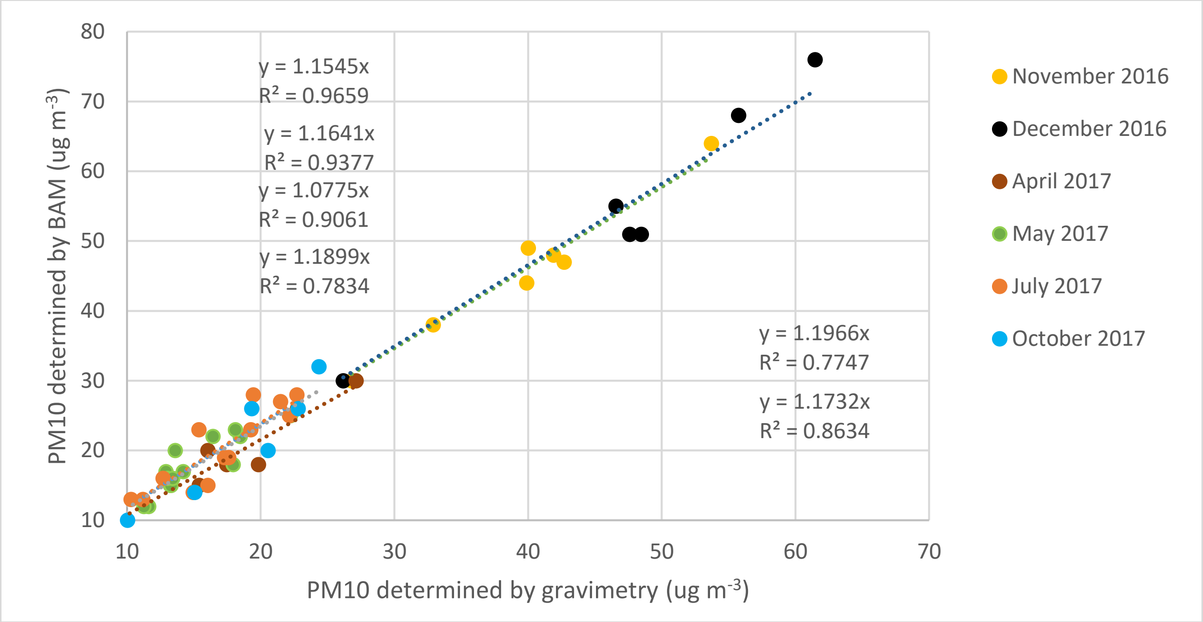


Figure 10 Comparison of PM10 concentrations as determined by the beta attenuation method and gravimetry at RH≈20%.

A very good correlation ($0.77<r^2<0.97$) was obtained between the two methods but the PM10 concentrations measured with the beta attenuation monitor (BAM) were higher in all campaigns. In October, November and December the dry PM10 mass concentrations were overestimated by 17%, 15%, 16%, respectively, as indicated by the slope of the regression lines while in April, May and July the differences were 8%, 19% and 20%, respectively. Several reasons may lead to discrepancies in PM10 concentrations obtained with the two methods including (1) differences in the cutoff aerodynamic diameter of the inlets, (2) differences in the water uptake of the filters (3) deliquesence of aerosol components, and (4) evaporation of volatile and semivolatile aerosol constituents. Although differences in the cutoff aerodynamic diameter of the inlets and the water uptake of the filter materials cannot be completely excluded there are probably two more phenomena that contribute to the discrepancies: The average ambient relative humidity during the campaigns were 69%, 69%, 82% and 86% in May, October, November and December, respectively. Although in May and October the average RH was lower than in November and December, the maximum RH reached or even exceeded 85% on each day of the campaigns (with 1 exception) in these months as well resulting in deliquescence of the dominant inorganic components and thus substantial water uptake of the particles. According to Chang et al. (2003) when the ambient RH exceeds ca. 85% the water content does not evaporate from the particles during the BAM measurement and thus the mass concentration values obtained by the BAM are higher than those derived from gravimetry.

A different phenomenon may have led to the overestimation of PM10 mass concentration by the BAM monitor in July: during this campaign the temperature was high, often approaching to or even exceeding 30 ^{0}C. The monitor operated in an air-conditioned (t=20 ^{0}C) container. Although the ambient RH was relatively low (average RH=55%) the warm air cooled down quickly after entering the air-conditioned container and thus RH increased sharply resulting in considerably higher RH in the BAM monitor than outside. E.g. 45% ambient RH at 30 ^{0}C ambient temperature turns into RH=82% at 20 ^{0}C inside the monitor leading to water uptake of the particles collected on the filter material of the BAM monitor.

In the campaign in April the average ambient RH (59%) was substantially lower than in November and December thus the water uptake of the aerosol particles was considerably lower than in the cold months. On the other hand, the average ambient temperature was substantially lower than 20 ^{0}C (11.6 ^{0}C) and thus, contrary to the July campaign, most of the time the air conditioning of the measurement container did not increase but decreased the RH of the sampled air. Thus the difference between the PM10 mass concentrations determined by the BAM and the gravimetric method was minor.

Similar results were reported by Chang et al. (2001) who found good agreement for urban samples collected under moderate environmental relative humidity (RH<70%) in Taiwan. The ratio of the mass concentrations determined by the BAM and GRM was found to be 1.08±0.06. However, under conditions with high ambient RH when the deliquescence RH of the dominant inorganic component was exceeded the deviation between the two methods increased to 1.21±0.22 (BAM/GRM). They estimated that under high RH conditions (RH>95%) the water content of the aerosol particles accounts for more than 40% of PM10 mass. However, due to partial evaporation of water from the particles collected on the filter of the BAM the overestimation of PM10 mass concentration obtained with the monitor is less than calculated by simulation. Lazaridis et al. (2008) found also similar results for PM10 under urban background/semi-rural area on the island of Crete, Greece. The BAM/GRM ratio was found to be 1.17±0.11 in a summer campaign with relative humidity and temperature averages being 64.4±8.0% (49.4–78.3%) and 25.1±1.9°C (21.8–28.0°C), respectively. It must be emphasized that in contrast to the above literature data in our work the BAM results are compared to the gravimetric results obtained at 20% RH. As shown in section 2.3, these values are lower than the PM10 concentrations determined with the GRM at 50% RH. It means that the BAM/GRM (at RH=50%) ratio would be closer to 1 than those shown in Figure 2 but in this case both methods would be biased by the water content of the aerosol particles.

2.5 Chemical analysis of the aerosol samples

In addition to the study of water uptake the chemical analysis of 92 high volume samples collected in eight campaigns from May 2016 to February 2018 was also carried out. The amount of the dominant inorganic ions (ammonium, potassium, sodium, calcium, magnesium, sulphate, nitrate, chloride) and oxalic acid (as the dominant individual organic acid) in the samples was determined with a combination of ion chromatography, spectrophotometry and atomic absorption spectroscopy and thus the atmospheric concentration of these species was obtained. Furthermore, the concentration of total and water-soluble carbon in the aerosol samples was also determined by using a TOC analyser.

In Figure 11 and 12 the atmospheric concentration and relative contribution of the analysed water-soluble inorganic ions in different seasons are summarized. Both the overall concentration of the ionic species and the share of the individual ions showed seasonal variation. The overall concentration of the ions averaged for the given campaign was in the range of 2.8-5.6 μg/m^3 in the case of spring and summer samples but it reached 16 μg/m^3 and 19.3 μg/m^3 in November and December, respectively. The average concentration of TC showed similar pattern: it ranged from 3.4 μg/m^3 to 5.6 μg/m^3 in spring and summer and it reached 14 μg/m^3 and 17.1 μg/m^3 in November and December, respectively. The higher concentrations in November and December can be explained with the decreased mixing height in the cold months.

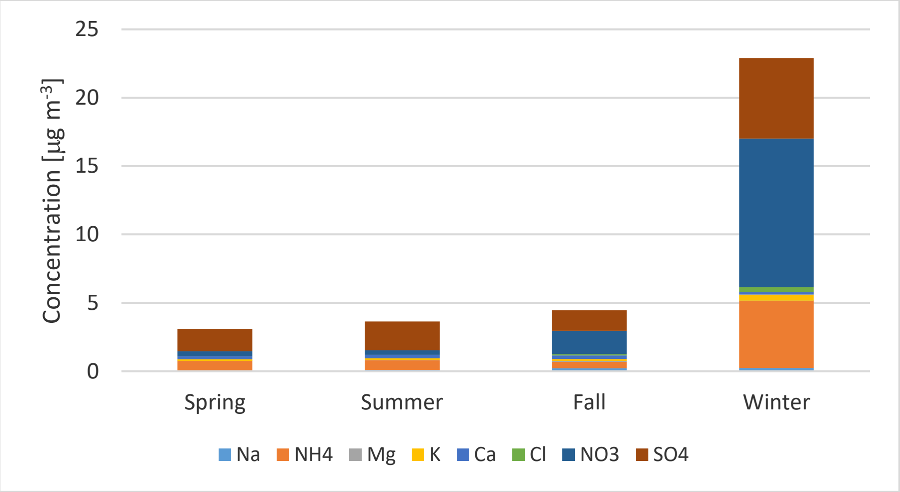


Figure 11 The concentration of the analysed water-soluble inorganic ions in atmospheric aerosol in different seasons.

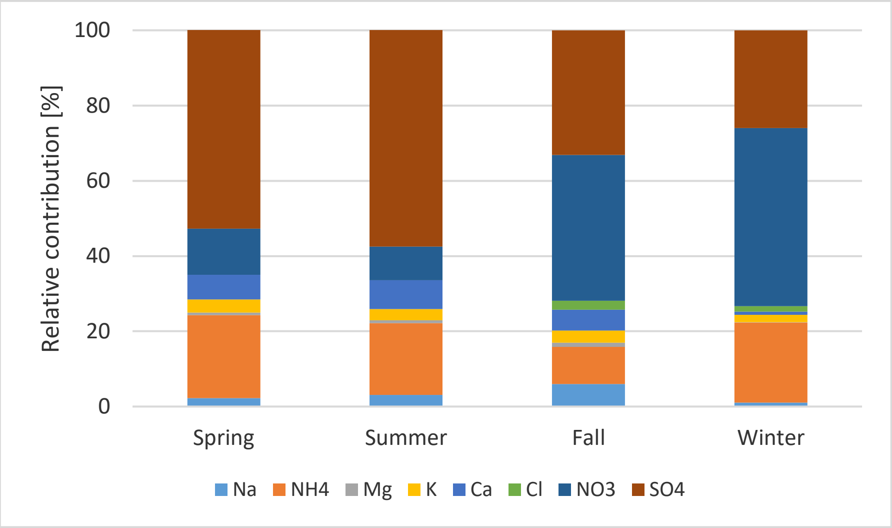


Figure 12. Relative contribution of the analysed water-soluble inorganic ions in atmospheric aerosol in different seasons.

Ammonium was the dominant cation in the spring and summer samples (average contribution in the campaigns ranging from 52% to 63%) followed by calcium (19-23%). Sodium (6.2-12%) and potassium (7.7-9.4%) contributed to the cation mass concentration to similar extents while magnesium (1.8%-4.1%) was present in the lowest concentration among the analysed cations. However, in the samples collected in November and December the contribution of ammonium raised to 75-79%, followed by potassium (11%), calcium (5.6-9.3%), sodium (2.8-3.4%) and magnesium (1.2-1.9%). The composition of anions showed seasonal changes, too. The average contribution of sulphate in the campaigns increased with increasing temperature from 32% in December to 79% in July. Oxalic acid changed similarly from 1.5% in December to 8.2% in July. Nitrate followed an opposite trend, its contribution decreased with increasing temperature from 60% in December to 12% in July. The increase of ammonium and nitrate in cold weather can be explained with the shift of ammonium-nitrate from gas phase to aerosol phase while the higher potassium contribution in winter can be the consequence of biomass burning. The relative increase of oxalic acid in July is most probably connected to enhanced photochemistry in summer. By converting the mass concentrations into equivalent concentrations a cation excess was found in the spring and summer samples and anion excess in November and December. The cation excess in spring and summer was probably counterbalanced by the anions of organic acids (not analysed in our study) while the anion excess in the cold months indicated the acidity of the aerosol (extracts).

WSOC accounted for 35-45% of TC but in this case seasonal trend was not observed (Fig 13.) However, the WSOC/TC ratio was below 30% in the winter samples when TC exceeded 18 μg/m^3. The lower WSOC/TC ratio can be explained partly with higher soot emission (e.g. from domestic heating or cars with cold-start engines) but also with the lower oxidizing potential of the atmosphere in winter.

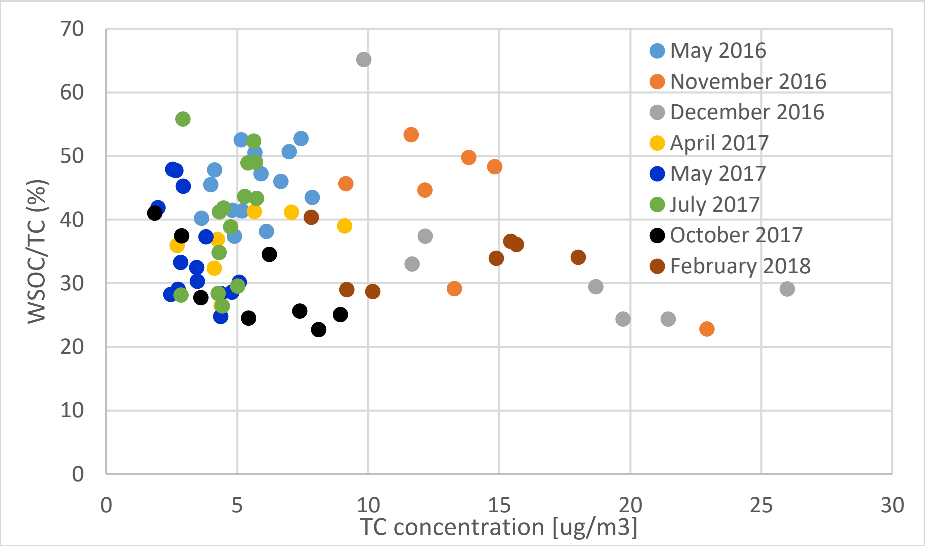


Figure 13 The WSOC/TC ratio as a function of TC concentration in different campaigns

The chemical composition of the samples was used to model the water content of the particles with the extended AIM thermodynamics model (see in section 2.6).

2.6 Relevance of the hygroscopic growth rate derived from visibility observations in PM10 measurements

Nowadays aerosol mass concentration serves as a basic parameter in air quality control. The consideration of hygroscopic growth of the aerosol mass has great importance since water vapor may considerably influence standard PM measurements. In order to eliminate the effect of aerosol hygroscopicity in PM10 several possibilities are available; and in this work we aimed to discuss and compare three of these methods including the estimation derived from visibility data. The aim of our work is to answer the following questions:

a. How hygroscopic growth factors obtained from different methods are related?
b. What is the relevance of the hygroscopic growth rate derived from visibility observations in PM10 measurements?

1. How hygroscopic growth factors obtained from different methods are related?
In the comparison of the individual mass growth rates, all rates concern to the same samples (weighting, AIM model) and strictly the same time intervals (visibility). First, the methods applied in this work to estimate the hygroscopic growth of the aerosol particles are compared and the advantages/disadvantages of their application are briefly summarized in Table 2. Despite that, the use of visibility data raises several questions; the broad availability of these data has great potential in environmental applications.

Table 2: Advantages and disadvantages of methods of hygroscopic mass growth rate.

Method	Abbrevation	Advantages	Disadvantages
Gravimetry: weighting the mass change of aerosol filters due to RH variation	GM_{filter}(h,c)	Provides direct mass growth rates	Time demand is huge Limited time resolution (24-hours samples) Limited RH range Precision of mass measurements Filter artefact
Application of AIM model	GM(AIM)	Provides direct mass growth rates Based on thermodynamics	Limited time resolution (24-hours samples) Restricted information on the compounds considered Artificial compounds are constructed from the ionic composition Not clear: deliquescence or crystallization pathway is considered
Use of visibility data	GM(VIS)	Worldwide availability of data High spatial and temporal resolution	Observation (based on human eye, daytime/nighttime observation, horizontal inhomogeneity of visibility, etc.) Based on empirical relationship between extinction coefficient and RH. Provides indirect mass growth rates

In Figure 14 the mass growth rates are given as a function of relative humidity. In all cases their general increase with increasing RH are given, but with different degrees. We can conclude that:

- The aerosol mass starts to increase according to the AIM model at the highest RH, around 65%, while a continuous increases from 20% and 35-40% RH are indicated by GM(VIS) and GM_{filter}(h), respectively. The importance of the hysteresis cannot be ignored since the crystallization (GM_{filter}(c)) takes place at significantly different path than humidification (GM_{filter}(h)). According to GM_{filter}(c) water release continues until 20% RH.
- These data suggest a rather important (ca. 30%) shift between the prediction of AIM model and GM(VIS), GM_{filter}(h, c). Considering this ca. 30% RH shift in GM(AIM), a rather good agreement can be found among the mass growth factors obtained by three

different methods. The question is that how this shift can be attributed to the other aerosol compounds which are not involved in the AIM model calculation.

- At high relative humidity (RH>80%), GM(VIS) and GM(AIM) converge and even above 95% are in rather good agreement.
- Under RH=50-60% GM(VIS) has similar values as GM_{filter}(c) in contrast to GM_{filter}(h). We suppose that mass growth factors derived from visibility data represent rather the crystallization paths of the aerosol hygroscopicity. On the other hand, at higher relative humidity (RH>60%) GM_{filter}(c) rate is much smaller than GM(VIS). We assume that the reason of this disagreement can be the “relative humidity history” of the aerosol. Our theory on RH history is the following. We presume that the extent of hysteresis (difference between GM_{filter}(h) and GM_{filter}(c)) depends on the highest RH the ambient aerosol particles exposed to. This means that the difference between GM_{filter}(h) and GM_{filter}(c) at a given relative humidity can be much higher if the maximum ambient RH reached e.g. 95-100% than in the case of lower (e.g. 80%) RH. It can have real relevance in the evaluation of our data since during the humidity-controlled measurements filters were exposed to RH≤80%, while the filter sampling the maximum ambient relative humidity could exceed this value. The clarification of this theory is in progress and the results will be reported.

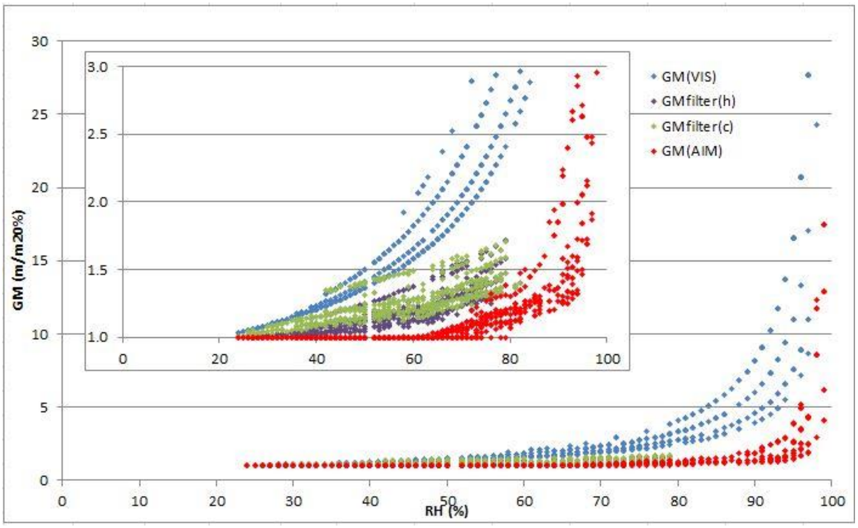


Figure 14: Mass growth rates derived from different methods as a function of RH (%)

The excess water uptake compared to the prediction of AIM model is regarded introducing the parameters of ΔGM:

$$\Delta GM(VIS) = GM(VIS) - GM(AIM)$$

$$\Delta GM_{filter}(h,c) = GM_{filter}(h,c) - GM(AIM)$$

In Fig. 15 the change of ΔGM as a function of the relative humidity is presented. In the cases of filters (h and c) the excess water uptake linearly increases with RH; the regression between the parameters rather good. The variation of ΔGM(VIS) due to RH increase is more complex (exponential function); but gives the best estimate of the excess water uptake. Taking into account this relationship the possible role of non-regarded species is discussed briefly in the case of ΔGM(VIS).

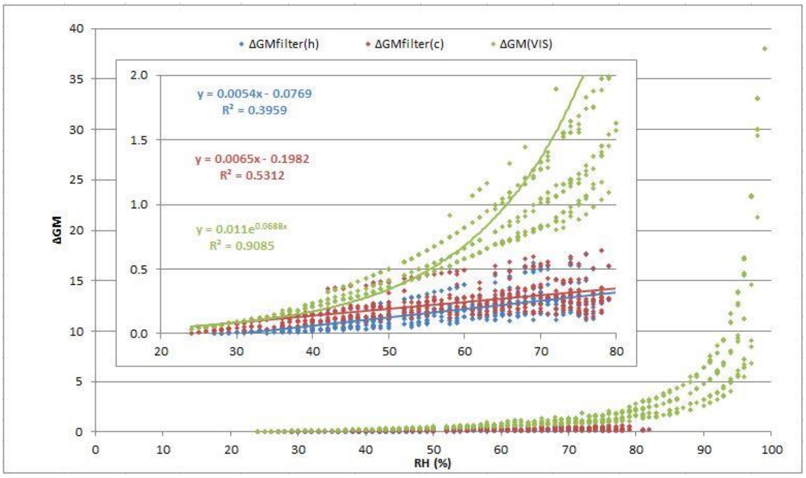


Figure 15: Excess water uptake (ΔGM) as a function of relative humidity.

Carbonaceous compounds (total carbon) are the most important aerosol compounds that are not concerned in AIM model calculations. Here we suppose that total carbon (TC) as a group of broad sorts of different organic compounds –including water soluble organic carbon (WSOC)– can have significant effect on aerosol hygroscopic behavior. In Fig. 16a-b the estimation of their role is attempted. In the further discussions the RH ranges of ≤90% and >90% are separated. The data in Fig. 16a indicates that with increasing relative humidity the excess water uptake also grows.

- Under 90% RH: a minimum in ΔGM(VIS) is found at the TC concentration of 5-6µgm^{-3}. We may conclude that in the concentration range of below 5-6µgm^{-3} increasing TC concentration hinders. Above 6µgm^{-3} the excess water increases.
- Over 90% RH: below 5-6µgm^{-3} with increasing TC the ΔGM(VIS) rises as under 90% RH, while over 6µgm^{-3} the increase reaches extremely high values. We suppose that this high mass growth may indicate a process like aerosol activation.

In Fig. 16b a clear relationship can be observed: at RH ≤90% the higher the WSOC/TC the lower the ΔGM(VIS). At RH>90% the excess water uptake significantly increases with higher WSOC fraction also implying aerosol activation-like process.

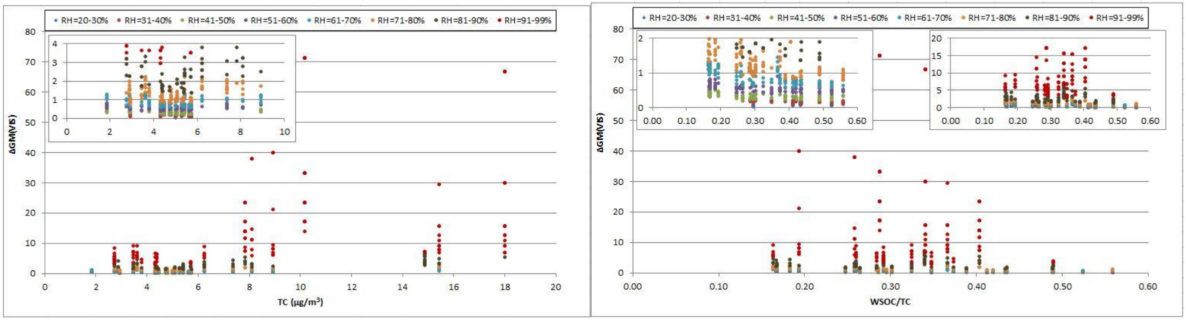


Figure 16: Role of carbonaceous compounds (a: total carbon; b: water soluble ratio of TC) in ΔGM(VIS) as a function of relative humidity.

2. What is the relevance of the hygroscopic growth rate derived from visibility observations in standard PM10 measurements?

In standard PM measurements, the consideration of hygroscopic growth of the aerosol mass have great importance. For this reason in standard PM monitoring a quasi-real time, appropriate and simple method would be desirable that covers the whole relative humidity range. In this work by comparing the hygroscopic mass growth rates derived from different approaches, we estimate the relevance of the use of GM derived from visibility instead of filter-based or modelled growth rates. Its feasibility is based on the wide availability of VIS measurements.

First, the comparison with filter-based method is presented (see Fig. 17a). We found statistically significant linear relationship between $GM_{filter}(h,c)/GM(VIS)$ and the relative humidity. Its use would be ideal and reasonable since filter mass measurements provides direct mass growth rates while RH and VIS data are widely available. Unfortunately mass change measurements were available under 80% RH and this linear function cannot be extended for higher RHs. For this reason, we also made the comparison with the mass growth rates obtained by AIM model (Fig. 17b). $GM(AIM)/GM_{filter}(h,c)$ *vs*. relative humidity also show relatively good but weaker relationship than above. Excellent linear linkage is found, however, in the case of GM(AIM)/GM(VIS) over the whole relative humidity range. Taking account all the foregoing results we can hypothesize that GM(VIS) can be widely used in standard PM monitoring to estimate the dry PM concentrations.

In standard PM measurements the consideration of the hygroscopic growth of the aerosol mass a quasi-real time and simple method would be necessary. We found that visibility derived mass growth rate could serve as a simple basis to construct a proxy for it for the whole relative humidity range. This due to that GM(VIS) can be related to the methods providing direct mass growth rates. We suppose that an extended survey could provide an appropriate database for a widely usable PM hygroscopicity proxy.

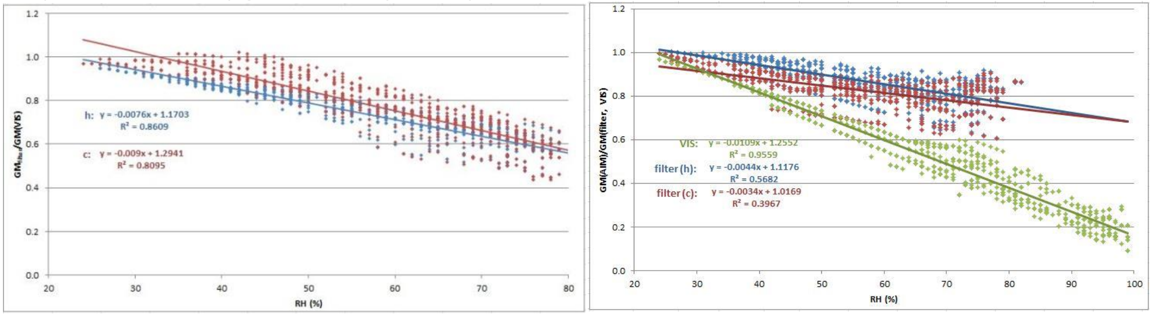


Figure 17a-b: Comparison of mass growth rates from different methods in RH range of 20-100%. Part a: relationship between filter-based and visibility methods; part b: comparison of AIM model to filter-based and visibility derived growth rates.

Beside aerosol hygroscopicity, visibility data can also be used in the estimation of ambient PM10 concentration. This is due to that light extinction (visibility) is controlled by the aerosol concentration and consequently variations in aerosol concentration result in changes of dry extinction (visibility). This is the reason why visibility (extinction) data provide an efficient (and inexpensive) tool for the study of long-term variations of air quality, PM10 concentration. The relationship between PM10 and aerosol extinction makes possible to use visibility in retrospective studies to estimate PM10 concentration. On the other hand, the worldwide availability of visibility data can provide information on the spatial distribution and temporal variation of extinction coefficient that can have great importance in climate models.

2.7 Consequences of the bias made in the determination of PM10 concentration

The mass concentration of particulate matter serves as a base for air quality control both on national and European scale. According to the regulations of the European Commission operative at present the daily average concentration of PM10 should not exceed 50 $\mu g\ m^{-3}$ and the number of transgressions of this daily limit should not exceed 35 days in a year. Violation of this upper limit may lead to legal consequences so it is important to have reliable PM data. The water content of the aerosol particles can influence the number of transgressions if the PM10 concentration is just somewhat higher than 50 $\mu g\ m^{-3}$. In order to show the effect of particle-bound water on the number of transgressions of the daily limit a survey of the daily PM10 concentrations was made for the sampling site used in this study. PM10 data for the last

12 years were retrieved from the database of the Hungarian Air Quality Network. In Fig. 18 the monthly distribution of transgressions of the daily limit is shown in black columns for years 2007-2018. It can be seen that most exceedances happened from October till February. The number of transgressions decrease considerably if it is assumed that particle-bound water accounted for 5%, 10%, 15% or 20% of aerosol mass. This has a dramatic effect on the yearly total transgressions as summarized in Figure 19. If the water content of the aerosol particles is neglected than the maximum number of transgressions (35/year) was exceeded 10 times in the last 12 years. However, if we assume that PM10 mass concentration was overestimated by 5% as a consequence of particle bound water then the number of exceedances falls to 5 for the examined period. Similarly, the maximum number of transgressions (35/year) was exceeded only in 2010 if we assume 10% bias due to the water content of the particles. Finally, if an overestimation of 11% or more is assumed due to the water content of PM10 samples then the maximum number of transgressions was not exceeded at all between 2006 and 2018 at the sampling site.

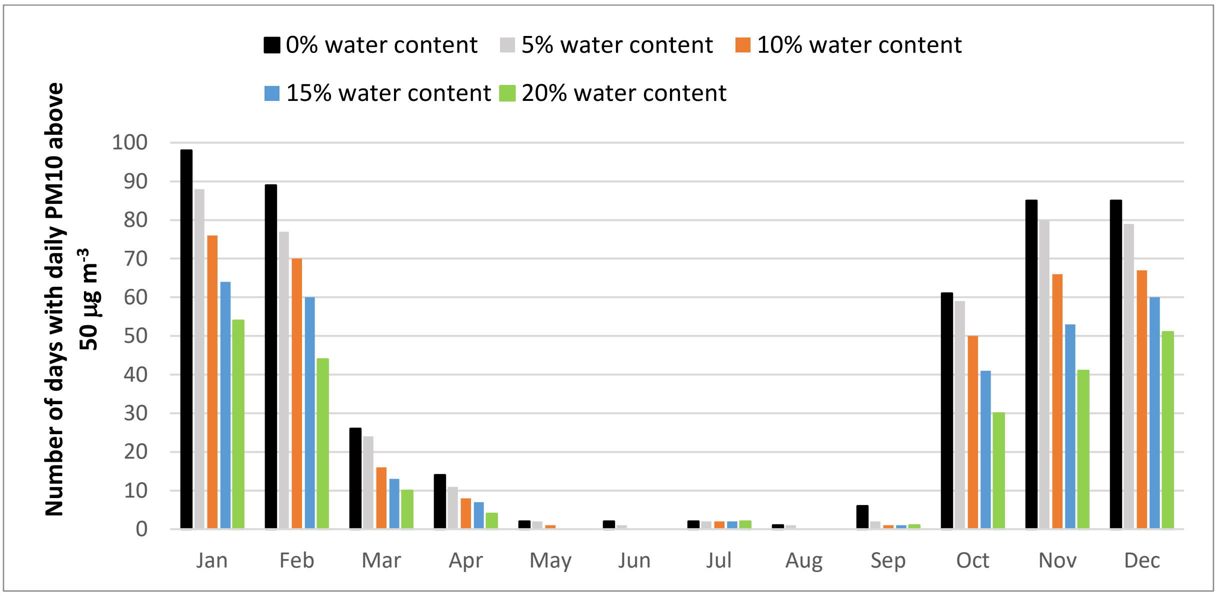


Fig. 18 The monthly distribution of transgressions of the daily health limit of PM10 cumulated for years 2007-2018 measured at Gilice square, Budapest, Hungary assuming 0%, 5%, 10%, 15% and 20% water content of particles.

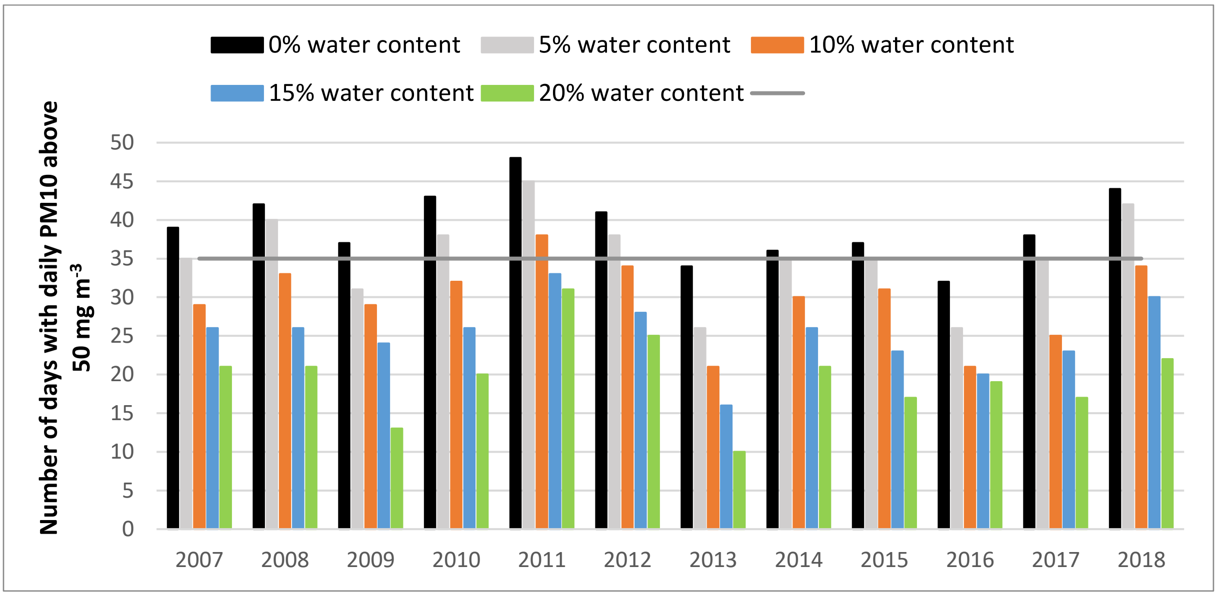


Fig. 19 The annual total transgressions of the daily health limit of PM10 for years 2007-2018 measured at Gilice square, Budapest, Hungary assuming 0%, 5%, 10%, 15% and 20% water content of particles.

These results of the project draw the attention to the remarkable fact that under moderately polluted conditions when daily PM10 mass concentrations slightly exceed the EU health limit (50 mg m^{-3}) the water content of the aerosol particles play a critical role. These distorted PM10 mass concentrations may lead to false transgression of the annual limit of 35 days.

Two more manuscripts have been prepared from the results of the project with submission scheduled for February 2019:

1. Exceedances of the health limits: the role of atmospheric water in PM10 mass concentration
2. Aerosol hygroscopicity: visual range an essential tool in standard PM monitoring?

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