Bias caused by water adsorption in hourly PM measurements

Gyula Kiss, Kornélia Imre, Ágnes Molnár and András Gelencsér

MTA-PE Air Chemistry Research Group, University of Pannonia, Egyetem 10, 8200 Veszprém, Hungary

Correspondence to: Gyula Kiss (kissgy@almos.uni-pannon.hu)

Abstract. Beta attenuation monitors are used worldwide to monitor PM concentration with high temporal resolution. Hourly PM10 and PM2.5 dry mass concentrations are publicly available with the tacit assumption that water is effectively removed prior to the measurement. However, as both the filter material of the monitor and the

10   aerosol particles are capable of retaining significant amount of water even at low relative humidities, the basic assumption may not be valid resulting in significant bias in reported PM10 and PM2.5 concentrations. Here we show that in PM10 measurement particle-free air can produce apparent hourly average PM concentrations in the range of $-13 - +21$ µg m^{-3} under conditions of fluctuating relative humidity. Positive and negative apparent readings are observed with increasing and decreasing relative humidities, respectively. Similar phenomena have

15   been observed when the instrument filter was previously loaded with atmospheric aerosol. As a result, the potential measurement biases in hourly readings arising from the interaction with water may be in the range of -53% − $+69\%$.

1 Introduction

Air pollution has a considerable impact on the quality of life and it is a permanent problem in cities leading to

20   considerable health risk. The respirable fraction of atmospheric aerosol (particulate matter with aerodynamic diameter <10 µm, PM10) is one of the most hazardous 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). In addition to their adverse health effects particulate pollution has significant impact on visibility which is

25   an important issue for road transport, aviation, tourism and landscape protection (Hand et al., 2011; Malm et al., 2013.)

The environmental legislation on ambient air quality is based on the monitoring of mass concentration of aerosol particles sized below a specified limit (PM10 or PM2.5). According to the regulation of the European Commission operative at present (Directive 2008/50/EC) the daily average concentration of PM10 should not exceed 50 µg

30   m^{-3}, while the upper limit for the annual average is 40 µg m^{-3}. In case the measured concentrations exceed the alert threshold (100 µg m^{-3}) special measures are implemented in order to reduce the level of pollution (smog alert), that affect the life and economic activities in the city and its surroundings. Hence knowledge on the reliability and environmental sensitivity of the measurement method used for monitoring and reporting PM10 mass concentrations is of great importance from the viewpoint of air quality legislation, health issues as well as

35   economy. As a result of multiple efforts PM10 concentration has been reduced in many developed countries in the past two decades (Report on the Environment, European Environment Agency, Bigi and Ghermandi, 2014).

However, as PM10 mass concentrations are decreasing, the potential relative bias caused by water interactions is likely becoming more significant.

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). The magnitude of water retention strongly depends on the filter material as known for decades (Chow, 1995; Perrino et al., 2013). Tierney and Conner (1967) concluded that the effect of relative humidity on glass fibre filters was insignificant, but at RH (relative humidity) >55% the effect on collected particulates was significant. Demuynck (1975) demonstrated that during 1-hour high volume sampling in urban area on a foggy day the amount of water irreversibly retained by cellulose filters is comparable to or even higher than the mass of particulate matter collected. Brown et al. (2006) compared the behaviour of quartz fibre, glass fibre and PTFE-bonded glass fibre under different RH conditions and found that the deviation in mass of certain unexposed 47 mm filters exceeded 450 µg while RH ranged between 30% and 81%. They concluded that in terms of water uptake and mass stability glass fibre was more suitable filter material than quartz but the best results were obtained with PTFE-bonded glass fibre.

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 concentrations. For this reason, particulate monitors, such as tapered element oscillating microbalance (TEOM, Patashnick and Rupprecht, 1980; Allen et al., 1997) or instruments working on the beta-attenuation principle (BAM, Maclas and Husar, 1976) were developed for the continuous measurement of atmospheric particulate mass. By today these monitors have been standardized and used worldwide and in many countries hourly PM data and air quality indices (AQI) are also publicly available (Air Pollution in World, Air Quality in Europe). Obviously, the particulate mass collected in one hour 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. This may be one reason why in some countries hourly air quality indices are derived by the combination of hourly trace gas concentrations and *daily* PM values.

The equivalence of the daily and annual PM data obtained with continuous particulate monitors and the 24-hour gravimetric reference method (GRM) has been investigated in numerous studies. Chang et al. (2001) found good agreement for the samples collected under moderate environmental relative humidity (RH<70%). The ratio of the mass concentrations determined by the BAM and GRM methods was found to be 1.08±0.06. However, with increasing RH– especially if the deliquescence RH of the dominant inorganic component was exceeded – the deviation between the two methods also increased reaching 1.22±0.22 (BAM/GRM). Salminen and Karlsson (2003) found similar results, ambient temperature below 0 $^{\circ}$C associated with high RH resulted in BAM/GRM ratio of up to 1.3. On the basis of data collected for 7 years Takahashi et al. (2008) found that in wintertime the gravimetric method yielded higher values than the BAM while in summertime the relationship was the opposite. They suggested that the differences were likely related to the chemical composition of the aerosol particles, both inorganic salts and organic compounds. This is in agreement with other studies concluding that organic aerosol constituents affect the hygroscopicity of the aerosol particles (Gysel et al. 2004). In addition to the composition of the particulate matter the filter material may also be the reason for the discrepancy observed. In a recent study Triantafyllou et al. (2016) compared PM10 and PM2.5 data obtained with BAM and GRM using different filter

materials (glass fibre, quartz fibre and Teflon) and found best correlation when glass fibre filter was used in both measurements (glass fibre was the material of the filter tape of the beta attenuation monitor).

PM monitors are used in long-term air quality monitoring networks as well as intensive air quality studies (e.g. Pittsburgh air quality study PAQS; Wittig et al., 2004). Thus, the equivalence of the monitors is also of great importance. Solomon and Sioutas (2008) summarized the continuous and semicontinuous monitoring techniques for PM mass of the U.S. EPA PM Supersites program including standard (original) TEOM, D-TEOM and FDMS (the latter two designed to measure PM including semivolatile compounds as well) and beta-attenuation methods. In the case of original version of the TEOMs (filters are intentionally heated to 30 or 50 °C) they found enhanced losses of semivolatile material from the collected particles. Grover et al. 2005 showed that in the case of 50 °C almost all semivolatile matter was lost in the TEOM while with D-TEOM and FDMS total PM2.5 including semivolatile compounds was measured. In beta-attenuation monitors the filter is not heated directly leading to minor loss of semivolatile compounds (Solomon and Sioutas, 2008). The study of Chung et al. (2001) provided similar results. Measurements made with TEOM resulted in lower values than the filter based reference measurements, while BAM appeared to be suitable for real-time continuous PM2.5 monitoring during their study. Hauck et al. (2004) also studied the equivalence of the gravimetric reference method (EN 12341) with TEOM and beta-attenuation measurements at four Austrian sites and concluded that PM values measured with TEOM and beta-attenuation monitors were not significantly different from each other. In summer the PM data measured by the monitors agreed reasonably well with those derived from the gravimetric method but in winter the monitors gave significantly lower results. In order to harmonize daily and annual PM data obtained by TEOM, BAM and GRM Gehrig et al. (2005) suggested a correction procedure that led to more coherent values.

All the above results indicate that under unfavourable conditions daily PM measurements can be biased significantly by the interaction of water with the filter material and/or the aerosol particles collected. This applies especially to hourly PM data obtained with aerosol particulate monitors although such studies are rare (Huang and Tai, 2008) probably due to the lack of a reliable reference method to compare to. The objective of this study is to quantify potential biases in hourly readings of PM10 of standard beta attenuation monitors which are caused by interaction with water.

2 Experimental

Investigations were carried out in a temperature controlled (at 20 °C) air monitoring container located at the Marczell György Observatory of the Hungarian Meteorological Service in the south-eastern part of Budapest, Hungary (GPS coordinates: 47°25'52.9"N, 19°10'56.4"E) in July, September and November 2015. The observatory is a standard synoptic weather station where meteorological parameters, temperature and relative humidity are measured on an hourly basis. In the Observatory, an urban background air pollution monitoring site is operated by the Hungarian Air Quality Network (www.levegominoseg.hu) which reports hourly PM10 mass concentration values.

A Thermo Scientific FH62C14 continuous ambient particulate monitor working on the beta attenuation principle was used for the experiments. The monitor was operated at a flow rate of 1 m^3 h^{-1}. However, in order to study the water uptake of the filter material of the PM monitor, particles were removed by replacing the PM10 inlet with a

HEPA filter. Thus, only gas phase components including water vapour were allowed to be collected on the glass fibre filter band of the instrument. The effect of heating the sampling inlet on water vapour adsorption/desorption was also studied by sampling with heated (at 40 °C) and non-heated inlet tube.

The experiment was also repeated with a pre-loaded glass fibre filter. From 19 to 25 September 2015 the filter was first exposed to ambient air and a total of 327 µg particles were collected with the ambient particulate monitor then the PM10 inlet was replaced with a HEPA filter and sampling was continued with particle-free air and with inlet heated at 40 °C. During the experiment the automatic filter change function was switched off.

3 Results and discussion

In July 2015 a sampling campaign was carried out to study the effect of inlet heating on water vapour adsorption of the filter used in the PM monitor. In this study aerosol particles were removed from the ambient air by a HEPA filter. 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) showed considerable fluctuation in the hourly average values (Fig. 1.) since the incremental mass change was obviously close to the lower limit of concentration determination of the monitor. The term 'apparent PM' is used here since zero mass concentration would have been expected since particle-free air was sampled. 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 were 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}.
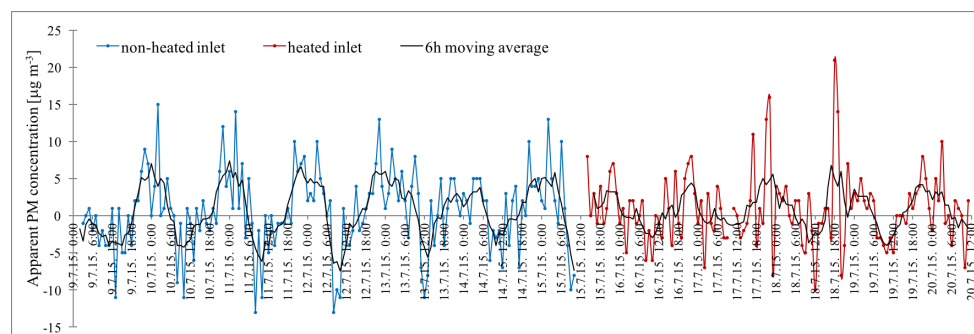
Figure 1: Temporal variation in the apparent PM mass concentration measured with particle-free air under ambient conditions in July 2015 with heated (red) and non-heated (blue) sampling inlet.

In order to demonstrate diurnal variations the apparent mass concentrations measured at each hour of the days were averaged over the entire sampling period. In Fig. 2a. negative apparent PM concentrations appear in the morning, while the largest positive values are found in the evening and at night. This diurnal variation of the apparent PM concentration can be explained by the operating principle of the instrument combined with interactions of water and the filter material. In Fig. 2b. it can be seen that the filter mass varied significantly during

the day with a maximum around 5 a.m. and a minimum between 11 a.m. to 5 p.m. The measured filter mass is largely in phase with the daily variation of ambient relative humidity (RH, Fig. 2b.). However, the apparent mass concentration is shifted as compared to the filter mass and RH since the instrument determines PM mass concentration as the incremental change of filter mass per unit air volume passed through the filter. Given the fact that particle-free air was sampled and filter mass correlates with ambient relative humidity water vapour must be the main condensable species causing positive and negative apparent PM concentrations. Not to mention that water vapour is by far the most abundant condensable gas in the atmosphere (present in absolute mass concentrations of 5-17 g m^{-3} at 20 ^{o}C). It should not be ruled out that other semi-volatile species (e.g. ammonium nitrate) co-condense with water and contribute to the observed apparent mass up to a few percent. The adsorption of nitric acid could also contribute to the mass change; however, at 40 °C this compound is rather volatile (e.g. Stelson et al., 1979; Harrison and Msibi, 1994). In addition to water vapour and gaseous inorganic species volatile organic compounds may also adsorb on the filter of the PM monitor. Vecchi et al. (2009) reported as high gas phase OC artefacts in polluted urban air of Milan, Italy during filter sampling in summer and winter as 2.4 µg m^{-3} and 3.8 µg m^{-3}, respectively. Significantly lower values were obtained in other studies. Viana et al. (2006, 2007) investigated the OC artefact in European cities both in winter and summer and found it in the 0.16-0.7 µg m^{-3} range. However, as revealed by OC/EC analysis, the organic compounds causing the abovementioned OC artefacts evaporate from the filter only above 150 ^{o}C (Kirchstetter at al., 2001) or even above > 310 ^{o}C (Vecchi et al., 2009). Consequently, the fraction composed of strongly retained organic compounds cannot be the reason for the periodic mass change observed at 20 ^{o}C. It must be added that in organic artefact studies related to PM measurements the filters are analysed subsequent to sampling and thus there is no information about potential mass change in the course of sampling.

It is worth noting that in the case of heated sampling inlet the measured apparent PM mass concentrations were generally smaller (in both positive and negative directions) than when non-heated inlet was applied (Fig. 2a.). This clearly indicates that heated inlet can considerably lower the bias caused by fluctuating RH although the temperature should be kept as low as possible in order to avoid losses of semivolatile compounds.
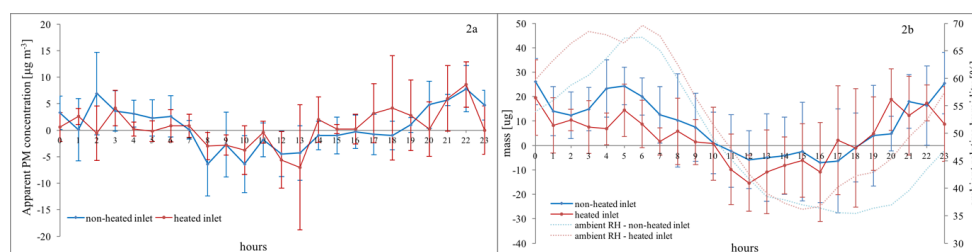
Figure 2: Daily variation of average apparent PM mass concentration (a) and filter mass (b) measured by sampling particle-free air on a blank glass fibre filter in July 2015 with heated (red) and non-heated (blue) sampling inlet. The diurnal variation of ambient relative humidity is also shown (b).

The experiment with blank filter and particle-free air was repeated with a heated sampling inlet in November 2015 and similar results were obtained: The 1-hour apparent PM concentrations ranged from −11 to +13 µg m^{-3} and even the 6-hour moving average PM concentration values varied between −4 and +4 µg m^{-3} with similar periodicity as shown above. These results clearly show that water vapour significantly biases 1-hour PM measurements in all seasons.

It should be noted, however, that the coincidence of the change in ambient RH and filter mass gives only an indirect evidence for the adsorption and desorption of water vapour. In order to confirm the role of water vapour an additional experiment was carried out. First, the ambient air was sucked through a dryer filled with $CaSO_4$ then a HEPA filter and finally entered the monitor. This way both water vapour and particles were removed from the air stream and, as a consequence, the periodicity of the 6-hour moving average disappeared and only the noise of the instrument was measured in the ca. ± 2 µg m^{-3} range.

In addition to sampling on blank filter the effect of water uptake was also studied with a filter band previously exposed to ambient aerosol. Similarly to the results of the experiments with blank filters the temporal variation of the apparent mass concentration showed considerable fluctuations but the diurnal variations were also observed. The magnitude of the 1-hour average apparent PM concentration ranged from −13 to +17 µg m^{-3} and even the 6-hour moving average concentration values varied between −5 and +5 µg m^{-3} (Fig. 3a.). The mass of the filter spot varied between 287 µg and 363 µg (remember the filter spot was pre-loaded with 327 µg aerosol) during the sampling period as a consequence of adsorption and desorption of water vapour. The daily variation of apparent mass concentrations averaged over the measurement period is presented in Fig. 3b. The data show that the daily variations of both the mass concentration and the filter mass were similar to those measured with the blank filter (Fig. 2 a-b.). In the morning hours the gradual evaporation of water caused a decrease in the mass of filter resulting in considerable negative apparent mass concentrations (down to −7 µg m^{-3}) while in the evening the gradual condensation of water led to positive artefacts of similar magnitude.
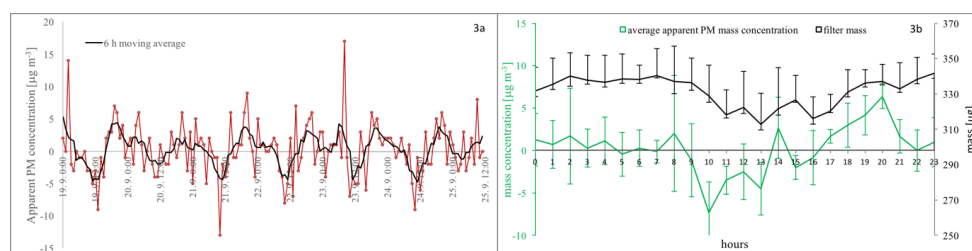
Figure 3: Temporal variation in the apparent PM mass concentration measured by sampling particle-free air on a pre-loaded glass fibre filter with heated sampling inlet in September 2015 (a). Diurnal variation of the average apparent PM mass concentration and filter mass (b).

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 as part of the Hungarian Air Quality Network.

In the first half of the 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 69%.

210 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 considerably but still relative errors exceeding 35% were observed occasionally. It should also be noted that the decrease of relative error experienced with heated sampling inlet can be attributed partly to higher ambient PM10 concentrations that

215 occurred during the second half of the campaign.
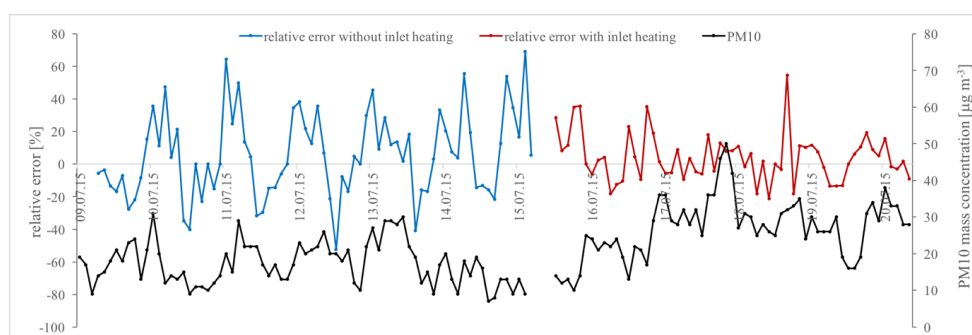
Figure 4: Relative errors in ambient hourly PM10 measurements due to the condensation and evaporation of water onto the glass fibre filter of the monitor.

In contrast to the above observations negative relative errors were found during the morning hours although their

220 magnitude (21% − 53%) was somewhat lower than during the night. The highest negative values were observed around 10 a.m. as a consequence of fast evaporation of previously condensed water vapour. The lower relative errors can be explained by the higher ambient PM10 concentrations in this period of the day (15 − 22 µg m^{-3}). Similarly to the positive relative errors observed during the night the heating of the inlet tube decreased the magnitude of the negative relative errors as well but this can be partially attributed to the elevated ambient PM

225 concentrations in the second half of the campaign.

4 Conclusions

Adsorption and desorption of water vapour under periodically changing ambient relative humidities cause considerable diurnal variation in the mass of the filter band of the beta attenuation monitor. This leads to positive and negative apparent PM concentrations even if particle-free air is sampled. In the evening hours —when

230 adsorption of water vapour occurs due to the increasing ambient RH even inside the monitor— the increased filter mass resulted in positive apparent concentrations, while in the morning —when water is desorbed due to decreasing ambient RH— negative apparent concentrations were measured. This phenomenon was observed with empty glass fibre filter but deviations of similar magnitude were also found with a filter previously loaded with ambient aerosol. Heating of the sampling inlet at 40 ^{0}C reduces but cannot completely eliminate this artefact related

235 to water vapour adsorption/desorption. This artefact can severely bias 1-hour ambient PM10 measurements in either direction. This was studied by comparing apparent PM concentrations to ambient PM10 concentrations measured simultaneously. Positive relative errors of 38% − 69% were observed during the night when ambient

PM10 concentrations were low (9 − 15 µg m^{-3}). On the other hand, in the morning negative relative errors of 21 − 53% were measured. The smaller negative relative errors can be explained by the gradual release of water from the filter material as well as the generally higher PM10 concentrations in this period of the day (15 − 22 µg m^{-3}).

These results clearly show that 1-hour PM10 concentrations should be used with extreme caution since significant measurement bias may occur at low ambient PM10 concentrations as a consequence of water vapour adsorption on or desorption from the filter material of the beta attenuation monitor. On the other hand, at high ambient PM10 concentrations water vapour uptake and release by the collected aerosol particles may also bias the reported 1-hour PM10 data. The effect of water vapour adsorption/desorption is even more pronounced when PM2.5 or PM1 concentrations are to be determined. In addition to water vapour organic and inorganic trace gases might also contribute to the mass change of the filter and thus increase the magnitude of the bias. Lower time resolution (e.g. 24-h) measurements are likely much less affected since much larger particle mass is collected and the change in ambient relative humidity is generally much less pronounced at the very same hour of the day from one day to another.

5 Acknowledgements

The financial support of the National Research, Development and Innovation Office – NKFIH 113059 project is gratefully acknowledged. We thank the Hungarian Air Quality Monitoring Network for the technical support and the data availability.

References

Air Pollution in World: Real-time Air Quality Index Visual Map http://aqicn.org/map/world/#@g/47.551/18.9621/7z

Air Quality in Europe - http://www.airqualitynow.eu/

Albert, C., Chang D. P. Y., Kleeman, M. J., Perry, K. D., Cahill, T.A., Dutcher, D., McDougall E. M., and Stroud K.: Comparison of Real-Time Instruments Used To Monitor Airborne Particulate Matter, J Air Waste Ma, 51:1, 109-120, DOI: 10.1080/10473289.2001.10464254, 2001.

Allen, G., Sioutas, C., Koutrakis, P., Reiss, R., Lurmann, F. W., and Roberts, P. T.: Evaluation of the TEOM(R) method for measurement of ambient particulate mass in urban areas, J Air Waste Ma, 47, 682-689, 1997.

Bigi, A. and Ghermandi, G.: Long-term trend and variability of atmospheric PM10 concentration in the Po Valley, Atmos. Chem. Phys., 14, 4895–4907, doi:10.5194/acp-14-4895-2014, 2014.

Brown, A. S., Yardley, R. E., Quincey, P. G., and Butterfield, D. M.: Studies of the effect of humidity and other factors on some different filter materials used for gravimetric measurements of ambient particulate matter, Atmos. Environ., 40, 4670–4678, 2006.

Chang, C. T., Tsai, C. J., Lee, C. T., Chang, S. Y., Cheng, M. T., and Chein, H. M.: Differences in PM10 concentrations measured by beta-gauge monitor and hi-vol sampler, Atmos. Environ., 35, 5741–5748, 2001.

Chow, J. C.: Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles. J Air Waste Ma, 45, 320–382 1995.

275 Demuynck, M.: Determination of irreversible absorption of water by cellulose filters, Atmos. Environ., 9, 523–528, doi:10.1016/0004-6981(75)90113-4, 1975.

Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, OJ L 152, 11.6.2008, 1–44, 2008 http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:32008L0050

280 Donaldson, G., Seemungal, T., Bhowmik, A., and Wedzicha, J.: Relationship between exacerbation frequency and lung function decline in chronic obstructive pulmonary disease. Thorax 57: 847–852, 2002.

European Environment Agency: Trends in PM10 and PM2.5 annual concentrations per station type http://www.eea.europa.eu/data-and-maps/figures/trends-in-pm10-top-graph

Gehrig, R., Hueglin, C., Schwarzenbach, B., Seitz, T., and Buchmann, B.: A new method to link PM10
285 concentrations from automatic monitors to the manual gravimetric reference method according to EN12341, Atmos. Environ., 39, 2213–2223, 2005.

Grover, B.D., Kleinman, M., Eatough, N.L., Eatough, D.J., Hopke, P.K., Long, R.W., Wilson, W.E., Meyer, M.B. and Ambs, J.L.: Measurement of Total PM2.5 Mass (Nonvolatile Plus Semi-Volatile) with the Filter Dynamic Measurement System Tapered Element Oscillating Microbalance Monitor; J. Geophys. Res., 110, D07S03, doi:
290 10.1029/2004JD004995, 2005.

Gysel, M., Weingartner, E., Nyeki, S., Baltensperger, U., Galambos, I., and Kiss, G.: Hygroscopic properties of water soluble matter and humic-like organics in atmospheric fine aerosol, Atmos. Chem. Phys., 4, 35–50, 2004.

Hand, J. L., Copeland, S. A., Day, D. E., Dillner, A. M., Indresand, H., Malm, W. C., McDade, C. E., Moore, C.
295 T. Jr., Pitchford, M. L., Schichtel, B.A., and Watson, J. G.: Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States. Report V: June 2011. IMPROVE report, Cooperative Institute for Research in the Atmosphere, Colorado State University, Fort Collins, USA., 2011.

Hauck, H., Berner, A., Gomisceka, B., Stoppera, S., Puxbaum, H., Kundi, M., and Preining, O.: On the equivalence of gravimetric PM data with TEOM and beta-attenuation measurements, Aerosol Science 35, 1135–1149, 2004.

300 Harrison, R. M. and Msibi, M. I.: Validation of techniques for fast response measurement of HNO3 and NH3 and determination of the [NH3] [HNO3] concentration product, Atmos. Environ. 28(2), 255, 1994.

Hoek, G., Krishnan, R. M., Beelen, R., Peters, A., Ostro, B., Brunekreef, B., and Kaufman, J. D.: Long-term air pollution exposure and cardio- respiratory mortality: a review. Environ. Health 12:4, 2013.

Huang, C. H. and Tai, C. Y.: Relative humidity effect on PM2.5 readings recorded by collocated beta attenuation
305 monitors, Environ. Eng. Sci., 25, 1079-1089 doi:10.1089/ees.2007.0142, 2008.

Kirchstetter, T. W., Corrigan C. E., and Novakov T.: Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters, Atmos. Environ., 35, 1663-1671, 2001.

Maclas, E. S. and Husar, R. B.: Atmospheric particulate mass measurement with beta attenuation mass monitor, Environ. Sci. Technol., 10, 904, 1976.

310 Malm, W. C., Schichtel, B. A., Barna, M. G., Gebhart, K. A., Rodriguez, M. A., Collett Jr., J. L., Carrico, C. M., Benedict, K. B., Prenni, A. J., and Kreidenweis, S. M.: Aerosol species concentrations and source apportionment of ammonia at Rocky Mountain National Park, J Air Waste Ma. 63, 1245-1263, doi: 10.1080/10962247.2013.804466, 2013.

Natusch, D. F. S. and Wallace, J. R.: Urban aerosol toxicity: The influence of particle size. Science 186: 695–699, 315 1974.

Patashnick, H. and Ruppecht, G.: New real-time monitoring instrument for suspended particulate mass concentration – TEOM, Abstract of papers of the American Chemical Society, 179, 1980.

Perrino, C., Canepari, S., and Catrambone, M.: Comparing the Performance of Teflon and Quartz Membrane Filters Collecting Atmospheric PM: Influence of Atmospheric Water, Aerosol Air Qual Res, 13, 137-147, doi: 320 10.4209/aaqr.2012.07.0167, 2013.

Solomon, P. A. and Sioutas, C.: Continuous and Semicontinuous Monitoring Techniques for Particulate Matter Mass and Chemical Components: A Synthesis of Findings from EPA's Particulate Matter Supersites Program and Related Studies, J Air Waste Ma, 58:2, 164-195, DOI: 10.3155/1047-3289.58.2.164, 2008.

325 Report on the Environment - Particulate Matter concentrations https://cfpub.epa.gov/roe/indicator_pdf.cfm?i=9

Salminen, K. and Karlsson, V.: Comparability of low-volume PM10 sampler with beta-attenuation monitor in background air, Atmos. Environ., 37 (26), 3707–3712, 2003.

Stelson, A. W., Friedlander, S. K., and Seinfeld, J. H.: A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate. Atmos. Environ., 13, 369–371, 1979.

330 Takahashi, K., Minoura, H., and Sakamato, K.: Examination of discrepancies between beta-attenuation and gravimetric methods for the monitoring of particulate matter, Atmos. Environ., 42, 5232-5240, 2008.

Tierney, G. P. and Conner, W. D.: Hygroscopic effects on weight determinations of particulates collected on glass-fiber filters, Am. Ind. Hyg. Assoc J., 28, 363-365, doi:10.1080/00028896709342537, 1967.

Triantafyllou, E., Diapouli, E., Tsilibari, E. M., Adamopoulos, A. D., Biskos, G., and Eleftheriadis, K.: Assessment 335 of factors influencing PM mass concentration measured by gravimetric & beta attenuation techniques at a suburban site, Atmos. Environ., 131, 409-417, 2016.

Vecchi, R., Valli, G., Fermo, P., D'Alessandro, A., Piazzalunga, A., and Bernardoni, V.: Organic and inorganic sampling artefacts assessment, Atmos. Environ., 43, 1713‑1720, 2009.

340   Viana, M., Chi, X., Maenhaut, W., Cafmeyer, J., Querol, X., Alastuey, A., Mikuška, P., and Večeřa Z.: Influence of Sampling Artefacts on Measured PM, OC, and EC Levels in Carbonaceous Aerosols in an Urban Area. Aerosol Sci Tech. 40, 107–117, DOI: 10.1080/02786820500484388, 2006.

Viana, M., Maenhaut, W., ten Brink, H. M., Chi, X., Weijers, E., Querol, X., Alastuey, A., Mikuška, P., and Večeřa
345   Z.: Comparative analysis of organic and elemental carbon concentrations in carbonaceous aerosols in three European cities, Atmos. Environ., 41, 5972‑5983, 2007.

Wittig, A. E., Anderson, N., Khlystov, A. Y., Pandis, S. N., Davidson, C. I. and Robinson, A. L.: Pittsburgh Air Quality Study Overview, Atmos. Environ. 38, (20), 3107-3125, 2004.