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Atmospheric Measurement Techniques Discussions

Interactive comment on "Bias caused by water adsorption in hourly PM measurements" *by* Gyula Kiss et al.

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We thank the referee for his/her careful and critical review of our paper. The following are our responses to the referee's comments.

Comments from Referee:

1. Very little detail is provided about the measurement techniques themselves. The beta attenuation principle is not really described in the manuscript. It is unclear what corrections, if any have been applied to the raw data.

Author's response: The experimental part has been extended with a more detailed description of the instrument and the beta attenuation principle. The monitor measures alpha particle emissions directly from the ambient aerosol being sampled and excludes

negative mass artefacts from the daughter nuclides of radon gas decay to achieve a refined mass measurement.

Author's changes in manuscript Original version: 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 m3 h-1. Revised version: A Thermo Scientific FH62C14 continuous ambient particulate monitor was used for the experiments. The instrument uses the radiometric principle of beta attenuation. Beta rays are attenuated according to an approximate exponential function of aerosol mass, while passing through deposited aerosol particles on a glass fibre filter tape. First the attenuation through the unexposed part of the filter tape is measured to correct for blank attenuation. The tape is then exposed to a constant ambient air flow maintained by a variable controlled rotary vane pump and aerosol particles are accumulated. The beta attenuation is measured again and the blank corrected attenuation is converted to mass concentrations. Additionally, the monitor measures alpha particle emissions directly from the ambient aerosol being sampled and excludes negative mass artefacts from the daughter nuclides of radon gas decay to achieve a refined mass measurement. Finally, PM10 concentration is obtained by using the corrected mass and the exact volume of sampled air. The monitor was operated at a flow rate of 1 m3 h-1.

2. The reference against which the biases are calculated in Figure 4 are apparently the reported hourly PM10 mass concentration values from the monitoring station. It is unclear by which method these are determined, nor is it clear how accurate these values are to serve as reference.

Author's response: The hourly PM10 concentrations shown in Figure 4. are the official values reported by the Hungarian Air Quality Network and measured also by a BAM monitor. This instrument is regularly calibrated and compared to the reference gravimetric method.

Author's changes in manuscript Original version: 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. Revised version: 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.

3. One of the most puzzling aspects is the principle of the inlet heater. It is unclear by what mechanisms inlet heating would remove the bias of absorbed water on the filter or particles. The heating would temporary lower the RH in the inlet, but not the water vapor mixing ratio. However, the temperature in the instrument is unchanged, and this the RH over the filter should not respond to inlet heating. After browsing through the manual of the used instrument (Thermo Scientific FH62C14), the manual states that an internal heater maintains an RH threshold above the filter tape. This heater is presumably different from the inlet heater. If that is true, then RH effects on particle mass are even more difficult to explain with the information provided. Furthermore, since the commercial instrument used already uses RH correction, the question investigated is a second order effect: to which extent does the RH correction in a specific commercially available instrument fail.

Author's response: Contrary to the present FH62C14 instruments our model (purchased in 2014) does not incorporate a dynamic heating system designed to maintain the relative humidity of the air passing through the filter tape below a preset threshold value. Instead, these models of the monitor were equipped with a regulated sample tube heater by the manufacturer to avoid condensation of water vapour at critical sampling conditions when warm, humid air is being sampled in a cooler air-conditioned cabin. As a consequence of the inlet heating the temperature of the air is somewhat higher in the short pathway from the entrance point of the instrument to the filter holder than it would be without heating and this results in slightly lower RH above the filter

band.

Author's changes in manuscript Original version: 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 a heated (at 40 °C) and non-heated inlet tube. Revised version: Thus, only gas phase components including water vapour were allowed to be collected on the glass fibre filter band of the instrument. Contrary to the present FH62C14 instruments the model used in this study does not incorporate a dynamic heating system designed to maintain the relative humidity of the air passing through the filter tape below a preset threshold value. Instead, this model of the monitor was equipped with a regulated sample tube heater by the manufacturer to avoid condensation of water vapour at critical sampling conditions when warm, humid air is being sampled in a cooler air-conditioned cabin. As a consequence of the inlet heating the temperature of the air is somewhat higher in the short pathway from the entrance point of the instrument to the filter holder than it would be without heating and this results in slightly lower RH above the filter band. In winter the effect of inlet or internal heater is negligible as internal temperature is significantly higher than outside resulting in very low RH over the filter band anyway. The effect of heating the sampling inlet on water vapour adsorption/desorption was studied by sampling with a heated (at 40 °C) and non-heated inlet tube.

4. A revised version of the manuscript needs to include (1) significantly more information about the instrumental techniques and how they are applied in this study, (2) a coherent hypothesis on why the instrument internal corrections are insufficient, and (3) some general recommendation on how the bias can avoided in monitoring networks.

Author's response: 1. The manuscript has been completed with more information about the instrumental techniques as detailed above at points 1 and 3. 2. As discussed at point 3 above no internal RH correction is incorporated in the monitor used in this study. 3. The aim of this paper is to draw the attention to the anomalies of reporting hourly PM

measurements even if we have no recommendation how to overcome them. It seems that hourly PM readings are strongly biased by water adsorption and desorption due to diurnal variations in ambient RH and should not be relied on. However, since these RH change-driven variations are largely cancelled over a period of one day (i.e. the cumulative value of the positive and negative biases is close to zero over the course of one day) it can be concluded that the water adsorption on and desorption from the filter may have only negligible effect on the 24-hour PM10 average values.

Âă 5. Ln 37: "However, as PM10 mass concentrations are decreasing, the potential relative bias caused by water interactions is likely becoming more significant." Why is this the case?

Author's response: The manuscript has been completed with an explanation as follows.

Author's changes in manuscript Original version: However, as the PM10 mass concentrations are decreasing, the potential relative bias caused by water interactions is likely becoming more significant. Revised version: However, as the PM10 mass concentrations are decreasing, the potential relative bias caused by water interactions is likely becoming more significant. This is simply due to the fact that the bias caused by adsorption or desorption of water on and from the filter medium becomes proportionally more significant relative to the aerosol mass deposited on the filter.

6. Ln 55: "By today these monitors have been standardized" By whom and how?

Author's response: These monitors have been standardized and recommended by several organizations (e.g. EPA, California Air Resources Board, EMEP): U.S. EPA Reference and Equivalent Methods for Ambient Air EQPM-0990-076, EQPM-0404-151, EQPM-1102-150, EQPM-0609-181, EQPM-0609-182, EQPM-1090-079.

Author's changes in manuscript Original version: 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).

Revised version: By 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).

7. Ln 57: "Obviously, the particulate mass collected in one hour is small thus the bias caused by water may be excessive." To which technique does this refer to? BAM, TEOM?

Author's response: Both instruments use filters for particle collection and are therefore subject to the same artefacts as other filter-based methods such as positive artefacts from absorption or adsorption of gaseous components on deposited particles and/or the filter media (Solomon and Sioutas, 2008).

Author's changes in manuscript Original version: Obviously, the particulate mass collected in one hour is small thus the bias caused by water may be excessive. Revised version: 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 one hour is small thus the bias caused by water may be excessive.

8. Ln 163: 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. I don't see this in the figure. The two series look about the same. Can this be quantified objectively? What is the mechanism by which the inlet heater should reduce water absorption?

Author's response: We have determined the minimum and maximum of the 6-hour

averages and calculated the standard deviations as well. Without heating: average value 0.7 μg m-3, SD: 3.6 μg m-3, minimum: -7.4 μg m-3, maximum: 7.4 μg m-3. With heating: average value 0.7 μg m-3, SD: 2.2 μg m-3, minimum: -4.0 μg m-3, maximum: 5.6 μg m-3.

Author's changes in manuscript Original version: 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. Revised version: Without inlet heating 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-hour 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)Âăthan when a non-heated inlet was applied.

9. Figures 1-4: The Figures need to be reworked. Blending the data with the time labels is distracting. The font size of the axis elements is too small for print.

Author's response: We have prepared new and improved figures that consider all suggestions from the reviewer.

10. Figure 4: If a relative error is given, the type and quality of the data for the reference method must be clearly indicated.

Author's response: As discussed above (Point 2) the hourly PM10 concentrations shown in Figure 4 are the official values reported by the Hungarian Air Quality Network and measured also by a BAM monitor. This instrument is regularly calibrated and compared to the reference gravimetric method.

Author's changes in manuscript Original version: 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. Revised version: Figure 4: Relative errors in ambient

hourly PM10 measurements due to the condensation or evaporation of water onto or from 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.

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