Near-Continuous $PM_{2.5}$ Mass Measurements at the Pittsburgh Air Quality Study Supersite

Beth Wittig, CUNY City College of New York, New York NY 10031
Spyros Pandis and Allen Robinson, Carnegie Mellon University, Pittsburgh PA 15213

AAAR PM Supersite Meeting, February 7 - 11, 2005

1. Abstract

The Rupprecht and Patashnick, Co. (RPCO) Tapered Element Oscillating Micro-Balance with Sample Equilibration System (TEOM with SES) was evaluated during the Pittsburgh Air Quality Study (PAQS) from July 2001 to June 2002. The TEOM uses an inertial approach to measure $PM_{2.5}$ mass on a 5-minute average basis. The SES uses Nafion diffusion dryers to dehumidify the ambient air before collection of ambient aerosol onto a 30 deg-C filter surface. This diffusion-based approach allows the TEOM to dehumidify the aerosol stream without use of heat, minimizing the loss of semi-volatile aerosol species that can occur when the instrument is operated in the typical configuration without a SES and with a filter maintained at 50 deg-C.

The TEOM with SES was evaluated throughout the study period using collocated measurements of fine particle mass. Integrated 24-hour samples of $PM_{2.5}$ were collected at ambient conditions using a Partisol FRM Sampler and Dichotomous Sampler, both of which were operated according to EPA guidelines.

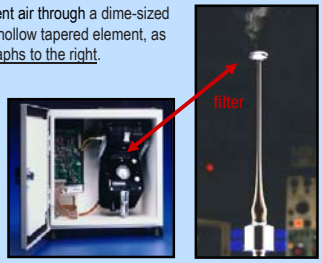
Throughout the study period, the TEOM with SES performed reliably and with excellent data capture. Its measurements were well correlated to the collocated measurements, with major axis regression R^2 values greater than 90%. Overall, the instrument bias was approximately +2% relative to the FRM and Dichotomous Sampler measurements. However, on particular days during the winter or when the 24-hour average fine particle mass was less than 20 μg m^{-3}, this bias was greater. The near-continuous TEOM with SES measurements have been used in conjunction with temporally resolved measurements of the particle size distribution to estimate the bulk 'effective' aerosol density, and with aerosol-bound water and inorganic and organic aerosol species to investigate the closure of the mass balance at the PAQS Supersite.

2. Problem statement

A TEOM is designated by the USEPA to be both an equivalent method for PM_{10} mass monitoring (EQPM-1090-079) and a correlated acceptable continuous method for $PM_{2.5}$ mass monitoring.

A TEOM draws ambient air through a dime-sized filter mounted onto a hollow tapered element, as shown in the photographs to the right.

As aerosol mass collects on the filter surface, the element oscillates. The frequency of oscillation is proportional to the mass loading by Hooke's Law.



In the EQPM-1090-079 configuration of the TEOM, the filter temperature is maintained at 50 deg-C. Allen *et al.* suggested that this elevated filter temperature may result in losses of semi-volatile aerosol species during months when ambient relative humidity is high and temperature is low.

To address this issue, RPCO designed a sample equilibration system that dehumidifies the ambient air using Nafion membranes instead of excessive heat. The SES allows the instrument to sample aerosol at 30 deg-C, minimizing both the positive artifact associated with the condensation of water vapor onto ambient aerosol before collection and the negative artifact due to loss of semi-volatile aerosol species.

3. Our goal?

Evaluate the ability of the TEOM with SES to minimize losses of semi-volatile aerosol species by comparing its measurements over multiple seasons to those collected by samplers operating at ambient conditions.

4. Approach

Supersite logistics

- Mass measurements were collected at the PAQS Supersite for 12 months from July 1, 2001 to June 30, 2002 (Wittig *et al.*).

- The Supersite (photographed above and denoted by a star in the illustration to the right) was located in an urban park, nearly 5 km from downtown Pittsburgh.
- $PM_{2.5}$ measured at this site is likely to be influenced by both local (fresh) and regional (aged) sources.

Mass measurement methods

- Tapered Element Oscillating Micro-Balance with sample equilibration (Series 1400a TEOM with SES, RPCO)

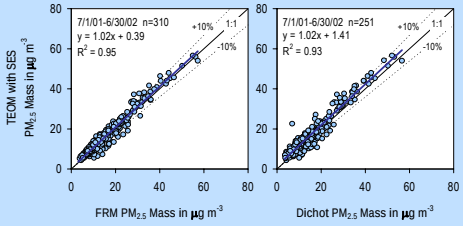
The TEOM with SES was operated according to manufacturer guidelines and was subjected to periodic quality control audits. The instrument was used to measure 5 minute average $PM_{2.5}$ mass.

- Partisol FRM Sampler (Model 2000 FRM, RPCO)
- Dichotomous Sampler (Series 241 Dichot, Thermo Anderson)

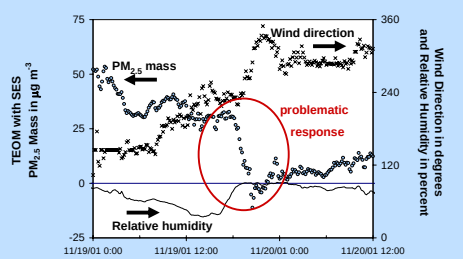
Both samplers were operated following manufacturer and USEPA guidelines and were subjected to periodic audits. The samplers were used to collect $PM_{2.5}$ onto Teflon filters at ambient conditions for 24 hour periods of time (from midnight to midnight). Before gravimetric analysis, the filters were conditioned in a humidity and temperature-controlled environmental chamber.

5. Method evaluation

- The 5 minute average $PM_{2.5}$ mass concentration reported by the TEOM with SES was averaged to 24 hours and compared with the 24 hour $PM_{2.5}$ mass collected using the FRM and Dichot samplers.
- Over the twelve month period, the TEOM with SES, Dichot, and FRM measurements compared well, although the bias was greater on particular days. As shown below, the major axis regression R^2 values were above 0.9, and the regression slopes were within 2% of the 1:1 line.



- The study average data capture from the TEOM with SES was 93%. While this data capture rate was on par with that observed for the FRM, it was achieved with a mere fraction of the time investment required for the FRM. Periods of reduced data capture did occur, but usually when the instrument was challenged with maintaining the relative humidity of the sampled air despite dramatic changes in the ambient relative humidity. The figure below illustrates the resulting negative instrument response.



6. Application of TEOM with SES measurements

The TEOM with SES measurements were used in conjunction with measurements of gas phase species and particle size distributions and $PM_{2.5}$ chemical composition to investigate a host of issues. Among others, the TEOM with SES measurements were used to investigate issues with other measurement methods, and investigate physical and chemical phenomena observed at the PAQS Supersite.

- Investigate issues with other measurement methods

Rees *et al.* used the TEOM with SES measurements with $PM_{2.5}$ chemical composition measurements to investigate discrepancies between the average FRM-measured mass and the sum of the mass of the individual aerosol chemical components.

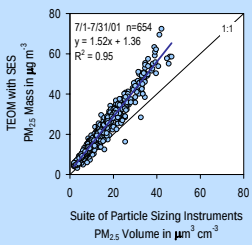
The TEOM with SES measurements were used to demonstrate that measurement uncertainty in $PM_{2.5}$ mass did not explain the observed discrepancies in the mass balance. Instead, the seasonal discrepancies in the mass balance were explained by water retention on conditioned FRM filters and volatilization losses of semi-volatile aerosol species during sampling and post-sampling filter handling.

- Estimate bulk 'effective' particle density

Khlystov *et al.* estimated the bulk aerosol density by comparing the $PM_{2.5}$ mass concentration measured using the TEOM with SES with the aerosol volume concentration from 3 nm-2.5 μm measured using a suite of TSI particle sizing instruments (Ultrafine SMPS 3936N25, SMPS 3936L10, and APS 3320). A shape factor of 1 was assumed.

As indicated to the right, the bulk aerosol density given by the slope of the regression relationship, was roughly 1.5 g cm^{-3}.

This effective density is similar to values reported in the literature, and is in good agreement with the density estimated from the chemical composition of the aerosol observed at the Supersite.



7. Conclusions

- The TEOM with SES compared well to the FRM and Dichot samplers. However, in locations like Pittsburgh, where the annual average $PM_{2.5}$ concentration is close to the 15 μg m^{-3} NAAQS, a 2% difference in $PM_{2.5}$ mass may mean the difference between compliance and noncompliance.
- The instrument performed reliably and required far less time investment than either of the samplers it was compared to. However, the instrument did not respond well to dramatic changes in ambient humidity.
- The data obtained by the instrument was valuable and was used to evaluate instrument issues as well as physical and chemical phenomena.
- Volatilization losses did not appear to significantly impact the instrument performance at the PAQS Supersite, perhaps due to the mild winter experienced in 2001-2002, and likely due to the fact that most of the organic aerosol is aged and aerosol nitrate concentrations are small. The performance of the instrument may be different in other areas.

8. References

G Allen, C Sioutas, P Koutrakis, R Reiss, F Lurmann, P Roberts (1997). Evaluation of the TEOM method for measurement of ambient particulate mass in urban areas. *JAWMA* 47: 682-689.

A Wittig, N Anderson, A Khlystov, S Pandis, C Davidson, A Robinson (2004). Pittsburgh Air Quality Study Supersite program overview. *Atmos. Environ.* 38: 3107-3125.

S Rees, A Robinson, A Khlystov, C Stanier, and S Pandis (2004). Mass balance closure and the Federal Reference Method for $PM_{2.5}$ in Pittsburgh PA. *Atmos. Environ.* 28: 3305-3318.

A Khlystov, C Stanier, and S Pandis (2004). An algorithm for combining electrical mobility and aerodynamic size distribution data. *Aerosol Sci. and Technol.* 38(S1): 229-238.

9. Acknowledgments

This research was conducted as part of the Pittsburgh Air Quality Study, which was supported by US Environmental Protection Agency under contract R82806101 and the US Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This poster has not been subject to EPA's peer and policy review, and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.