Interactive comment on “Evaluation and application of a semi-continuous chemical characterization system for water soluble inorganic PM$_{2.5}$ and associated precursor gases” by K. J. Godri et al.

K. J. Godri et al.

Received and published: 25 February 2009

The reviewer is thanked for comments and suggestions. Point-to-point author responses are included below in italics.

Anonymous Referee 1 Received and published: 18 December 2008

This paper reports measurements of gas and particle chemical composition over an extended period of time. The paper essentially has two parts, the first part deals with instrument performance through various comparisons with other measurements, and the second part discusses the ambient results.
Unfortunately, significant instrumentation problems were encountered during the study and many of the instruments compared showed large discrepancies. To account for this, the results from filter samples were taken as a gold standard and the various results scaled. Although the data reported is of some interest, many issues with the data quality should be addressed.

1) Why is it appropriate to use the filter as the standard; on what basis is this made. For example, can references be cited that show this is reasonable; that this filter sampling/analysis technique compares well with other methods and is free of artifacts, include citations. Some quantitative measure of the filter precision and or accuracy would put this in perspective.

GPIC particulate concentrations were standardized with NAPS filter measurements. Validation of this assumption to use filters as a standard is provided in Yao et al., (2008) where GPIC discrepancies on the particle side are also discussed. Moreover, GPIC data that were standardized with NAPS filter data were also compared with independent TEOM measurements collected at two locations in proximity to the sampling site (Section 3.1.3, Page 219). The good agreement of this high time resolution mass reconstruction provided further evidence that using the filters as a standard to correct the GPIC data provided accurate results. All NAPS measurement methods are accredited by the Canadian Association for Laboratory Accreditation (CALA). Detailed standard operating procedures are available:

Method 6.05/2.0/M: Determination of Gaseous and Particulate Inorganic Air Pollutants by Ion Chromatography; Rev. Date: September 24, 2007, Environmental Science and Technology Centre, Environment Canada

Method 6.08/1.3/M: Determination of the Weight of Particulate Matter Collected on Teflon Filters; Rev. Date: February 7, 2006, Environmental Science and Technology Centre, Environment Canada

Because theses standard operating procedures are not openly accessible to readers
they were not referenced.

2) Throughout the paper, very little information is supplied regarding measurement uncertainty. Given that much of the paper deals with comparisons between various instruments, discussions of measurement uncertainty are critical. This should include error bars on plots and discussions whether instruments are within or out of combined measurement uncertainties. An estimate should be made of the resulting uncertainty in the data once corrected based on the filter measurements, and uncertainties should be combined and reported in the mass balance analysis.

The authors agree with Referee 1 that further discussion on measurement uncertainty would be useful to the reader. Additional details have been added through Section 2.2:

Section 2.2.1 (Page 210 Line 11): The measurement uncertainty for individual GPIC species was determined over a period of stable operating conditions and concentrations. As the magnitude of sampled component concentrations governs the associated uncertainty, it is useful to note that these uncertainties were determined for blank samples of high purity water with much lower ionic content than typical ambient samples. Hence these blanks samples provided an upper estimate of the uncertainty. For GPIC particulate species the measurement reproducibility was found to be \( \text{pCl}^- = 8\% \), \( \text{pSO}_4^{2-} = 9\% \), \( \text{pNO}_3^- = 11\% \), \( \text{pNH}_4^+ = 13\% \) and the following for gas phase compounds: \( \text{HCl} = 6\% \), \( \text{SO}_2 = 6\% \), \( \text{HNO}_3 = 10\% \), and \( \text{NH}_3 = 5\% \). The number of samples included for each uncertainty calculation ranged between 75 to 192 replicates.

Section 2.2.2 (Page 211, Line 13): The detection limit for gravimetric measurements was 0.3 \( \mu \text{g m}^{-3} \) which represented 1 to 2% of mean aerosol mass.

Section 2.2.2 (Page 211, Line 17): A total carbon loading of less than 0.2 \( \mu \text{gC cm}^{-2} \) in the analyzer oven was achieved prior to field sample analysis. In addition, before analyzing a sample batch, the instrument was calibrated for \( \text{CH}_4 \) or \( \text{CO}_2 \). EC and OC concentrations were determined to have a detection limit of 140 and 610 ng m\(^{-3}\), respectively. The uncertainty for OC was determined to be 20% and 30% for EC.
**Section 2.2.2 (Page 211, Line 27):** NIST-traceable calibration standards were run prior to field sample analysis and every 10 to 15 samples. Anions and cations were found to have detection limits in the range of 2 to 30 ng m$^{-3}$ and 1 to 6 ng m$^{-3}$, respectively. Uncertainty for sulphate, nitrate and ammonium were in the order of 10%.

**Section 2.2.4 (Page 212, Line 19):** The uncertainty for EC and OC measurements by the Sunset OCEC was determined to be 4% and 8%, respectively.

**Section 3.1.1 (Page 215, Line 7):** The total propagated uncertainty associated with these particulate GPIC results calibrated with NAPS filter measurements are 13, 15, and 16% for pSO$_2$$^-4$, pNO$_3^-3$, and pNH$_4^+$, respectively.

**Section 3.1.2 (Page 216, Line 8):** These calibrated gas phase GPIC results have propagated measurement uncertainties of 12, 14 and 11% for SO$_2$, HNO$_3$, and NH$_3$, respectively.

**Section 3.1.3 (Page 219, Line 19):** The propagated total measurement uncertainties on average for the reconstructed Walberg Building and NAPS 24 hour Partisol PM$_{2.5}$ mass concentrations were 12% and 18%, respectively.

3) There is considerable discussion on the various limitations of many of the methods but few specific details are provided, such as citations and discussions of results from other investigators. This is especially true for possible TEOM semi volatile losses, e.g., nitrate and OC, see for example (Willson et al., 2006).

The authors take note of Referee 1’s concern for more discussion of results from other investigators regarding TEOM semi-volatile losses. More details have been added to Section 3.1.3 paragraphs 4 and 5):

To evaluate both the Gage and MoE TEOM semi-continuous mass measurements, a comparison was conducted with 24 hour NAPS Dichot filter mass data. Lower PM$_{2.5}$ mass measurements were made by both TEOM instruments as compared to the NAPS Dichot filter mass. Furthermore, high particulate mass concentrations were more se-
riously underpredicted by both TEOMs. It is possible that episodic values influenced this divergence given that the mean difference between the NAPS Dichot and each of the TEOMs was greater than the median concentration difference. Underprediction of PM mass concentrations by TEOMs has been well documented (Allen et al., 1997; Ayers et al., 1999; Green et al., 2001; Charron et al., 2004); the heated inlets of this instrument act as an effective denuder, removing all semi-volatile compounds (in particular ammonium nitrate and OC) from the PM sample. Wilson et al., (2006) have further noted that semi-volatile compounds losses by the TEOM is a function of meteorological conditions; cold and humid conditions better stabilize ammonium nitrate and OC, minimizing TEOM PM mass concentration underestimation. Although TEOMs suffer from semi-volatile material losses, it is also pertinent to recall that gravimetric filter measurements may also experience losses of ammonium nitrate and OC ranging from less than 10% to greater than 50% (Wilson et al., 2006).

Individual monthly comparisons between each TEOM and the NAPS Dichot filter further elucidated the discrepancy noted between the two measurement techniques (Fig. 2). TEOM mass concentrations illustrated maximum underpredictions in the winter months and showed approximately equivalent measurements to the NAPS Dichot mass filters during the summer. As the Partisol mass filter measurements were taken as the standard for evaluating the semi-continuous measurement techniques, all semi-continuous TEOM mass concentrations were calibrated to the NAPS Dichot measurements on a month to month basis.

4) Either I missed it or there was very little discussion on how the various NAPS filters were used, ie, was the OC mass corrected for OC on the quartz filter behind the nylon filter. Was the mass corrected in any way? This is very important since this data is taken as the gold standard.

The OC mass measured by the NAPS Partisol sampling setup was corrected for with the concentration of ambient gaseous organic species collected on a backup quartz fibre filter - the authors appreciate this is information is very important and was therefore
5) The discussion in the last section of the paper on caused for various trends are mainly speculation, they need to be highly qualified possibly with phrases like, consistent with the idea that8230;., or give more details or data to support the assertions.

Additional details have been provided in Section 3.3.3 to support the assertions reported. The section now reads as follows:

No statistically significant diurnal variation was noted for sulphate and gaseous SO2 as both these species did not likely originate from local urban emission sources. Long range transport, generally from sources west or southwest of the sampling site, governed the magnitude of SO2 and sulphate concentrations observed in this urban environment. Sulphate results are in line with previous studies: Fisseha et al., (2006) also noted that sulphate lacked any diurnal trend and Drewnick et al., (2004) only observed a weak diurnal pattern. The late afternoon peak reported by the latter study was postulated to be the result of regional pollution episodes coupled with in situ SO2 photochemical processing. However, disagreement between studies exists in the literature regarding diurnal sulphate behaviour: a pronounced broad morning (7:00 to 12:00) sulphate peak identified by Weimer et al., (2006) was attributed with a rising boundary layer. pNH4+ and pSO42− diurnal trends were both insignificant in the summer. This was expected as the NH4)2SO4 was mostly likely in the form of either (NH4)2SO4 or NH4HSO4 (Zhang et al., 2006). Conversely, winter pNH4+ favoured nitrate association (Harrison and MacKenzie, 1990; Wexler and Seinfeld, 1990); thus diurnal variation of pNH4+ was observed in January.

As temperatures declined, gas phase ammonia concentrations also decreased. Interestingly, the diurnal profile for ammonia also shifted with season: a pronounced morning maximum rush hour peak (9:00 to 10:00) was noted in July which shifted to occur later in the day as the overall ambient temperature dropped: in January, the daily maximum was observed at 18:00. This profile likely implied that NH3 originated from
a local source, possibly vehicle traffic since this maximum did not occur on weekends. Furthermore, significant statistical correlation between NH$_3$ with CO was found ($r = 0.60$). The morning rise in the NH$_3$ may not have been observed in January due to increased conversion of NH$_3$ to NH$_4$NO$_3$ as a result of the colder temperatures. The late afternoon rise in the NH$_3$ diurnal profile for January appears to coincide with a drop in pNO$_3^-$ and pNH$_4^+$ concentrations. This observation potentially suggests that the same NH$_3$ from the vehicles that condensed in the morning subsequently evaporated once the temperature rose. Diurnal NH$_3$ trends have previous been reported in urban centres and were attributed to traffic emissions. Nowak et al., (2006) reported that during the summer in Atlanta, NH$_3$ concentration increased at 8:00 and remained consistently elevated throughout the day. However, during the winter in New York City, Li et al. (2006) noted a bimodal diurnal ammonia pattern; a rise in NH$_3$ commenced at 6:00 and attained peak levels at 9:00 which was followed by a gradual decline in concentration until 17:00 when a second peak was noted.

Although vehicle emissions appeared to influence the ammonia diurnal profile, agricultural fertilizer and livestock emissions also likely contributed to measured concentrations as monthly median NH$_3$ concentrations declined with temperature. This hypothesis was further investigated by comparing the total ammonium concentration (calculated as the sum of pNH$_4^+$ and NH$_3$) variation for the period when livestock and agricultural ammonia emissions were likely contributing (June to October) with that for the months of when minimal livestock or agricultural emissions were assumed present (December 2006 to March 2007). Given total ammonium concentrations were significantly lower ($p < 0.0001$) during the colder months ($N=4787$) than the warmer months ($N=5088$), with mean total ammonium concentrations and associated standard errors of $3.07 \pm 0.3$ and $5.21 \pm 0.3 \mu g m^{-3}$ respectively, agricultural and livestock source potentially influence the total measured ammonium measurements in downtown Toronto.

On weekends, the traffic density passing the sampling site was reduced and this is possibly reflective of the weaker daytime rise in gaseous NH$_3$. In addition, a gradual
midday decline due to a rise in the planetary boundary layer mixing height, which effectively diluted concentrations, was more apparent, particularly in July. As the depth of the mixing height weakened in the winter as compared with summer months, the degree to which this primary gas emission was diluted during the day was expected to be accordingly reduced.

For the entire duration of the sampling period HNO$_3$ concentrations were consistently less than those of pNO$_3^-$ . Gaseous nitric acid reached a peak concentration of 1.08 $\mu$g m$^{-3}$ in the early afternoon (12:00 to 13:00) for the month of July coinciding with maximum daily solar radiance and temperatures. Particulate nitrate in July peaked at 2.1 $\mu$g m$^{-3}$ between 10:00 and 11:00, prior to the HNO$_3$ peak. Diurnal HNO$_3$ formation and pNO$_3^-$ removal in the summer was the most pronounced diurnal trend observed. HNO$_3$ was likely formed during the night via N$_2$O$_5$ + H$_2$O reaction yielding pNO$_3^-$ in the early morning hours provided sufficient NH$_3$ was present (Ansari and Pandis, 1999; Weimer et al., 2006). As local vehicle sources further emitted primary NO$_x$ and NH$_3$ in the morning, more NH$_4$NO$_3$ may have been produced through oxidation of the NO$_x$ to HNO$_3$. As temperature and solar radiance increased throughout the day, gaseous HNO$_3$ concentrations continued to rise due to the evaporation of morning rush hour derived PM nitrate and the rapid oxidation of NO$_x$. The concentration of both species declined in the afternoon, suggestive of HNO$_3$ dry deposition and removal by advection (Fisseha et al., 2006).

Particulate nitrate exhibited a strong seasonal dependence: the greatest contribution of particulate nitrate (in the assumed form of ammonium nitrate) to total nitrate (calculated as the sum of HNO$_3$ and pNO$_3^-$) was observed in March (85%) and the lowest fraction was found in August (34%). Furthermore, the proportion of the total PM$_{2.5}$ mass, as measured by the TEOM, that was due to pNO$_3^-$ was on average 11 times higher in March than in August. Similar seasonal and diurnal variation were also observed in Zurich where the pNO$_3^-$ content of measured PM$_{10}$ was five times greater in March as compared to August (Fisseha et al., 2006).
Specific Comments. In section 2.2.1 It may be good to discuss the HNO₃ inlet tubing losses here. For example, what type of inlet Teflon tubing was used. Cite references and discuss sampling losses of HNO₃, eg (Neuman et al., 1999).

*The authors acknowledge that HNO₃ sampling is challenging due to elevated adsorption rates to certain inlet material wall surfaces. The suggested reference (Neuman et al., 1999) notes no adsorption loss differences between types of Teflon fluoropolymer tubes tested (FEP, PFA and TFE): all Teflon tubes encountered <5% HNO₃ losses from a 5.6 ppbv stream at 22°C. As the GPIC sampling setup described in this manuscript used 0.6 cm i.d. Teflon tubing, it is likely HNO₃ adsorption losses on the inlet tubing are not significant compared to losses described in other parts of the system. Neuman et al., (1999) did however mention HNO₃ loss on inlet lines was a function of tube temperature. Details regarding this experimental parameter were added to Section 2.2.1:

**Section 2.2.1 (Page 208, Line 16):** The use of Teflon lines for gas species sampling was to minimize the loss rate of HNO₃ which is known to readily adsorb onto many sampling inlet materials. All sampling lines were located indoors where a temperature of 23°C was maintained; increased HNO₃ adsorption to Teflon inlet tubing has been noted to occur at temperatures below 10°C (Neuman et al., 1999).

**Section 2.2.2. (Page 210, Line 26):** Aluminum inlets were used on cartridges A and B while a Teflon inlet was installed on cartridge C.

Section 2.2.3. Known losses from heated TEOM inlets should be discussed and cited.

*Additional details were added to Section 2.2.3 (line 6) to describe the known losses from heated TEOM inlets:

**Section 2.2.3 (Page 212, Line 6):** The heated inlet however, causes volatilization losses of pNO₃⁻ and OC (Wilson et al., 2006). Additional details are discussed in Section 3.1.3.

Section 2.2.4. The lines 5 and 6 on Applied optical detection 8230; it is unclear what is
being discussed.

Additional details have been included in the text to describe the Sunset OCEC measurement methods. **Lines 5 - 8 of section 2.2.4 have been removed and replaced with the following:**

EC and OC concentrations were measured using thermal methods: particles were heated in the quartz oven to oxidize the carbon aerosol into CO$_2$ which was measured using a Non-Dispersive Infrared detection system. Heating was conducted in various staged temperatures, each volatizing different carbonaceous components. The first stage raised ambient temperatures to a maximum of 840 °C and introduced pure helium gas into the oven in an effort to minimize the amount of black carbon (BC), also known as EC, oxidation while enhancing OC volatilization (Chow et al., 2005). Measured carbon during this stage was classified as OC. The oven temperature was reduced to ambient conditions and purged of helium before the commencement of the second stage. Oxygen was then introduced into the system and temperatures were increased to a maximum of 850 °C such the remaining carbonaceous content (BC) of the collected bulk aerosol could be quantified (Chow et al., 2005).

In addition to thermal measurements of EC and OC concentrations, this Sunset instrument also used optical methods to correct thermal measurements. Although OC charring should be avoided in non-oxidizing environments, losses are still possible given the operating oven temperatures. By transmitting the beam of a laser through the collected aerosol sample, the intensity of light transmitted or reflected at each stage of thermal analysis was used to quantify the amount of OC charred: as OC became increasingly charred, light absorption was enhanced. While elevating BC evolution resulted in increased laser transmission. However, it is reasonable to expect some BC volatilization will occur prior to the second stage heating phase as the temperature at which this species evolves is dependent on the aerosol's chemical compositions and a number of other factors (Reid et al., 1998). Therefore, given this optical detection method, the Sunset Laboratory OCEC instrument is able to better estimate the true concentra-
tion of each type of carbonaceous aerosol present in the sample and minimize errors from sampling processing.

Last line of section 3.1.2. The regression results have slope of 1, so no correction was applied?

The regression results presented in the last line of Section 3.1.2 are calibrated GPIC values.

A general question; were the filter holders located outside or inside, were they at ambient temperature?

Filter holders were in Partisol sampling platform located outside at ambient temperatures.

Last part of section 3.3.1 Be specific on what agricultural activities contributed to the measured pollutants. Also, on page 22 why are there no livestock or agricultural emissions in the winter?

Subzero temperature in Southern Ontario prevent much agricultural activity to continue through the winter. The very cold temperatures also limit outdoor livestock activity (Table 2).


Green, D., Fuller, G., Barratt, B.: Evaluation of TEOM 8216;correction factors8217; for assessing the EU stage 1 limit values for PM10. Atmos. Enviro., 35: 25898211;2593, 2001.


