**Atmospheric
Measurement
Techniques
Discussions**

Evaluation and application of a semi-continuous chemical characterization system for water soluble inorganic PM$_{2.5}$ and associated precursor gases

K. J. Godri[1], G. J. Evans[1], J. Slowik[1], A. Knox[1], J. Abbatt[1], J. Brook[1,2], T. Dann[3],
and E. Dabek-Zlotorzynska[3]

[1]Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto,
200 College Street, Toronto, Ontario, M5S 3E5, Canada
[2]Environment Canada, Downsview, Ontario, Canada
[3]Analysis and Air Quality Division, Environmental Science and Technology Centre,
Environment Canada, 335 River Road, Ottawa, ON K1A OH3, Canada

---

AMTD

1, 205–248, 2008

**Evaluation of a PM$_{2.5}$
chemical
characterization
system**

K. J. Godri et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄◄ | ►►|
|◄ | ►|

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Water soluble inorganic particles components (Cl^-, SO_4^{2-}, NO_3^-, and NH_4^+) and concentrations of their associated precursor gases (HCl, SO_2, HNO_3, NH_3) were semi-continuously measured using the Dionex Gas Particle Ion Chromatography (GPIC) system. Sampling was conducted adjacent to a high traffic street in downtown Toronto, Canada from June 2006 to March 2007. This study evaluated the precision and accuracy of field sampling measurements with the GPIC both relative to filter based measurements and other co-located semi-continuous instruments (R&P 8400N Nitrate Monitor, API Fluorescent SO_2 Gas Analyzer, and Aerodyne C-ToF-AMS). High temporal resolution $PM_{2.5}$ mass reconstruction is presented by combining GPIC measured inorganic species concentrations and Sunset Laboratory OCEC Analyzer determined organics concentrations. Field sampling results were also examined for seasonal and diurnal variations. HNO_3 and particulate nitrate exhibited diurnal variation and strong partitioning to the gas phase was observed during the summer. Ammonia and particulate ammonium also demonstrated seasonal differences in their diurnal profiles. However, particulate sulphate and SO_2 showed no diurnal variation regardless of season suggesting dominant transport from regional sources throughout the year.

1 Introduction

Exposure to atmospheric aerosols has been implicated in mortality from cardio-pulmonary causes (Dockery et al., 1993; Pope et al., 1995; Hoek et al., 2002; Pope et al., 2002). Moreover, degradation in visibility (Watson, 2002) and environmental damages (Schindler, 1988; Jacobson, 2001; Driscoll et al., 2003) also result from atmospheric aerosols. These negative consequences may only be addressed once variations in the chemical composition, size distribution and mixing state of aerosols are better understood. Specifically, the mass, composition and size of fine particulate matter can be influenced by the partitioning of species between the gas and particle

phase.

Two limiting factors in understanding dynamic atmospheric processes have been the low time resolution associated with many existing aerosol and gaseous chemical characterization instruments and the inability to measure chemical components in both the gaseous and particulate phases simultaneously. Instrument measurement inadequacies prompted the first objective of this study: commissioning the semi-continuous Dionex Gas Particle Ion Chromatography (GPIC) system. The GPIC simultaneously measured bulk concentrations of ambient water soluble inorganic species in particulate matter with an aerodynamic diameter smaller than $2.5\,\mu$m (PM$_{2.5}$) and the associated precursor gases with a fifteen minute time resolution. A number of additional semi-continuous instruments, including an R&P TEOM, R&P 8400N Nitrate Monitor, API SO$_2$ Analyzer and Aerodyne C-ToF-AMS, were deployed along side of the GPIC to evaluate this recently developed instrument.

The second objective of this paper was to use GPIC measurements to better understand temporal fluctuations in the chemical composition observed for urban aerosols and their precursor gases. Focus was given to studying the diurnal and episodic variation of inorganic species within and between seasons.

2 Experimental

2.1 Sampling site

This study sampled air collected from downtown Toronto, Ontario, Canada in the University of Toronto's Wallberg Building located at latitude 43.66 N and longitude 79.40 W (Fig. 1). The Wallberg Building is situated on the north side of College Street, which experiences weekday traffic of about 33 000 vehicles per day, a volume representative of traffic on many major streets in downtown Toronto. The sampling inlet was approximately 15 m from College Street and 5 m above the ground.

Filter, denuder and TEOM measurements used for comparison were collected on

the roof top of the three story Gage building located approximately 170 m west of the Wallberg Building sampling site. A second TEOM operated by the Ontario Ministry of the Environment (MoE) was situated at the high traffic intersection of Bay and Wellesley Streets with an inlet 10 m above ground, approximately 875 m from the Wallberg Building sampling site.

2.2 Sampling methods

2.2.1 Gas Particle Ion Chromatography (GPIC) System

The GPIC system was used to obtain semi-continuous measurement of soluble gaseous and particulate phase species simultaneously. Monitored species included particulate chloride (pCl^-), particulate sulphate (pSO_4^{2-}), particulate nitrate (pNO_3^-), particulate ammonium (pNH_4^+), $HCl_{(g)}$, $SO_{2(g)}$, $HNO_{3(g)}$, and $NH_{3(g)}$. Each of the gas phase and particulate phase constituents were independently analyzed on two separate channels each sampling at $5\,L\,min^{-1}$ operating with 15 min time resolution. The gas channel sampled ambient air via a 0.6 cm diameter, 3 m long piece of Teflon tubing while the particle channel employed 0.9 m diameter stainless steel tubing of the same length for sampling.

On the particle channel, the air stream passed through a $PM_{2.5}$ sharp cut cyclone prior to introduction into the etched plexiglass parallel plate wet denuder (PPWD). A $0.5\,mM\,H_2O_2$ solution wetted the denuder and served to collect soluble gaseous constituents from the ambient air. All liquid flow was controlled using an eight channel peristaltic pump. Gas species dissolved in the dilute H_2O_2 solution were collected from the denuder and sent to waste. Gas denuded air was then routed to a plexiglass airtight particle collector vessel (PC), which was outfitted with a polytetrafluoroethylene (PTFE) filter located at the exit of the chamber. This hydrophobic filter prevented particles from leaving the PC and aided in the process of capturing soluble particulate matter. An $18.2\,M\Omega$ dionized water stream was injected into the high velocity sample air flow path in the PC. Upon entrance into the collection vessel the water formed a fine

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

mist. Any water soluble particulate matter was dissolved into solution. Negative arti-facts, due for example to evaporation after sampling, were minimized since the volatile aerosol species were continuously being dissolved. Mist quickly accumulated in the PC causing the water droplets to coalesce due to the chamber's high humidity. The base of the PC was conical allowing for the liquid to be easily aspirated from the bottom of this reflux-condenser-like vessel. Once extracted from the PC, components within the dissolved particulates were routed into a series of cation and anion concentrator columns for conductivity and IC analysis, respectively.

Cation concentrators were eluded with a 15 mM NaOH solution. Liquid subsequently passed through a porous membrane device (PMD) (Dionex, CRD-200). A concentra-tion gradient was the acting driving force behind this shell and tube like exchanger; any NH_3 in the concentrated alkaline sample passed through the PMD shell diffusing into the inner stream. The high purity water, which was flowed through the inner PMD tubing, served to hydrolyze the collected NH_3 back into NH_4^+. Flow was then routed through a conductivity detector (Dionex, CD25A) providing a measure of the total am-monium content. The anion concentrators were eluded with 20.5 mM KOH and then pumped (GS50) into the ion chromatography system (Dionex, ICS-2000) for analysis of the remaining species. Once in the dissolved anion form, particles were routed into the anion guard column (AG11-HC, 2×50 mm) and then the separator column (AS11-HC, 2×250 mm), both of which were heated in an oven maintained at 30°C. Following these columns, the sample solution passed through an ASRS-Ultra 52mA suppressor and 2 mm carbonate removal device (Dionex, CRD) prior to entering the thermally stabi-lized conductivity cell. The system used electrodialytically generated (EG40) 20.5 mM KOH mobile phase. It should be noted that the GPIC system was modified from its orig-inal form to function with the additional post suppressor carbon dioxide removal device to minimize the magnitude of the carbonate in the sample stream, consequentially re-ducing interference with sulphate and nitrate peaks. This enhanced peak resolution hence also improved detection limits for the nitrate and sulphate related atmospheric gases and particle components measured on the IC system.

The air stream in the gas channel was directly introduced into another PPWD which collected soluble gases in a weak H_2O_2 solution. The peroxide solution, now containing dissolved gas species, was drained from the denuder and then sent to a series of cation and anion concentrator columns for subsequent analysis identical to that on the particle side.

A computer using Dionex Chromeleon Software was connected to the GPIC system and allowed continuously automated valve control in 15 min intervals. This software package was also used to collect both conductivity detector signals and the ion chromatography output. The limits of detections were established as $100\,ng\,m^{-3}$ for all particle anion species, $25\,ng\,m^{-3}$ for all gas anion species and $100\,ng\,m^{-3}$ for both gas and particle cation constituents. Further details regarding this instrument's design have been previously described by Al Horr et al. (2003) and Ullah et al. (2006).

2.2.2 NAPS sample collection and analysis

Integrated 24 h ambient aerosol samples, acid gases (HNO_3, HNO_2, SO_2) and ammonia were collected on the rooftop of the Gage Building in Toronto, one of the National Air Pollution Surveillance (NAPS) sites. All PM samples were collected in parallel with R&P Partisol-Plus 2025-D sequential dichotomous particulate samplers (Dichot) and with the R&P Partisol Model 2300 Speciation samplers (Partisol) once every three days (Rupprecht & Patashnick Co., Inc.,). The dichotomous particulate sampler was operated at a total flow rate of $16.7\,L\,min^{-1}$ which was split between two channels: $PM_{2.5}$ and coarse PM ($PM_{2.5-10}$). Two separate mass flow controllers maintained the flow rates of the fine and coarse particle stream at $15\,L\,min^{-1}$ and $1.7\,L\,min^{-1}$, respectively. The Partisol speciation sampler was comprised of three distinct Harvard designed Chemcomb® cartridges (A, B, and C) connected to a low volume air sampler operating with a total flow rate of $30\,L\,min^{-1}$. Each channel maintained a flow rate of $10\,L\,min^{-1}$. The Chemcomb cartridge A contained pre-fired quartz fiber filter for collecting $PM_{2.5}$ for the analysis of elemental carbon (EC) and organic carbon (OC). Cartridge B contained a Teflon filter and a backup pre-fired quartz filter in series. The Teflon filter

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

was analyzed for $PM_{2.5}$ and archived for other analyzes. The backup quartz fiber filter samples particle-free ambient air and provided an estimate the amount of gaseous organic species adsorbed on the quartz fiber filter (Cartridge A). The cartridge C had two honeycomb glass denuders placed upstream of two filter packs with Teflon and nylon filters. Na_2CO_3-coated denuder was used for collection of acid gases (HNO_3, HNO_2, SO_2) and a citric acid-coated denuder was used for collection of ammonia. The Teflon filter was used for the collection of PM for the analysis of water-soluble anions and cations, and water-soluble trace metals. The volatile nitrate that was released from the Teflon filter was captured by the nylon backup filter.

PM mass was determined by weighing all Teflon filters, before and after sampling, at controlled temperature (23±3°C) and relative humidity (45±5%) with a Mettler 5 Microbalance (1-μg readability; MT-5, Mettler-Toledo Inc., Highstown, NJ), after the filters (samples and blanks) had acclimatized to these conditions for at least 24 h. Exposed quartz fiber filters were analyzed for OC and EC content using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc Calabasas, CA). In this study, the Interagency Monitoring of Protected Visual Environments thermal/optical reflectance protocol (Chow, 2001) was used. Ion chromatography analysis was used to determine the soluble ion contents of the various extracts applying a dual-channel Dionex DX-500 and/or DX-600 and/or ICS-3000 (Dionex, Sunnyvale, CA, USA) ion chromatographs. Each channel operated a self-regenerating SRS-ULTRA suppressor with internal DDW regeneration mode, a CD20 conductivity detector, and a GP50 gradient pump. For the water-soluble cations in extracts of Teflon filters (Cartridge C) and ammonium in the extracts of citric acid-coated denuders, IonPac CS-12 analytical columns with methanesulfonic acid as eluent were used. Water-soluble anions in the extracts of Teflon filters (Cartridge C) were analyzed using IonPacAS15 column. For the anions in extracts of nylon filters and carbonate-coated denuders, a Dionex-AS4A column was used with carbonate/bicarbonate eluent.

2.2.3 R&P TEOM monitor

Total $PM_{2.5}$ mass concentrations were measured using a tapered element oscillating microbalance (TEOM, Model 1400A, Rupprecht & Patashnick Co. Inc.) with five minute resolution. As the mass collected on the TEOM filter was very sensitive to ambient water vapour concentrations, the ambient air inlet stream was heated to 30 or 50°C to eliminate the effect of water associated with hygroscopic particles (Patashnick and Rupprecht, 1991; Mignacca and Stubbs, 1999). This study employed the use of two TEOMs: one run by Environment Canada on the rooftop of the Gage Building (30°C heater temperature) and the second operated by the Ontario Ministry of the Environment (MoE) with a 50°C heated inlet at another downtown location.

2.2.4 Sunset Laboratory Semi-Continuous OCEC Analyzer

The Sunset Laboratory OCEC Analyzer collected $PM_{2.5}$ on a quartz fibre filter in an oven at a flow rate of $8 \, L \, min^{-1}$ for a period of 108 min per sample. Following the completion of the aerosol sampling period, deposited particles were heated in the quartz oven where elemental and organic carbon concentrations were individually quantified. Applied optical detection methods allowed sampling processing errors to be minimized yielding a better estimate of the true concentration of each type of carbonaceous aerosol collected. Further optical methods were also used to correct thermal EC and OC measurements. Chow et al. (2005) provides an in depth discussion of this instrument's operating philosophy. The Sunset Labs OCEC was located in the Wallberg Building laboratory.

2.2.5 API Fluorescent SO_2 Gas Analyzer

Five minute averaged ambient SO_2 gas samples were collected at the Wallberg Building sampling site using this API SO_2 instrument (Model 100A).

2.2.6 R&P 8400N Nitrate Analyzer

The Ambient Particulate Nitrate Monitor (Model 8400N, Rupprecht and Patashnick Co. Inc.) sampled air through a PM$_{2.5}$ impactor which was then heated to 350°C. This temperature was adequately high to volatilize all collected nitrate, causing decomposition into NO$_x$ which was analyzed using the API chemiluminescent NO$_x$ analyzer (Model 200A) in 15 min averaged intervals.

2.2.7 Aerodyne C-ToF-AMS

An Aerodyne Compact Time of Flight Mass Spectrometer (C-ToF-AMS) (Aerodyne Research Inc., Billerica, MA) deployed at the Wallberg Building sampling site in January and February 2007. This instrument determined the size-resolved non-refractory chemical composition of particles with submicron vacuum aerodynamic diameter (PM$_{1.0}$, particulates with an aerodynamic diameter of less than 1 μm) with 1 min time resolution. This instrument has been previously described by Drewnick et al. (2005).

3 Results and discussion

3.1 GPIC data evaluation

3.1.1 GPIC comparison with NAPS filter measurements

Inorganic particulate and gas concentrations generated by the GPIC were compared with these 24 h PM$_{2.5}$ Partisol and Dichot filter and denuder samples collected by the NAPS program on the roof of the Gage Building. The proximity of the Gage Building suggested similar ambient air concentrations and previous study have indicated that the two sampling locations yielded similar inorganic particulate measurements upon comparison (Tsai, 2002).

GPIC fifteen minute particulate measurements were averaged to a 24 h basis comparable to the NAPS filters' resolution. At least 75% of the fifteen minute GPIC measurements were required for a daily average to be considered valid. For the entire campaign duration, raw GPIC particulate measurements were less than inorganic concentrations given by the corresponding filter data: overall linear regressions between raw GPIC particulate averaged measurements and NAPS Partisol filter measurements indicated a slope of 0.45, 0.41, and 0.49 $(\mu g\,m^{-3})_{GPIC}/(\mu g\,m^{-3})_{Gage\,Filter}$ for sulphate, nitrate and ammonium concentrations, respectively. However, good GPIC- NAPS Partisol filter temporal agreement was indicated by high Pearson r values of 0.93 (sulphate, N=76), 0.86 (nitrate, N=77) and 0.85 (ammonium, N=68) for each regression.

Consistency between the three main particle phase species and low month-to-month variation between the two measurement methods suggested a systematic bias. Non-unit GPIC/ NAPS Partisol filter ratios for all inorganic components of interest suggested incomplete particle collection, air flow leakage, low flow rate, or line losses in the semi-continuous instrument. The possibility of low flow in the GPIC itself as the cause was eliminated as the mass flow rates were verified intermittently throughout the sampling with an independent flow meter. The reason for the non-unit GPIC/ NAPS Partisol filter ratios could not fully be determined during the study as the issue was only identified at the end of the sampling period, once the filter results became available. However, in-leakage of air due to incomplete seals in the sampling lines upstream of the particle trap in the GPIC was one issue that was identified. This problem caused a 20–30% negative artifact that was aggravated by frequent maintenance-related disconnections. In a follow-up study, a discrepancy inherent in the GPIC design, relating to the fixed volume loop used for calibration was identified (Yao et al., 2008). This error caused a systematic 30% negative artifact in the GPIC concentrations results. Hence the difference between the GPIC and filter samples was eventually identified and accounted for.

To address the difference between the GPIC and NAPS results, NAPS Partisol filter measurements were selected as the basis for correcting the particulate mass concen-

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

trations. Given that the filter sampling methodology had been designed to minimize losses by volatilization species, specifically nitrate, it was reasonable to use the filters as a basis for semi-continuous instrument evaluation and calibration. Raw GPIC particulate concentrations were calibrated against the Gage Partisol filter particulate measurements on a month by month basis in an effort to obtain more accurate temporally resolved GPIC results. The final recoveries for pSO_4^{2-}, pNO_3^-, pNH_4^+ were 98% (r=0.93), 100% (r=0.93), 97% (r=0.94), respectively.

3.1.2 GPIC comparison with NAPS denuder measurements

Similarly to the GPIC particle channel measurements, all the fifteen minute data was averaged to a 24 h basis while implementing the same criteria for validating averaged results as for the particulate channel. Again the NAPS denuder measurements for HNO_3, NH_3 and SO_2 gases were assumed to be accurate and the GPIC concentrations were calibrated to these standards. Comparison of the denuder and GPIC concentrations indicated an overprediction by the GPIC for NH_3 and SO_2 measurements and underprediction for HNO_3: overall linear regression slopes and corresponding Pearson r values of 0.25 (r=0.76, N=39), 1.43 (r=0.83, N=56), and 1.42 (r=0.97, N=70) (($\mu g\,m^{-3}$)$_{GPIC}$/($\mu g\,m^{-3}$)$_{Gage\,Denuder}$) were found for HNO_3, NH_3 and SO_2, respectively. The high Pearson r values showed the strong temporal consistency between the two sets of measurements. Significant in-leakage of lab air (54%) was found at the end of the study on the gas channel. However, there was no reason to suspect that the indoor lab air had higher concentrations of NH_3 and SO_2 than the outside air. Consequently it was not clear why this in-leakage could cause the NH_3 and SO_2 species to be overpredicted. HNO_3 line losses likely contributed to low GPIC measurements for this species. Losses may have occurred along the walls of the inlet sample air tubing and any water droplets accumulated in the inlet line may have caused further losses. Furthermore, comparison of nitric acid measurements made at other locations to this study indicated that the GPIC concentrations were lower than those typically observed (Hering et al., 1988; Boring et al., 2002; Huang et al., 2002; Fischer et al., 2006; Lin et

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

al., 2006; Morino et al., 2006; Ullah et al., 2006).

For the gaseous species, the ratio of the GPIC to NAPS concentrations did not show as much month to month variability as the particle channel. Hence the GPIC-NAPS denuder calibrations were made based on two seasonal linear correlations: Summer–Fall (June 2006 to December 2006) and Winter (January 2007 to March 2007). GPIC calibration with seasonal denuder measurements yielded final relationships of: $y=1.0x$ ($r=0.9$, $N=70$), $y=1.0x$ ($r=0.61$, $N=35$), and $y=1.1x$ ($r=0.81$, $N=56$) for SO_2, HNO_3, and NH_3 respectively.

3.1.3 Mass closure study

$PM_{2.5}$ mass in Toronto is composed of the major secondary inorganic species, including sulphate, nitrate, and ammonium, and organic matter and elemental carbon. Crustal elements and other inorganic species have been reported to account for the remaining $PM_{2.5}$ mass (approximately 8%) on an annual basis in Toronto (Brook et al., 1999a). As a further verification of the accuracy of the GPIC measurements, the particulate mass was reconstructed using the inorganic GPIC particulate measurements and EC and OC mass concentrations made by the Sunset Laboratories OCEC instrument, both co-located in the Wallberg Building for the months of July 2006 and October 2006 to January 2007.

Measurements collected by the Sunset Laboratory OCEC Analyzer included OC and EC which were both validated against 24 hour NAPS Partisol filter results in a separate study. A recovery of 0.71 for Sunset OCEC's OC measurements to filter results was found with an associated Pearson $r=0.73$. Loss of semi-volatile organic species during sampling may have caused a negative artifact in the Sunset OCEC results. Conversely, condensation of semi-volatile organic carbon overnight on the particulate matter already collected on the filters may have created a positive artifact for the NAPS Partisol results. Comparison of the EC measured by the Sunset OCEC to the Partisol filter EC resulted in a slope of 1.08, Pearson $r=0.58$.

On average for this period, the major inorganic species represented 62% of the total

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

reconstructed mass and carbonaceous compounds accounted 26%. It should be re-called that all the inorganic GPIC concentrations used in the mass closure study were corrected against the monthly NAPS filter measurements as previously described. To-tal reconstructed PM$_{2.5}$ mass from the Wallberg Building GPIC and OCEC instrument measurements were compared to both the Gage and Ministry of the Environment Downtown TEOMs. Successful comparison between the semi-continuous and filter-based measurement techniques required the Sunset OCEC's organic carbon results to be converted to an organic mass (OM) concentration. A factor of 1.4 was used to account for the contribution of elements other than carbon to this mass (Watson, 2002; Harrison et al., 2003). This conversion factor was expected to have a seasonal depen-dence; however, the degree to which the relative amounts of primary and secondary organic carbon varied between seasons was unknown and thus a constant conversion ratio was employed.

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. This observation has been frequently documented (Allen et al., 1997; Ayers et al., 1999; Charron et al., 2004). Furthermore, high particulate mass concentrations were more seriously 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.

Differences in instrument design, specifically the heated TEOM inlet air steam, po-tentially caused semi-volatile constituent losses, particularly for nitrate. Individual monthly comparisons between each TEOM and the NAPS Dichot filter further eluci-dated the discrepancy noted between the two measurement techniques (Fig. 2). TEOM mass illustrated maximum underpredictions in the winter months and showed approxi-mately equivalent measurements to the NAPS Dichot mass filters during the summer. As the Partisol mass filter measurements were taken as the standard for evaluating

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

the semi-continuous measurement techniques, all semi-continuous TEOM mass concentrations were calibrated to the NAPS Dichot measurements on a month to month basis.

The cause for this winter underprediction was likely increased loss of semi-volatile species induced by the TEOM's heating of the air stream: as the contribution of semi-volatile species to the total particulate mass increased at the colder ambient temperatures, more particulate semi-volatile species removal would have occurred (Table 1). Hence, the magnitude of the TEOM mass overprediction was a function of particle composition, if all other factors are considered to be equal: as nitrate production was thermodynamically favoured at lower temperatures, the highest particulate nitrate concentrations were measured during the winter months. Elevated ambient relative humidity may have also contributed to increased differences between the two mass measurement methods as this controls particle liquid water content and therefore the partitioning of semi-volatile species such as nitrate. Measured particulate nitrate was assumed to all be in the form of ammonium nitrate.

The TEOM experienced maximum particulate loss during the winter which corresponds to the standard NAPS Dichot mass filter trends and peak concentrations of volatile nitrate species. Least square linear regressions were conducted between the PM$_{2.5}$ mass reconstructed from the GPIC and Sunset OCEC measurements and (1) calibrated and (2) raw TEOM results for the months of November 2006 to March 2007. These months were associated with the greatest contribution of ammonium nitrate to the total Wallberg PM$_{2.5}$ mass measurement. Figure 3 was used to evaluate if the deviations of the TEOM measurements from the NAPS Dichot filter were approximately equivalent to the mass of ammonium nitrate present within the particulates. The linear relationship established between the reconstructed PM$_{2.5}$ mass and raw TEOM PM$_{2.5}$ measurements was $y=1.55x$ and $y=1.57x$ for the MoE and Gage, respectively (Fig. 3a and b). With a slope greater than 1, raw TEOM values underpredicted the reconstructed mass from the Wallberg measurements which only included major secondary inorganic and carbonaceous species, excluding the inorganic soil species

which was estimated to account for approximately a further 8% of the total Toronto PM$_{2.5}$ mass (Brook et al., 1999a). Subtraction of the ammonium nitrate mass from the reconstructed Wallberg PM$_{2.5}$ mass yielded a significant reduction in the previously described slopes yielding values of about 0.8. The difference between the TEOM and NAPS Dichot filter mass measurements were attributed to partial volatilization of nitrate in the heated inlet air stream. It is worth noting that subtracting the ammonium nitrate slightly improved the correlation between the Wallberg PM$_{2.5}$ results and the TEOM measurements, suggesting that the day to day variation in the NH$_4$NO$_3$ mass contributed to the variation in accuracy of the TEOM measurements. Furthermore, the different temperatures used in the two TEOMs did not cause significant dissimilarities in the extent of semi-volatile mass loss; a temperature of 30°C should, in theory, have been sufficient to volatilize all the ammonium nitrate.

Comparison of the calibrated TEOM MoE and Gage data with reconstructed GPIC and OCEC Wallberg Building PM$_{2.5}$ mass concentrations for the entire study period yielded a relationship $y=0.93x$ and $y=0.95x$, respectively (Fig. 4). Excluded inorganic soil compounds possibly accounted for the non-unit slope in addition to instrument measurement errors. However, correlation of the filter mass measurements for the NAPS 24 h NAPS Partisol (y) and NAPS Dichot (x) filters also gave a slope of 0.95 (Pearson $r=0.93$). Hence the 5% difference was also within the range of the experimental error.

3.2 Semi-continuous inter-instrument comparison

To further verify the GPIC system was successfully measuring gaseous and aerosol species, particulate nitrate and gaseous SO$_2$ values from the GPIC were compared with co-located R&P 8400N Nitrate Analyzer and API Fluorescent SO$_2$ Analyzer measurements in the Wallberg Building for the entire sampling period: June 2006 to March 2007. Further intercomparison for all particulate species was conducted between the GPIC and C-ToF-AMS measurements for the period of 22 January 2007 to 4 February 2007.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀◀ | ▶▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.2.1 API SO$_2$ Analyzer comparison

Analysis of the API SO$_2$ Analyzer and GPIC results suggested that the former consistently overpredicted SO$_2$ concentrations: when the entire sampling period was considered (N=5345), linear regression yielded a slope and associated 95% confidence interval of 1.37±0.01 (ppb)$_{API}$/(ppb)$_{GPIC}$. Strong temporal agreement (Pearson r=0.87) was identified between the two measurement techniques based on a comparison of the entire sampling period. However this slope of 1.37 indicated that the API SO$_2$ Analyzer would have agreed well with the original uncalibrated GPIC SO$_2$ concentrations and hence that correcting the GPIC SO$_2$ data based on the NAPS denuders may actually have altered potentially more accurate values. The API SO$_2$ Analyzer offset measurements by 0.59±0.01 ppb as compared to the GPIC SO$_2$ concentrations which was at least in part due to API SO$_2$ Analyzer calibration challenges. It is worth noting that full calibrations were conducted on this instrument prior to the sampling collection period on 22 October 2005 and afterwards in July 2007. However some drift was observed between these two dates.

3.2.2 R&P 8400N Nitrate Analyzer comparison

Comparison of the co-located R&P 8400N Nitrate Analyzer and the GPIC in the Wallberg Building showed an overall good correlation between the two measurement techniques: 8400N versus GPIC regression (N=4099) yielded a slope and associated 95% confidence interval of 0.83±0.03 (μg m^{-3})$_{R\&P\,8400N}$/(μg m^{-3})$_{GPIC}$ with an intercept of 0.32±0.11 μg m^{-3} (Pearson r=0.86) and a recovery slope of 0.89. However, upon examination of the individual months, the ratio relating the two instruments was found to approach unity in the wintertime (December 2006 to March 2007) which suggested better agreement was possible when higher ambient nitrate concentrations were present. This good agreement provided support for the validity of correcting the GPIC particle channel results based on the NAPS Partisol filter. Both nitrate measurements tracked each other well (Fig. 6a and b); however, discrepancies between the GPIC and 8400N,

for both high and low nitrate concentrations, were noted for periods of elevated relative humidity. Toronto experienced a period of high temperature ($T>30°C$) and elevated relative humidity (RH>85%) from 25 July 2006 to 2 August 2006 and on 27 August 2007. The R&P 8400N may have suffered from incomplete flash volatilization resulting in underpredicted measurements during these times (Long and McClenny, 2006).

Although the 8400N and GPIC exhibited excellent temporal correlation, the apparent 8400N underprediction warrants discussion. Comparable underprediction of the 8400N as compared to other measurement techniques (noted as the slope in Table 2) has been cited previously at various US urban and rural centers (Harrison et al., 2004; Hogrefe et al., 2004; Wittig et al., 2004; Grover et al., 2006; Long and McClenny, 2006; Rattigan et al., 2006). A summary of instrument intercomparison relationships is presented in Table 2 where all centres were urban environments with the exception of Whiteface Mountain, NY. Consistent underpredication by the 8400N was evident for each intercomparison and this divergence was not limited to comparisons with the GPIC. Moreover, each summarized study reported a similar mass concentration range as that observed in the current study. Nitrate measurement loss by the 8400N may have been in part due to decreased Molydenum converter efficiency which was located in the system's pulse analyzer (Long and McClenny, 2006). Low efficiency may have resulted in incomplete NO_2 to NO conversion causing nitrate measurement underestimations. It is also worth noting that Long and McClenny (2006) observed only a negative bias with the 8400N as compared to the GPIC during ambient sampling; the 8400N accurately measured high nitrate concentrations when operating under controlled laboratory conditions. These results suggested that interfering species may have contributed to the divergence between measurement techniques at high nitrate concentrations. Additional differences between these techniques may be caused to the 95% maximum 8400N sampling efficiency for particle diameters between 100 and 800 nm (Stolzenburg and Hering, 2000).

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

3.2.3 Aerodyne C-ToF-AMS comparison

Co-located GPIC $PM_{2.5}$ and C-ToF-AMS $PM_{1.0}$ measurements were collected for the period of 22 January 2007 to 4 February 2007 and compared using 15 min averaged sulphate, nitrate, and ammonium particulate concentrations. Excellent temporal agree-
5 ment between the two measurement techniques was indicated from Pearson r values for each species: 0.92, 0.92, and 0.86 for sulphate, nitrate and ammonium, respectively (Table 3). However, the C-ToF-AMS concentrations were typically 40% lower than those from the GPIC. This difference was mostly due to the different size cut-points of the two instruments; $PM_{2.5}$ for the GPIC and $PM_{1.0}$ for the C-ToF-AMS. Mass
10 concentrations calculated from TSI 3321 Aerosol Particle Sizer (APS) measurements (assuming spherical particles with unit density) indicated that the ratio of $PM_{1.0}$ to $PM_{2.5}$ was on average 0.63±0.21 during the sampling period. The collection efficiency of the AMS may also have been lower than the value of one used in the calculations, and this also potentially contributed to the difference.
15   The time series for each particulate species indicated that the relationship be-tween the GPIC and C-ToF-AMS was not constant throughout the measurement period (Fig. 7). This variability was partially attributable to fluctuations in the aerosol size dis-tribution. However, scaling the C-ToF-AMS data based on the $PM_{1.0}$ and $PM_{2.5}$ ratio from the APS only improved the agreement some of the time, with some notable excep-
20 tions. For example, on 23 January 2007 the ratio of $PM_{1.0}$ to $PM_{2.5}$ rose to 0.9 while the C-ToF-AMS measurements remained 40% lower on average than those of the GPIC. A similar pattern occurred overnight on 1 February 2007 to 2 February 2007: the C-ToF-AMS to GPIC ratio was 0.55 whereas that for $PM_{1.0}$ to $PM_{2.5}$ was 0.83. Hence, particle size could explain the difference between the GPIC and C-ToF-AMS on average, but
25 other as of yet unidentified factors also contributed to the divergence at times. It is worth noting that the GPIC agreed with the R&P 8400N on 23 January 2007 and was higher overnight on 1 February 2007 to 2 February 2007 (Fig. 6).

3.3 Field data

3.3.1 Sampling conditions

Measured gas and particulate concentrations were to a large extent governed by meteorological parameters (wind speed, wind direction, temperature, relative humidity
5 and solar radiation). The measurement time of day and contributions from local and long range transported aerosol sources were also influential factors. NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) back trajectory analysis and plume dispersion modeling were used to elucidate the geographic origin of measured air masses.
10 Regarding local sources, the Wallberg Building sampling site was strongly influenced by vehicle traffic. Peak traffic densities of gasoline vehicles passing by the site occurred on weekdays between: 06:30 to 09:00 and 16:30 to 18:30. Nighttime vehicular traffic was significantly lower than during the day.

Long range transported air masses were frequently sampled at the Wallberg Build-
15 ing sampling site in downtown Toronto. The majority of industrial sources influencing sampled air masses were situated south and southwest of the sampling site. Thus, air masses which originated from the north and northwest were generally free from high aerosol concentrations. However, winds from the southwest had the potential to carry gases and particles from Hamilton, Ontario, Ontario Power Generation's Nanticoke
20 coal-fired power generation station, and the Ohio River Valley, into Toronto. Westerly winds were influenced by industries and power generating facilities in, or near, Detroit, Michigan and Sarnia, Ontario. Furthermore, agricultural activities located to the southwest and west of the city also contributed to measured pollutant gas and aerosol concentrations.

3.3.2 High time mass reconstruction

A high time resolution reconstruction of the $PM_{2.5}$ mass was created using inorganic and organic mass concentrations measured by the GPIC and Sunset Laboratory OCEC semi-continuous instruments. Each season was associated with a different signature of relative particulate concentrations dictated partially by temperature dependent chemistry. Fig. 8 compares variations in percent composition of inorganic and organic components of $PM_{2.5}$ mass for periods of elevated and reduced concentrations during different sampling periods: the entire sampling period (July 2006–March 2007, A), in the fall (October and November 2006, B) and winter (December 2006–March 2007, C) . Organic species dominated the $PM_{2.5}$ mass fraction when low $PM_{2.5}$ concentrations were measured, regardless of season. Furthermore, the percent mass contributed by organic species during the low $PM_{2.5}$ periods was the greatest during warmer months. Conversely, the percent contribution of pNO_3^- increased as temperature declined and during high $PM_{2.5}$ concentration periods.

Air mass geographic origin and meteorological parameters influenced resultant particulate concentrations. Large seasonal differences were observed, in particular for sulphate and nitrate, even though the seasonal variation in the emission rates from mobile and point sources was likely small. Southwestern winds typically brought elevated regional sulphate concentrations for all seasons. However, measured pSO_4^{2-} concentrations were higher during the summer as compared to the winter as the availability of OH and H_2O_2 for reaction with SO_2 increased during this season. Higher organic matter was measured during the summer and fall as compared to the winter. Summertime increases in biogenic emissions and photochemical activity allowed for enhanced volatile organic compound (VOC) reaction with OH, O_3 and NO_3 and consequently favoured the formation of secondary organic aerosols (SOA).

Stacked time series of inorganic particulates, elemental carbon and organic matter during October 2006 and January 2007 are shown in Figs. 9 and 10, respectively. These figures illustrate the rapid and extensive temporal variability that exists in the

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

mass and speciation of Toronto's fine particulate matter. During period of 18 October 2006 to 22 October 2006, three distinct air masses passed through Toronto resulting in large changes in $PM_{2.5}$ mass. Southwesterly winds first introduced a sulphate driven episode of elevated $PM_{2.5}$ which commenced on the morning of 18 October 2007 and lasted for approximately 24 h. A shift in winds midday on 19 October 2007 brought air from the north into Toronto producing a dramatic drop in $PM_{2.5}$ sulphate, nitrate and ammonium. This allowed local urban sourced pollutants to dominate measurements and resulted in reduced $PM_{2.5}$ concentrations as compared to air masses originating from southwest of the city. The third air mass, originating from east of the city, caused a nitrate dominated episode that started on the morning of 21 October 2007. It should be noted both sulphate and nitrate events contained approximately similar concentrations of ammonium and organics constituents. Owega et al. (2006) also observed the most significant difference in $PM_{2.5}$ aerosol mass occurred between air masses originating from the north/ northwest and south/southwest of Toronto.

The magnitude and frequency of pSO_4^{2-} episodes declined in the winter and pNO_3^- concentrations increased. This was attributed to the semi-volatile nature of ammonium nitrate, which should partition more extensively to the particle phase at low winter temperatures. Consistently elevated nitrate concentrations were observed during winter sampling months while the sulphate mass contribution varied depending on the geographic origin of the air mass. Similar to summer and fall measurements, winds from the southwest (17 January 2007 to 19 January 2007) were associated with higher sulphate concentrations than those from the other directions (13 January 2007 to 15 January 2007).

Episodes of high particulate concentrations resulting from long range transported air masses, independent of geographic origin or season, typically lasted for approximately two to three days. Particulate concentrations during these pollution periods were not continuously elevated, but instead exhibited a number of interwoven local minima and maxima values due to a series of separate plumes or fronts passing across the sampling site. Temperature driven diurnal variations, as described next, were also super-

imposed on top of the synoptic variability. A similar concentration variation was noted during the 2001 PMTACS-NY summer and winter sampling campaigns conducted in New York City (Weimer et al., 2006).

3.3.3 Seasonal diurnal variation

Hourly averaged GPIC HNO_3, pNO_3^-, NH_3 and pNH_4^+ concentrations are plotted as diurnal trends for the months of July 2006, October 2006 and January 2007 in Fig. 11. Measurements were subdivided into weekend and weekday categories and were conditioned to exclude outliers, defined as 1.5 times greater than the interquartile range of the monthly average of the measurements for the given time of day. Diurnal profiles were analyzed to better understand the influence of local and long range source contributions to the measured secondary aerosol species and their production pathways. Emissions, photochemical activity and the planetary boundary layer mixing height were parameters which affected diurnal patterns. Locally derived gas and particulate species would be expected to exhibit a distinct diurnal trend while long range transported pollutants would be more influenced by synoptic meteorology and therefore should not necessarily show a daily cycle.

No diurnal variation was observed for either pSO_4^{2-} or gaseous SO_2 as both these species did not predominantly originate from local urban emission sources. These results differ from other studies which reported SO_2 and pSO_4^{2-} fluctuations which were consistent with variations in the mixing height (Drewnick et al., 2004; Fisseha et al., 2006; Weimer et al., 2006). Long range transport, generally from sources west or southwest of the sampling site, governed the magnitude of SO_2 and sulphate concentrations observed in this urban environment. pNH_4^+ and pSO_4^{2-} diurnal trends were both insignificant in the summer. This was expected as the pNH_4^+ was mostly likely in the form of either $(NH_4)_2SO_4$ or NH_4HSO_4. Conversely, winter pNH_4^+ favoured nitrate association; thus diurnal variation of pNH_4^+ 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 (09:00 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 implied that NH_3 originated from a local source, possibly vehicle traffic since this maximum did not occur on weekends. Fur-
5 thermore, 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_4NO_3 as a result of the colder temperatures. The late after-noon rise in the NH_3 diurnal profile for January appears to coincide with a drop in pNO_3^- and pNH_4^+ concentrations suggesting the same NH_3 from the vehicles that condensed
10 in the morning subsequently evaporated once the temperature rose. Li et al. (2006) also noted similar wintertime diurnal ammonia trends in New York City using tunable diode laser absorption spectrometer measurements.

Although vehicle emissions appeared to influence the ammonia diurnal profile, agri-cultural fertilizer and livestock emissions also likely contributed to measured concen-
15 trations as monthly median NH_3 concentrations declined with temperature. This hy-pothesis 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–October) with that for the months of when no livestock or agricultural emissions were assumed present
20 (December 2006 to March 2007). Given total ammonium concentrations were signifi-cantly 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 ± 0.3 and $5.21\pm0.3\,\mu g\,m^{-3}$ respectively, agricultural and livestock source do po-tentially influence the total measured ammonium measurements in downtown Toronto.
25 On weekends, the traffic density passing the sampling site was reduced and thus the daytime rise in gaseous NH_3 was much weaker. 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

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

this primary gas emission was diluted during the day was 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
5　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 $N_2O_5 + H_2O$ reaction yielding pNO_3^- in the early morning hours provided sufficient NH_3 was present. As local vehicle sources
10　further emitted primary NO_x and NH_3 in the morning, more NH_4NO_3 may have been produced through oxidation of the NO_x to $HNO_{3(g)}$. As temperatures increased throughout the day, $HNO_{3(g)}$ 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
15　advection.

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 $PM_{2.5}$
20　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 was noted in Zurich, Switzerland (Fisseha et al., 2006).

4　Conclusions

Comparison of the GPIC results with other parallel measurements revealed excellent
25　temporal agreement demonstrating the potential of this technique. However, numerous challenges were encountered in the continuous operation of the GPIC producing systematic errors in accuracy. Many of the underlying causes were identified and resolved

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

but only after many months of sampling. Application of monthly and seasonal calibration factors to particle and gas species concentrations, respectively, provided accurate data while maintaining the high time resolution of the GPIC measurements.

A difference between TEOM and NAPS Dichot filter measured PM$_{2.5}$ mass concentrations was identified, in particular during the winter. The difference between the two measurement techniques was attributed to partial volatilization of nitrate in the TEOM's heated inlet air stream. Variation was normalized by calibrating the TEOM concentration to the NAPS Dichot filter data. Comparison of the calibrated TEOM data with reconstructed GPIC and Sunset Laboratory OCEC PM$_{2.5}$ mass concentrations exhibited excellent correlation.

Co-located inter-instrument comparison between the GPIC and API Fluorescent SO$_2$ Gas Analyzer showed an overall good correlation between the two measurement techniques ($r=0.87$); calibration challenges with the API SO$_2$ Analyzer likely contributed to an observed offset. Comparison of the GPIC with a co-located R&P 8400N Nitrate Analyzer ($r=0.86$) and Aerodyne C-ToF-AMS ($r\geq0.86$) showed overall good correlation between the measurement techniques.

High time resolution PM$_{2.5}$ mass reconstruction was possible via the GPIC and Sunset Laboratory OCEC measurements. This enabled rapid PM$_{2.5}$ inorganic and organic species and precursor gases fluctuations to be characterized within and between seasons.

The strongest diurnal HNO$_3$ and pNO$_3^-$ partitioning was observed during the summer: nighttime pNO$_3^-$ formation and morning rush hour derived PM nitrate was converted to nitric acid gas midday as daily temperatures peaked. In the winter, low temperatures and high relative humidity induced gaseous HNO$_3$ and NH$_3$ condensation yielding NH$_4$NO$_3$ aerosol. Consequently, the fraction of total nitrate (TNO$_3$ = HNO$_3$ + pNO$_3^-$) in gaseous form was the lowest during the winter months.

Ammonia and particulate ammonium (pNH$_4^+$) also demonstrated seasonal diurnal differences. During the summer, NH$_3$ exhibited a morning rush hour maxima on weekdays. The progression from summer to winter shifted the morning maxima to an af-

ternoon/evening diurnal peak and the overall magnitude of the NH_3 concentrations also decreased. Ammonium only demonstrated diurnal variation in the winter. pNH_4^+ and pSO_4^{2-} both showed little diurnal variation in the summer; these trends were coupled as the measured pNH_4^+ was mostly associated with pSO_4^{2-}, in the form of either $(NH_4)_2SO_4$ or NH_4HSO_4. Conversely, winter pNH_4^+ favoured nitrate association; thus a diurnal variation in pNH_4^+ was only observed during the winter.

References

Allen, G., Sioutas, C., Kourtakis, 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 Manage. Assoc., 47(6), 682–689, 1997.

Al Horr, R., Samanta, G., and Dasgupta, P. K.: A continuous analyzer for soluble anionic constituents and ammonium in atmospheric particulate matter, Environ. Sci. Technol., 37, 5711–5720, 2003.

Ayers, G. P., Keywood, M. D., and Gras, J. L.: TEOM vs. manual gravimetric methods for determination of $PM_{2.5}$ aerosol mass concentrations, Atmos. Environ., 33, 3717–3721, 1999.

Boring, C. B., Al-Horr, R., Genfa, Z., and Dasgupta, P. K.: Field measurements of acid gases and soluble anions in atmospheric particulate matter using a parallel plate wet denuder and an alternating filter-based automated analysis system, Anal. Chem., 74, 1256–1268, 2002.

Brook, J. R., Dann, T. F., and Burnett, R. T.: The relationship among TSP, PM_{10}, $PM_{2.5}$, and inorganic constituents of atmospheric particulate matter at multiple Canadian locations, J. Air Waste Manage. Assoc., 49, PM35–PM44, 1997.

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Brook, J. R., Dann, T. F., and Bonvalot, Y.: Observations and interpretations from the Canadian fine particle monitoring program, J. Air Waste Mange. Assoc., 49, 35–44, 1999a.

Brook, J. R. and Dann, T. F.: Contribution of Nitrate and Carbonaceous Species to $PM_{2.5}$ Observed in Canadian Cities, J. Air Waste Manage. Assoc., 49, 193–199, 1999b.

5 Charron, A., Harrison, R. M., Moorcroft, S., and Booker, J.: Quantitative interpretation of divergence between PM_{10} and $PM_{2.5}$ mass measurements by TEOM and gravimetric (Partisol) instruments, Atmos. Environ., 38(3), 415–423, 2004.

Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH Carbon Measurements, Aerosol Sci. Technol., 34, 23–34, 2001.

10 Chow, J. C., Watson, J. G., Chen, L.-W. A., Paredes-Miranda, G., Chang, M.-C. O., Trimble, D., Fung, K. K., Zhang, H., and Zhen Yu, J.: Refining temperature measures in thermal/optical carbon analysis, Atmos. Chem. Phys., 5, 2961–2972, 2005, http://www.atmos-chem-phys.net/5/2961/2005/.

Dockery, D. W., Pope, C. A., Xu, X. P., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., and

15 Speizer, F. E.: An association between air pollution and mortality in 6 United States cities, N. Engl. J. Med., 329, 1753–1759, 1993.

Drewnick, F., Hings, S. S., DeCarlo, P., Jayne, J. T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J. L., Demerjian, K. T., Borrmann, S., and Worsnop, D. R.: A New Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS) – Instrument Description and First Field Deployment, Aerosol

20 Sci. Technol., 39, 637–658, 2005.

Driscoll, C. T., Driscoll, K. M., Roy, K. M., and Mitchell, M. J.: Chemical responses of lakes in the Adirondack region of New York to declines in acidic deposition, Environ. Sci. Technol., 37, 2036–2042, 2003.

Fischer, E., Pszenny, A., Keene, W., Maben, J., Smith, A., Stohl, A., and Talbot, R.: Nitric acid

25 phase partitioning and cycling in the New England coastal atmosphere, J. Geophys. Res., 111, D23S09, doi:10.1029/2006JD007328, 2006.

Fisseha, R., Dommen, J., Gutzwiller, L., Weingartner, E., Gysel, M., Emmenegger, C., Kalberer, M., and Baltensperger, U.: Seasonal and diurnal characteristics of water soluble inorganic compounds in the gas and aerosol phase in the Zurich area, Atmos. Chem. Phys., 6, 1895–

30 1904, 2006, http://www.atmos-chem-phys.net/6/1895/2006/.

Grover, B. D., Eatough, N. L., Eatough, D. J., Chow, J. C., Watson, J. G., Ambs, J. L., Meyer, M. B., Hopke, P. K., Al-Horr, R., Later, D. W., and Wilson, W. E.: Measurement of both

Evaluation of a $PM_{2.5}$ chemical characterization system

K. J. Godri et al.

nonvolatile and semi-volatile fractions of fine particulate matter in Fresno, CA, Aerosol Sci. Technol., 40, 811–826, 2006.

Harrison, D., Park, S. S., Ondov, J., Buckley, T., Kim, S. R., and Jayanty, R. K. M.: Highly time resolved fine particulate nitrate measurements at the Baltimore Supersite, Atmos. Environ., 38, 5321–5332, 2004.

Harrison, R. M., Jones, A. M., and Lawrence, R. G.: A pragmatic mass closure model for airbourne particulate matter at urban background and roadside sites, Atmos. Environ., 37, 4927–2933, 2003.

Herring, S. V., Lawson, D. R., Allegrini, I., Febo, A., Perrino, C., Possanzini, M., Sickles II, J. E., Anlauf, K. G., Wiebe, A., Appel, B. R., John, W., Ondo, J., Braman, R. S., Sutton, R., Cass, G. R., Solomon, P. A., Eatough, D. J., Eatough, N. L., Ellis, E. C., Grosjean, D., Hicks, B. B., Womach, J. D., Horrocks, J., and Knapp, K. T.: The nitric acid shootout: field comparison of measurement methods, Atmos. Environ., 22, 1519–1539, 1988.

Hoek, G., Brunekreef, B., Goldbohm, S., Fischer, P., and van der Brandt, P.: Association between mortality and indicators of traffic related air pollution in the Netherlands: a cohort study, Lancet, 360, 1203–1209, 2002.

Hogrefe O., Schwab, J., Drewnick, F., Rhoads, K., Lala, G. G., Felton, H. D., Rattigan, O. V., Husain, L., Dutkiewicz, V. A., Peters, S., and Demerjian, K. L.: Semi-Continuous PM2.5 Sulfate and Nitrate Measurements at an Urban and a Rural Location in New York: PMTACS-NY Summer 2001 and 2002 Campaigns, J. Air Waste Manage. Assoc., 54, 1040–1060, 2004.

Huang, G., Zhou, X., Deng, G., Qiao, H., and Civerolo, K.: Measurements of atmospheric nitrous acid and nitric acid, Atmos. Environ., 36, 2225–2235, 2002.

Li, Y., Schwab, J. J., and Demerjian, K. L.: Measurements of ambient ammonia using a tunable diode laser absorption spectrometer: Characteristics of ambient ammonia emissions in an urban area of New York City, J. Geophys. Res., 111, D10S02, doi:10.1029/2005JD006275, 2006.

Lin, Y.-C., Cheng, M.-T., Ting, W.-Y., and Yeh, C.-R.: Characteristics of gaseous HNO_2, HNO_3, NH_3 and particulate ammonium nitrate in an urban city of Central Taiwan, Atmos. Environ., 40, 4725–4733, 2006.

Long, R. W. and McClenny, W. A.: Laboratory and field evaluation of instrumentation for the semicontinuous determination of particulate nitrate (and other water-soluble particulate components), J. Air Waste Manag. Assoc., 56, 294–305, 2006.

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Mignacca, D. and Stubbs, K.: Effects of Equilibration temperature on PM_{10} Concentrations from the TEOM Method in the Lower Fraser Valley, J. Air Waste Manage. Assoc., 49, 1250–1254, 1999.

Morino Y., Kondo, Y., Takegawa, N., Miyazaki, Y., Kita, K., Komazaki, Y., Fukuda, M., Miyakawa, T., Moteki, N., and Worsnop, D. R.: Partitioning of HNO_3 and particulate nitrate over Tokyo: Effect of vertical mixing, J. Geophys. Res., 111, D15215, doi:10.1029/2005JD006887, 2006.

Owega, S., Zaman, B. U., Evans, G. J., Jervis, R. E., and Fila, M.: Identification of long-range aerosol transport patterns to Toronto via classification of back trajectories by cluster analysis and neural network techniques, Chemometrics Intel. Lab. Sys., 83, 26–33, 2006.

Patashnick, H. and Rupprecht, E. G.: Continuous PM_{10} measurements using the tapered element oscillating microbalance, J. Air Waste Manage. Assoc., 41, 1079–1983, 1991.

Pope, C. A., Thun, M. J., Namboodiri, M. N., Dockery, D. W., Evans, J. S., Speizer, F. E., and Heath, C. W.: Particulate air pollution as a predictor of mortality in a prospective study of U.S. adults, Am. J. Respir. Crit. Care Med., 151, 669–674, 1995.

Pope, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewshi, D., Ito, K., and Thurston, G. D.: Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, J. Am. Med. Assoc., 287, 1132–1141, 2002.

Rattigan, O., Hogrefe, O., Felton, H.D., Schwab, J. J., Roychowdhury, U. K., Husain, L., Dutkiewicz, V. A., and Demerjian, K. L.: Multi-year urban and rural semi-continous PM2.5 sulphate and nitrate measurements in New York state: Evaluation and comparison with filter based measurements, Atmos. Environ., 40, S192–S205, 2006.

Schindler, D. W.: Effects of acid-rain on fresh-water ecosystems, Science, 239, 149–157, 1988.

Stolzenburg, M. R. and Hering, S. V.: A new method for the automated measurement of atmospheric fine particulate nitrate, Environ. Sci. Technol., 34, 907–914, 2000.

Tsai, J.: Chemical composition and source apportionment of Toronto summertime urban fine aerosol ($PM_{2.5}$), M.A.Sc. thesis, University of Toronto, Toronto, 2002.

Ullah, S. M. R., Takeuchi, M., and Dasgupta, P. K.: Versatile Gas/Particle Ion Chromatograph, Environ. Sci. Technol., 40, 962–968, 2006.

Watson, J. G.: Visibility: Science and Regulation, J. Air Waste Manage., 52, 628–713, 2002.

Weimer, S., Drewnick, F., Hogrefe, O., Schwab, J. J., Rhoads, K., Orsini, D., Canagaratna, M., Worsnop D. R., and Demerjian, K. L.: Size-selective nonrefractory ambient aerosol measurements during the Particulate Matter Technology Assessment and Characterization Study – New York 2004 Winter Intensive in New York City, J. Geophys. Res., 111, D18305,

Evaluation of a $PM_{2.5}$ chemical characterization system

K. J. Godri et al.

Printer-friendly Version

Interactive Discussion

doi:10.1029/2006JD007215, 2006.

Wittig, A. E., Takahama, S., Khlystov, A. Y., Pandis, S. N., Hering, S., Kirby, B., and Davidson, C.: Semi-continuous PM$_{2.5}$ inorganic composition measurements during the Pittsburg Air Quality Study, Atmos. Environ., 38, 3201–3213, 2004.

5 Yao, X., Shairsingh, K., Lam, P. H., and Evans, G. J.: Underestimation of sulfate concentration in PM$_{2.5}$ using a semi-continuous particle instrument based on ion chromatography, J. Environ. Monit., submitted, November 2008.

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.

Table 1. Mean monthly temperatures and Gage TEOM concentrations presented in conjunction with the percentage of volatile species in the reconstructed PM$_{2.5}$ mass by the GPIC and Sunset OCEC measurements in the Wallberg Building (WB).

	% Volatile Species of WB PM$_{2.5}$ Mass (±SD)	Mean Temp (°C) (min, max)	Mean Gage TEOM (μg m^{-3}) (min, max)
July 2006	4.6±3.6	23.7 (13.7, 34.1)	14.1 (0.1, 60.4)
October 2006	28±13	9.8 (1.9, 23.7)	5.3 (0, 38.3)
November 2006	39±13	6.5 (−0.2, 15.2)	8.3 (0, 40.5)
December 2006	51±17	3 (−10.9, 14)	5.2 (0, 19.4)
January 2007	47±15	−1.5 (−15.9, 11.8)	4.7 (0, 67.7)
February 2007	55±16	−6.5 (−17.8, 6.2)	5.8 (0.1, 21.9)
March 2007	50±13	1.7 (−20.6, 16.7)	6.3 (0.1, 66.5)

SD: Standard Deviation

Table 2. Intercomparison of studies between GPIC, Particle Into Liquid Samples (PILS), and Partisol 24 h Filter nitrate measurement instruments against the R&P 8400N Nitrate Analyzer at rural and urban centres in the United States. All presented slopes have units of $(\mu g\, m^{-3})_{R\&P\,8400N}/(\mu g\, m^{-3})_{Other\,Instrument}$.

	Site	Slope	Intercept	Pearson r Value	N	Min, Max ($\mu g\, m^{-3}$)	Sampling Period	Time Resolution
Hogrefe et al., 2004								
8400 vs. PILS	Whiteface Mountain, NY	0.49	0.13	0.81	16	0.1, 0.5	July 2002–August 2002	1 h
8400 vs. PILS	Queens, NY	0.57	0.18	0.95	285	0.2, 8.4	July 2001–August 2001	1 h
Rattigan et al., 2006								
8400 vs. Partisol Filter pNO$_3^-$	Whiteface Mountain, NY	0.73	0.01	0.95	~240	0.2, 2.7	July 2002–July 2005	24 h
8400 vs. Partisol Filter pNO$_3^-$	South Bronx, NY	0.59	0.28	0.94	~240	0.2, 13.5	July 2002–July 2005	24 h
Wittig et al., 2004								
8400 vs. Partisol Filter pNO$_3^-$	Pittsburg, PA	0.83	0.2	0.92	~240	0.2, 6	July 2001–March 2002	24 h
Grover et al., 2006								
8400 vs. GPIC	Fresno, CA	0.55	1.4	0.87	493	0.1, 25	December 2003	15 min
Long and McClenny, 2006								
8400 vs. GPIC	Rubidoux, CA	0.78	0.8	0.93	480	0.1, 24	July 2003	15 min

N: Sample Size

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀◀ | ▶▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 3. Summary of 15 min averaged regressions and recoveries (no intercept assumed) of calibrated GPIC particulate measurements with corresponding C-ToF-AMS results for the period of 22 January to 4 February 2007. All calculated slopes have units of $(\mu g\,m^{-3})_{AMS}/(\mu g\,m^{-3})_{GPIC}$.

	Slope ($\pm CI$)	Intercept ($\mu g\,m^{-3}$) ($\pm CI$)	Pearson r value ($\pm SE$)	C-ToF-AMS/GPIC Recovery ($\pm CI$)	N
Sulphate	0.54±0.03	0.11±0.06	0.92±0.28	0.58±0.01	1250
Nitrate	0.52±0.03	0.31±0.13	0.92±0.71	0.57±0.02	1239
Ammonium	0.46±0.04	0.69±0.08	0.86±0.38	0.7±0.04	891

CI: 95% Confidence Interval;
SE: Standard Error;
N: Sample Size
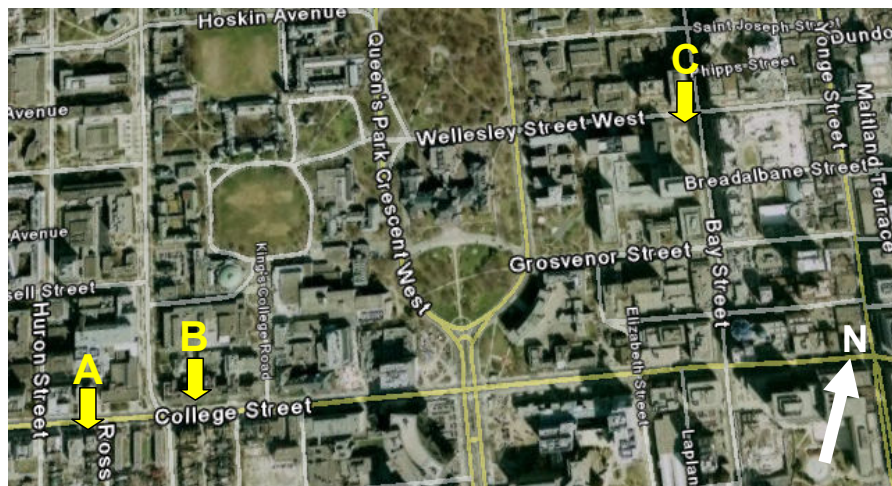
Fig. 1. Detailed map of downtown Toronto highlighting the Gage Building sampling location **(A)**, the Wallberg Building site **(B)**, and the MoE downtown sampling location **(C)**.

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.
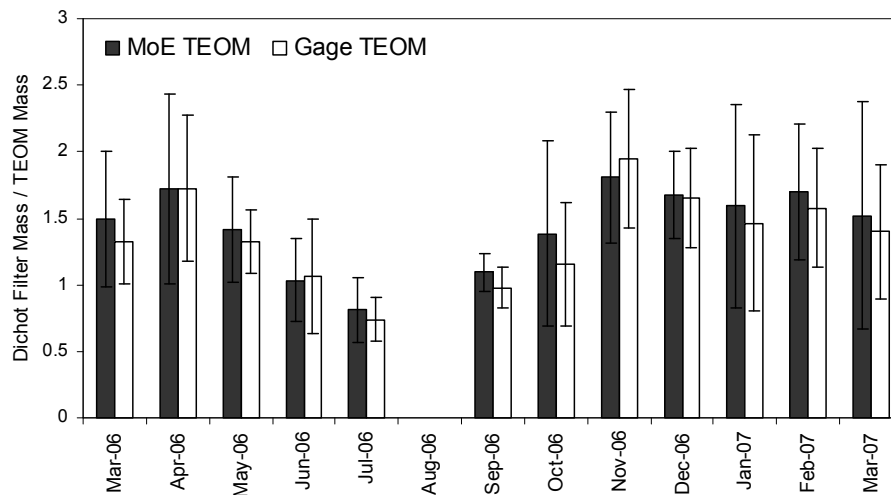
Fig. 2. Ratio of mass concentration as measured by the NAPS Dichot Filter to the TEOM for both the downtown Ministry of the Environment and Gage Building sampling sites. Standard deviation for each TEOM ratio is indicated by the error bars.
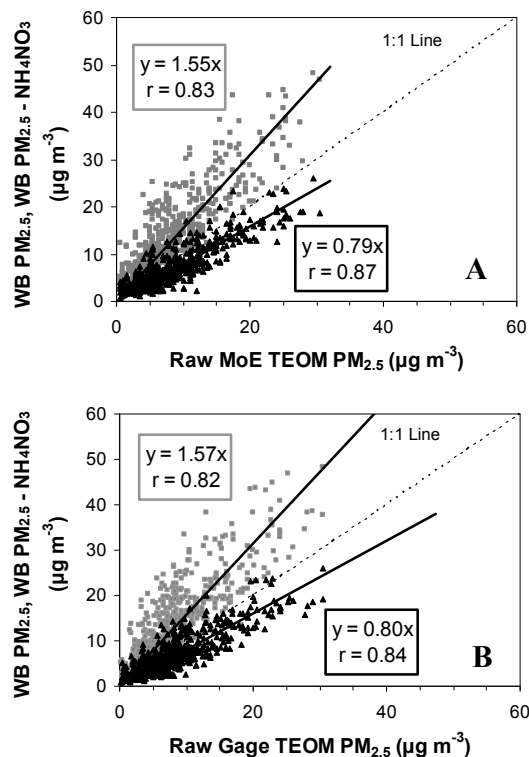
Fig. 3. November 2006 to March 2007, 2 h resolution least square regressions between raw Ministry of the Environment (MoE) **(A)** and Gage Building **(B)** TEOM measurements and reconstructed PM$_{2.5}$ mass (grey squares) and reconstructed PM$_{2.5}$ mass minus the NH4NO3 mass (black triangles) as measured by the GPIC and OCEC at the Wallberg Building (A and B). (N=566)
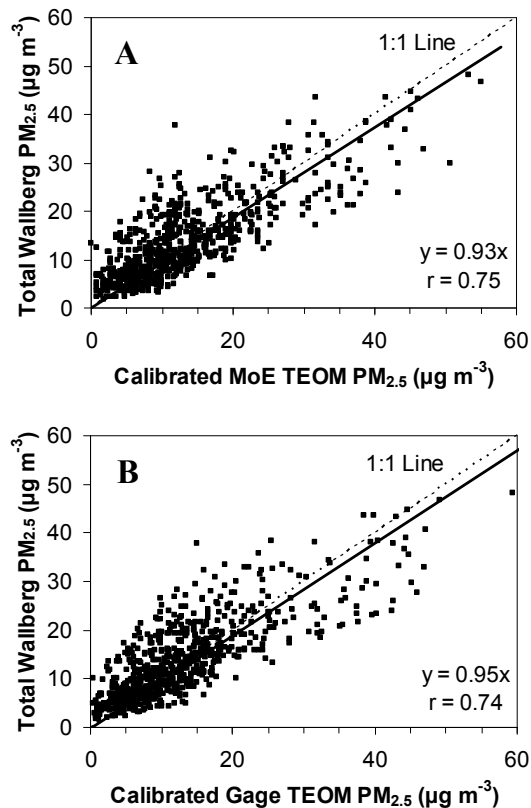
Fig. 4. Comparative analysis of the reconstructed PM$_{2.5}$ mass as measured by the GPIC and OCEC instruments in the Wallberg Building to the Ministry of the Environment (MoE) **(A)** and Gage Building **(B)** TEOMs for the entire study period: July 2006 to March 2007. (*N*=722)
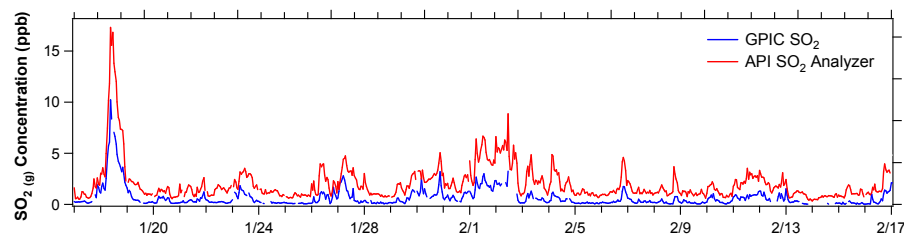
Fig. 5. Semi-continuous, 1 h resolution, SO$_2$ gas concentrations measured by the GPIC and API Fluorescent SO$_2$ Analyzer for the period of 17 January to 17 February 2007.
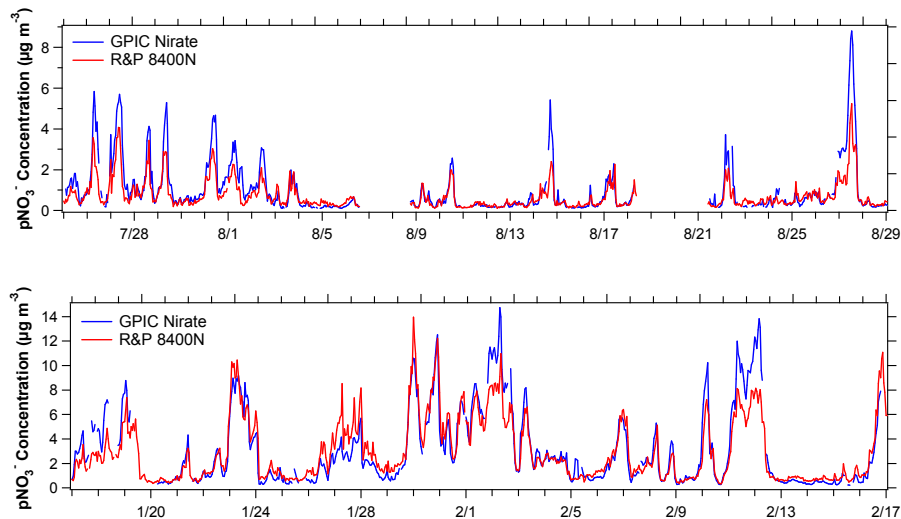
Fig. 6. Semi-continuous, 1 h resolution, PM$_{2.5}$ particulate nitrate concentrations measured by the GPIC and R&P 8400N Nitrate Analyzer for the period of 25 July to 29 August 2006 **(A)** and 17 January to 17 February 2007 **(B)**.

Evaluation of a PM$_{2.5}$ chemical characterization system

K. J. Godri et al.
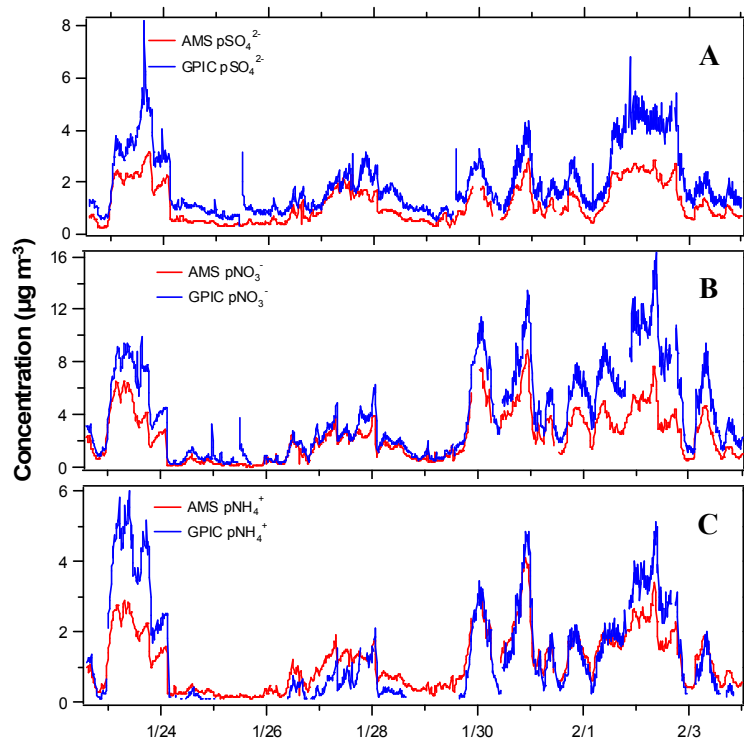
Fig. 7. Semi-continuous, 15 min resolution, GPIC PM$_{2.5}$ and PM$_{1.0}$ C-ToF-AMS measurements during the period of 22 January to 4 February 2007 for particulate sulphate **(A)**, nitrate **(B)** and ammonium **(C)**.
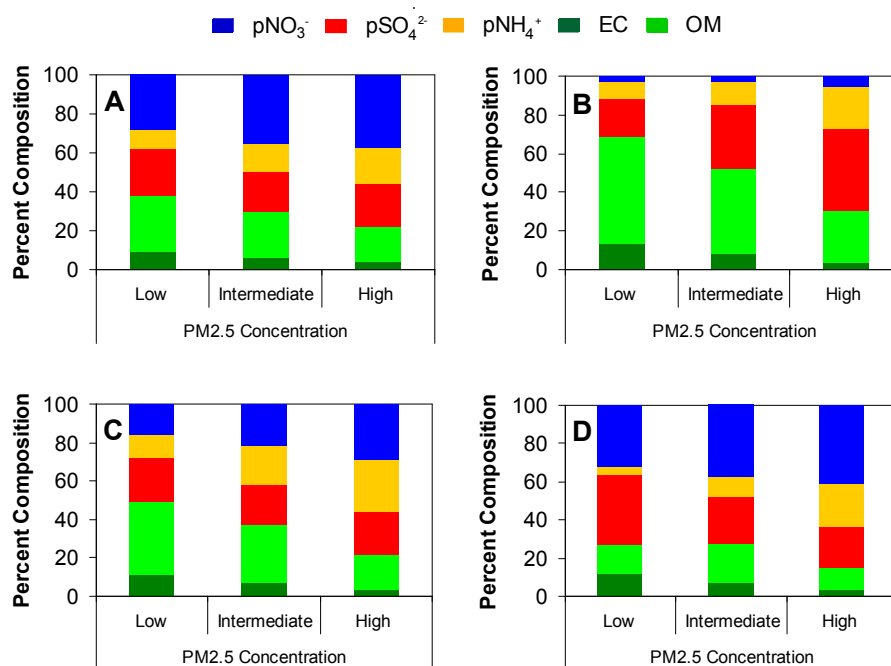
Fig. 8. Stacked percent composition of PM$_{2.5}$ subdivided by concentration shown for the entire sampling campaign, June 2006–March 2007 **(A)**, July 2006 **(B)**, October 2006 **(C)** and January 2007 **(D)**. Concentration regimes are defined as low PM$_{2.5}$ ($x < \bar{x} - \sigma$), intermediate PM$_{2.5}$ ($\bar{x} - \sigma < x < \bar{x} + \sigma$) and high PM$_{2.5}$ ($x > \bar{x} + \sigma$). Organic matter was calculated as 1.4 times organic carbon concentrations.
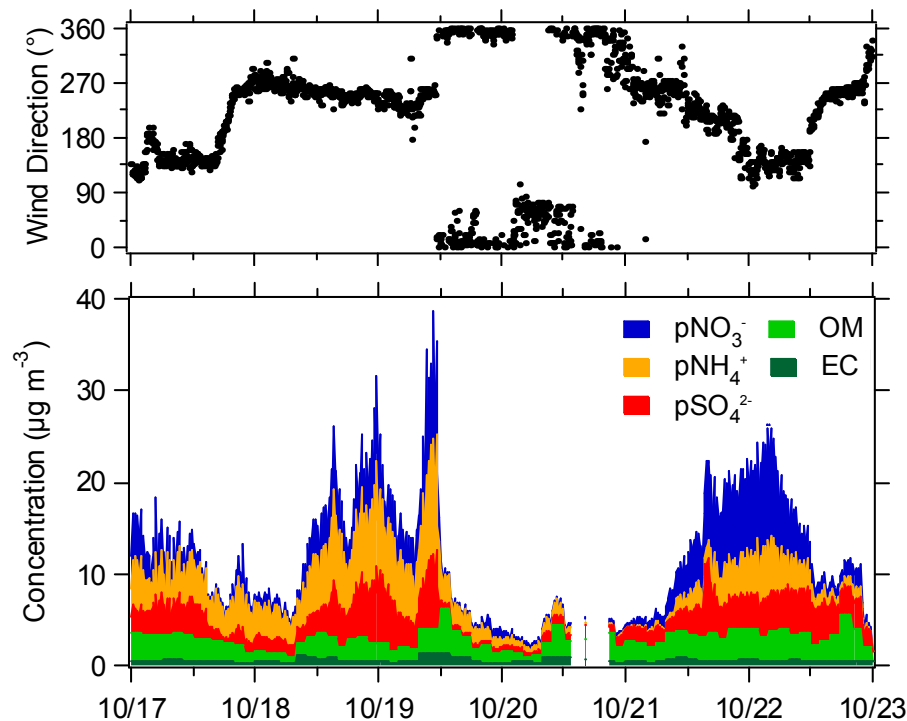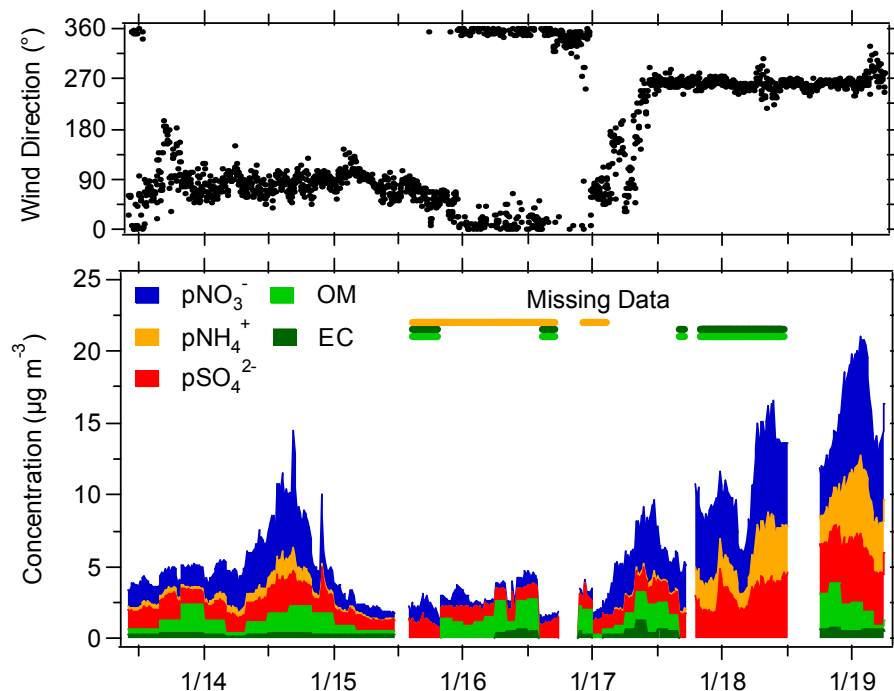
Fig. 9. Stacked fifteen minute resolution inorganic particulate concentrations and two hour resolution organic matter and elemental carbon concentrations as measured during October 2006 presented associated five minute averaged temporal wind direction. Organic matter was calculated as 1.4 times organic carbon concentrations.

Fig. 10. Stacked fifteen minute resolution inorganic particulate concentrations and two hour resolution organic matter and elemental carbon concentrations as measured during January 2007 presented associated five minute averaged temporal wind direction. Organic matter was calculated as 1.4 times organic carbon concentrations. Periods of missing data for specific species (organic matter, elemental carbon, and particulate ammonium) are indicated with horizontal bars along the upper axis.
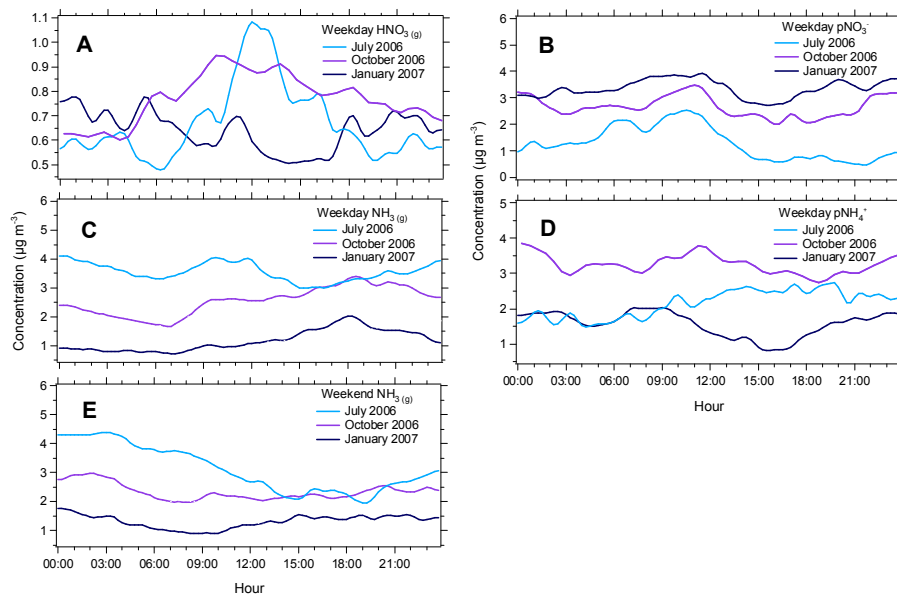
Fig. 11. Weekday and weekend hourly averages for July 2006, October 2006, and January 2007: weekday HNO$_{3(g)}$ **(A)**, weekday particulate nitrate **(B)**, weekday NH$_{3(g)}$ **(C)**, weekday particulate ammonium **(D)**, and weekend NH$_{3(g)}$ **(E)** observations.