

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.

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The authors thank the reviewer for comments. Point-to-point responses are included below highlighted in italics.

Anonymous Referee 2 Received and published: 29 November 2008

Referee Comment

This is a well-written paper that describes a long-term ambient monitoring study conducted in Toronto, Canada during 2006 and 2007. The goals of the paper seem to be to provide information about the sources and atmospheric transport that are rele-

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vant to Toronto and to provide in-field validation of the Dionex Gas Particle Ion Chromatography (GPIC) system by comparison to other instruments. This type of work is useful in the validation of relatively new instruments and represents the most difficult and discerning type of test. Unfortunately, this paper leaves some room for concern about the quantitative accuracy of the GPIC, so conclusions in that regard appear to be premature. Results pertaining to the temperature dependent partitioning of nitrate and ammonium nitrate from the particle to gas phase appear to be in agreement with other field studies. Variable mixtures of locally produced (including agricultural) and long-range transported PM were observed in downtown Toronto during the study.

Specific Concerns: It is odd that the NH₃ and SO₂ measurements by the gas phase portion of the GPIC instrument were systematically high (vs. the denuder) during the period when lab air was leaking into the system. Does this imply (as it appears to) that the GPIC has an even more substantial positive bias than it appears to? The fact that the API SO₂ instrument shows better agreement with the GPIC should probably be examined more fully, perhaps there were problems with the denuder system? It is not clear that the comparison is fair though, given the known problem with the GPIC inlet. The fact that the same sampling system underpredicts nitric acid gives little confidence in the quantitative accuracy of this part of the GPIC system. Since the major purported strength of the GPIC is that it can measure related particle and gas phase components, this appears to an issue that should be addressed in an instrument validation.

The authors agree with Referee 2 about GPIC gas measurements; the problems encountered do reduce confidence in the reported GPIC gas phase measurements. This will be discussed in further detail in a follow-up manuscript which will include an inter-instrument comparison study.

In a similar vein to the comment above, if the 8220; correction factor⁸²²¹; between the GPIC particle species and the ancillary measurements was adjusted on a monthly basis, can this be regarded as an absolute measurement? It would be comforting (if true) to note that the size and variability in the correction factor decreased during the

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study as the sampling line leakage and loop and other measurement problems were addressed.

Given that the issue of the proper calibration standard (e.g., denuder vs. API, etc.) appears to be open, the most honest presentation of the time-series data would seem to be a straight presentation of the raw GPIC and other measurements. Another alternative would be to present the evolving calibration factors, but that would probably be more difficult for the reader to interpret.

The evolving size and variability in the correction factors during the sampling campaign are available (Godri, 2008). Sampling line leakage and the negative artefact resulting in GPIC concentration results due to the calibration loop volume were only addressed after the completion of this study (Yao et al., 2008).

The lack of a diurnal dependence in the sulfate and sulfur dioxide concentrations is only partially explained by invoking long-range transport. As the authors note, the dependence of the particulate sulfate concentration on the mixing layer height, especially in an urban core, generally produces a diurnal pattern, even in the absence of diurnally varying local sources. This should be discussed with greater clarity.

The authors take note of Referee 2's comment with respect to sulphate and SO₂ diurnal variation. A modification has been made to the text:

Section 3.3.3, Paragraph 2 (Page 226): *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, disagree-*

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ment 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.

The interplay between the agricultural and vehicular sources of ammonia/ammonium is one of the more interesting aspects of the local emissions/transport situation and probably deserves further study.

Now that ammonium and ammonia measurements have been resolved, the authors intend to conduct a study which further investigates the interplay between the agricultural and vehicle sources measured at this Toronto sampling site.

Overall, this is a well-written paper with few typographical errors. It presents a large amount of data that can be useful in analyzing the trends in PM sources and transport in Toronto. The conclusions regarding the reliability of the GPIC instrument appear to be slightly overstated in my opinion. There still appears to be some room for exploration of the possible sources of error in and the absolute accuracy attainable with the particle and (perhaps more seriously with the) gas-phase concentrations determined by the GPIC.

The strength of the conclusions commenting on the reliability of the GPIC has been toned down to read:

Page 228, Line 24: *Comparison of the GPIC with other parallel measurements revealed good temporal agreement demonstrating the potential of this technique.*

Page 229 Line 2: *Application of monthly and seasonal correction factors to particle species concentrations, respectively, provided reasonably accurate data while maintaining the high time resolution of the GPIC measurements. Applying similar correction to the gas species data was less successful in resolving disagreement between different instruments.*

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 205, 2008.

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