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Atmospheric Measurement Techniques Discussions

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.

Anonymous Referee #2

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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 relevant 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.

In a similar vein to the comment above, if the “correction factor” 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 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.

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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 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.

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.

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