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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds" *by* I. C. Rumsey et al.

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Response to Referee 2:

We wish to thank the reviewer for their careful and thoughtful review of our manuscript. Our response to the reviewer's questions and recommendations is as follows:

Comment 1: In general, the manuscript is well written with logical flow of information. The key findings from the present assessment should contribute significantly to the

development of routine instruments for the monitoring of important parameters that are critical for the understanding of atmospheric processes, long-term air quality trends, and evidence-base policy formulation.

Response: Thank you.

Comment 2: Nevertheless, the limitation in scope of the assessment, including the limited study period (from 8 September-8 October 2010), limited and low concentration ranges of monitored soluble ions during the monitoring period, tests conducted in only one site, should also be highlighted.

Response: We acknowledge that the measured ambient concentrations are low in comparison to some areas of Europe and Asia and therefore can be considered as a limitation of the study. A sentence has been added to the end of the conclusion stating the limitation and also that our future work will help address this limitation.

We disagree that the study is conducted over a limited study period. We believe that a 30-day sampling period with rigorous quality assurance/quality control procedures is appropriate for the instrument evaluation.

Comment 3: RE: sampling site and scheme (lines 15 to 20, page 25072), it would help the readers to get a sense of the nature and characteristics of the AIRS site by providing a location map.

Response: Thank you for your suggestion. We have added maps of the location and surrounding area of the sampling site to the supplementary section as well as adding a description of the nature and characteristics of the AIRS site to the manuscript.

Comment 4: Lines 20-21, page 25072, "... The horizontal distance between the MU inlets and the denuder/filter packs was less than 2 m."... Exactly what was the distance between the MU inlets and the denuder/filter packs? Any potential interference as a result of the sample inlets being too close?

Response: Thank you. The distance between individual MARGA and denuder/filter

pack inlets ranged from 0.7 m to 2.9 m with an average distance of 1.9 m. For clarification, we have replaced the relevant sentence with this information.

We did not observe any indication of potential interference as a result of the sample inlets being too close.

Comment 5: Lines 8-9, page 25073; line 5, page 25075, I don't understand why an inlet with aerodynamic particle cutoff of 26 um was fitted with the MARGA system while the filter pack system was fitted with a particle size cutoff of 2.5 um. Any scientific or operational reasons behind this arrangement? More elaboration, clarification, and justification are needed.

Response: At the time of the comparison, the intended use of the MARGA was ultimately to augment measurements at select U.S. Clean Air Status and Trends Network (CASTNet) sites, which currently employ a weekly integrated filter pack approach to measure SO2, SO42-, HNO3, NO3-, and NH4+. Because the CASTNet filter pack measurements are used to calculate total deposition using a multi-layer inferential model, there is no particle size selection. A large particle size cutoff was chosen for the original MARGA inlet design to approximate the particle sampling characteristics of the CASTNet open-face filter pack measurement. During the intercomparison of the MARGA to the denuder/filter pack system, we chose to use the standard 2.5 um cutoff PM inlet for the filter pack and the original MARGA inlet (26 um). We knew that the difference in inlet sampling characteristics would not affect the comparison of ammonium sulfate and ammonium nitrate aerosol, which exist in the fine mode. However, we incorrectly assumed that the contribution of coarse nitrate to total nitrate would be small. Ultimately, the contribution of coarse nitrate, which was not measured by the filter pack, was significant and therefore caused substantial disagreement between the MARGA and filter pack NO3- results.

Comment 6: Lines 1 to 19, page 25075 under denuder/filter pack system, any idea about the collection efficiency of the denuder/filter pack system? Any spiking or evalu-

ation perform on this system before?

Response: Based on the widespread use of the annular denuder/filter pack system and its thorough characterization in the peer reviewed literature, it was viewed as a reference method in this study. Subsequently, there were no spiking or other performance characteristics evaluated during its comparison to the MARGA. Relevant articles describing the collection efficiency of annular denuders and filters for the gases and aerosols sampled in this study include:

Koutrakis, P., Wolfson, J.M., Slater, J.L., Brauer, M., Spengler, J.D., Stevens, R.K., and Stone, C.L. 1988. Evaluation of an annular denuder/filter pack system to collect acidic gases and aerosols. Environmental Science and Technology, 22, 1463-1468.

Allegrini, I., Desantis, F., Dipalp, V., Febo, A., Perrino, C., Possanzini, M., and Liberti, A. 1987. Annular denuder method for sampling reactive gases and aerosols in the atmosphere. The Science of the Total Environment, 67. 1-16.

Perrino, C., and Gherardi, M. 1999. Optimization of the coating layer for the measurement of ammonia by diffusion denuders. Atmospheric Environment, 33, 4579-4587.

John, W., and Reischl, G. 1978. Measurements of the filtration efficiencies of selected filter types. Atmospheric Environment, 12, 2015–2019.

Appel, B.R., Wall, S.M., Tokiwa, Y., and Haik, M. 1980. Simultaneous nitric acid, particulate nitrate and acidity measurements in ambient air. Atmospheric Environment, 14, 549.

Denuder collection efficiencies for the gases included in the comparison to the MARGA are >99%. Collection efficiency of the Teflon filter for aerosols and backup nylon filter for HNO3 volatilized from the primary Teflon filter are also near 100%. While spike tests were not performed on the annular denuder/filter pack systems, standard quality assurance procedures that were followed include periodic measurements of the sampling flow rate using a NIST traceable standard, the use of trip (field) blanks, the use of

analytical blanks and calibration standards, and duplicate analysis of individual samples.

Comment 7: Lines 22 to 24, page 25082; Lines 8-9, page 25073; line 5, page 25075, . . .As mentioned in Sec 2.2, the filter pack had a particle size cut-off of 2.5 um aerodynamic diameter, whereas the MARGA customized inlet had a cut-off of 6 um.". . .. This is very confusing. Was the MARGA unite fitted with a 26 um inlet or 6 um inlet should be clarified. Hope this is not just a typo error.

Response: The MARGA customized inlet had a cut-off of 26 um. This has been corrected in the manuscript.

Comment 8: Line 5, page 25088. '. . .Because of the larger particle cut-off (-26 ug) used in the present study. . .' 26 ug should read 26 um.

Response: Thank you. The correction has been made to the manuscript.

Comment 9: Line 25, page 25093, How would the proposed "bacterial consumption event" be handled in routine monitoring operation and data processing work? Bearing in mind that the present study was performed by a team of experts comprising personnel from USEPA and Metrohm Applikon.

Response: It is not known what factors cause 'bacterial consumption events' in MARGA systems. In ongoing field studies in North Carolina, U.S.A., 'bacterial consumption events' have occurred on average 2-3 times a year. In this study (particle size selection 26 μm) and in ongoing field studies in North Carolina, U.S.A. (no particle size selection), 'bacterial consumption events' have been associated with the sampling of coarse marine aerosols (though it does not occur every time the MARGA samples coarse marine aerosols). If the coarseness of the aerosol is a factor, we would expect a reduction in the extent and frequency of 'bacterial consumption events' in MARGA systems that sample using PM2.5 and PM10 inlets, which is a common application for MARGA systems. Biological, chemical and meteorological processes related to pro-

duction and transportation of the bacteria are expected to have a large influence on the occurrence of 'bacterial consumption events'. Obviously, these processes will vary with location, therefore it is unknown for a particular location the extent and frequency that 'bacterial consumption events' will occur. The US EPA is further investigating the 'bacterial consumption events' and will relate any significant findings to Metrohm Applikon. A potential solution for the handling of the 'bacterial consumption events' in routine monitoring would be for the MARGA software to calculate the ion balance (or ammonium/sulfate balance in areas of low nitrate) of the measured aerosols. During a 'bacterial consumption event', the ion balance will be in favor of the anions. When the anion dominated ion balance crosses a certain threshold, the MARGA software could provide a warning that a 'bacterial consumption event' could be taking place and flag the data. Furthermore, a valve could be installed within the MARGA sampling system that switches the MARGA from sampling absorption solution to prepared NH4+ external standard and cleaning solutions. This valve could be switched remotely using the MARGA software, allowing confirmation of the 'bacterial consumption event' and the ability to disinfect the system without visiting the monitoring site. The use of a remotely operated valve in conjunction with prepared NH4+ external standard and cleaning solutions has been successfully used for handling 'bacterial consumption events' remotely on a MARGA system in the Netherlands. The aforementioned potential solution has been discussed by some of the co-authors from the US EPA and Metrohm Applikon and if feasible may be introduced to the standard MARGA in the future.

Comment 10: Unit missing in Y-axis in Fig 7.

Response: Thank you. The figures has been corrected.

Comment 11: Typo: Line 13, page 25069, SO4- should read SO4 2-

Response: Thank you. The correction has been made to the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25067, 2013.