

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 1:

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

Comment 1: In general the manuscript is well structured and presents the results in

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quite a clear manner. The cited literature is relevant. The paper merits publication in ACP after consideration of the following general and minor remarks. The paper is written systematically and clearly, but unfortunately I cannot judge the quality of the English writing as I am not a native speaker.

Response: Thank you.

Comment 2: On page 19 “A noticeable difference can be observed between the denuder and MARGA (HNO₃) concentration trends, with typically the MUs measuring lower concentrations than the denuder during the day, and higher concentrations than the denuder at night.” – The higher night time concentrations may be caused by N₂O₅ artifact described by Phillips et al. 2013. (Phillips G. J., Makkonen U., Schuster G., Sobanski N., Hakola H., and Crowley J. (2012) The detection of nocturnal N₂O₅ as HNO₃ by alkali- and aqueous-denuder techniques, Atmos. Meas. Tech. 6, 231–237, www.atmosmeas-tech.net/6/231/2013/ doi:10.5194/amt-6-231-2013.)

Response: Thank you for your comment. We have now referenced the Phillips et al. (2013) paper and have added a discussion on the influence of the N₂O₅ artifact on the comparison between the sampling techniques and also on measured HNO₃ concentration levels. According to the Phillips et al. (2013) paper both the MARGA and the alkali denuder will be affected similarly by the N₂O₅ artifact. Therefore, we do not think it is likely that the higher nighttime concentrations measured by the MARGA in comparison to the denuder are due to the N₂O₅ artifact.

Comment 3: The results of the blanks, external standards and analytical bias are presented in the Supplement – It would be easier to read if they were included in the Manuscript. Instead the Table of data points >DL (but not detection limits) could be in Supplement.

Response: A summary of the blank and external standard results are provided in the text of the manuscript, therefore we think that adding the table to the manuscript would add little value to this already lengthy manuscript.

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Comment 4: MU data was adjusted based on the biases in (external?) calibration standard using one concentration for example for nitrate 1.7 ug m-3. The measured ambient concentrations were however much lower and it is a bit questionable if the bias (%) was of the same magnitude.

Response: Thank you for your comment. Yes, the calibration standard was external. A description of the external standard test is provided in the quality assurance/quality control section of section 2.2.1 in the manuscript.

We acknowledge that the external standard test is not comprehensive and that the NO₃- external calibration standard is higher than measured ambient concentrations. However, considering the large range of the ion conductivity detector, we feel that the calibration standard is close enough to the measured concentrations to suitably represent the performance of the ion conductivity detector and thus the analytical bias of the instrument.

Comment 5: p.1 r. 32, instead of SO₄- there should be SO₄²⁻

Response: Thank you, we have made the correction.

Comment 6: p.5: The ETV was conducted at the AIRS site located on the EPA campus in Research Triangle Park, North Carolina. – Could you add a very short description of the environment (suburban/rural/polluted/traffic)?

Response: Thank you for your comment. We have added a short description of the sampling site environment to the manuscript.

Comment 7: p. 6 and p. 8: What was the material of the custom inertial separator inlet (cutoff \approx 26 μ m) and the inlet cyclone (cutoff 2.5 μ m)?

Response: Thank you. The custom inertial separator inlet was composed of white acrylic and the inlet cyclone was composed of Teflon coated aluminum. This information has been added to the manuscript.

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Comment 8: p.16. r. 21: MARGA customized inlet had a cut-off of \approx 6 μ m (Should it be 26 μ m?)

Response: Thank you, we have made the correction.

Comment 9: p. 10 r. 10: C (d/f)l - Should be C(d/f)i ?

Response: Thank you. The 'i' in this equation is not displaying correctly in MS word and looks like a 'l'. However, the 'i' in the equation looks correct in the pdf version of this manuscript, which will be used for the publication.

Comment 10: p.11-> The analytical bias for NH₃ and NH₄⁺ was not so good, with values ranging from -22.7% to -14.5 % for MU1 and - 24.4% to -21.1% for MU2 - NH₃ denuder blank high: 1.38 \pm 0.43 ug. -> inaccuracy in the NH₄⁺ and NH₃ results. However, this was discussed later. These values could also be compared with the value of direct manual injections to the MARGA IC.

Response: Thank you for your comment. In our experience, there is considerable error in direct manual injections using the manual injection valve on the MARGA and therefore they are not a reliable way to accurately determine concentration differences of this magnitude. Furthermore, if there is bacteria in the analytical part of the MARGA (e.g. on the guard column filters or inline filters) this will not help in determining the analytical bias of NH₃ and NH₄⁺.

Comment 11: Move blanks before bias: p. 11 r. 10-11 Move "Blanks were subtracted from the measured concentrations, and the SO₂, SO₄²⁻, HNO₃ and NO₃⁻ measurements were adjusted for their respective analytical biases." to r. 6 before "The analytical bias for SO₂, SO₄²⁻, HNO₃ and NO₃⁻ was acceptable ranging from +4.5% to +11.2% for MU1 and +3.5% to +10.7% for MU2."

Response: Thank you. We have now modified the section appropriately.

Comment 12: p. 11 r.16-17. Blank values were zero or small. – better under/close to the DLs..

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Response: Thank you for your suggestion, the sentence has been modified appropriately.

Comment 13: p.12, r 12-13: MARGA blank as four times the noise of anion and cation IC detector signal. Does this mean from the peak height?

Response: Yes, the noise of the anion and cation IC detector signal was determined in the direction of peak height.

Comment 14: p. 13 r. 4: "For the Teflon filter, $\approx 57\%$ of NO_3^- concentrations were below the DL and... the nylon filter had $\approx 3\%$ of concentrations below the DL", so was most of NO_3^- on the nylon filter (or was the Teflon filter blank higher than that of the nylon filter)? In Supplement: p. 3 Teflon filter typically captures majority of NH_4NO_3 , did it in this case? Or is it probably dependent on temperature?

Response: Thank you for your comment. In the sentence, 'the nylon filter had $\approx 3\%$ of concentrations below the DL' the 3% is a typographic error and should be 33%. It has now been corrected. During this study the majority of NO_3^- was captured on the nylon filter (58%) in comparison to the Teflon filter (42%). We have now also examined the relative contributions of the Teflon and nylon filters to total NO_3^- concentrations during two periods with different average air temperatures. These results support that NH_4NO_3 volatilization is influenced by temperature. A section has been added to the supplemental that discusses the volatilization of NH_4NO_3 from the Teflon filter and the influence of temperature. The sentence 'Teflon filter typically captures the majority of NH_4NO_3 ' has been removed from the supplemental.

Comment 15: p. 13. r. 16: temperatures varying from 17 to 26_C – Temperature was lower, but 17 to 26_C is not cool! (r. 18: nor 18 to 26_C cooler...)

Response: Thank you. We have modified the relevant sentences appropriately.

Comment 16: p.22 r. 18: ...larger particle cut-off ($\approx 26 \mu\text{m}$) used... should be μm .

Response: Thank you, we have made the correction.

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Comment 17: Table 1: Detection limits column: move $\mu\text{g m}^{-3}$ to the heading row. Decimal numbers are varying. (oliko tarkoituksella?)

Response: Thank you for your comment. As suggested, we have moved $\mu\text{g m}^{-3}$ to the heading row. We have also made the decimal numbers consistent.

Comment 18: Table 2: Precision MARPD %: is it calculated from duplicate MARGA units (1 h) resolution, except HNO_3 12 h and 24 h? If so why?

Response: Thank you for your comment. The inclusion of 24-hour HNO_3 precision in the manuscript was an error, therefore this information has been removed from the manuscript. Table 2 has now been modified appropriately to indicate that precision for all compounds was calculated using 1 hour averaged data and that accuracy for all compounds was calculated using 12-hour averaged data, with the exception of HNO_3 accuracy, which was additionally calculated using 24-hour data.

Comment 19: Figure 10: Units missing.

Response: Thank you. We have made the correction.

Comment 20: In the Supplement Table S2 there is an error in NO_3^- MU % analytical bias.

Response: Thank you. We have made the correction.

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

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