

[Interactive
Comment](#)

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.

Anonymous Referee #1

Received and published: 9 December 2013

The manuscript presents an assessment of the performance of the online ion chromatograph MARGA for particulate sulphate, nitrate and ammonium as well as for three precursor gases sulphur dioxide, nitric acid and ammonia. In the validation work ambient concentrations measured with MARGA (1 h time-resolution) at the EPA campus in North Carolina for thirty days were compared with those measured using denuder/filters (12 h time-resolution). The motivation of the paper is the interest of U.S. EPA in supplementing CASTNet with semi-continuous monitoring systems at selected sites to characterize atmospheric chemistry of N and S compounds at higher time res-

C8108

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



olution than is provided by the filter pack. In the scientific community there is in general a wider interest to shift towards measurements with higher time resolution to be able to characterize atmospheric processes.

Unlike SO₂, HNO₃ and NH₃ are difficult gases to sample and measure due their ‘sticky’ nature and reactivity. In this study there were also some difficulties likely caused by the growth of bacteria in the MARGA units leading to under-estimation of NH₃/NH₄⁺. The comparison of NO₃⁻ with the filters (cutoff 2.5 μm) was most problematic because of the large cutoff used (26 μm) in the MARGA units. Furthermore, the concentrations of the parallel MUs varied with each other especially during the highest peaks, which can be influenced by slightly different cutoffs and local influence. The amount of coarse-NO₃ in was estimated by using Na⁺ results and after that the concentration levels agreed better with filters. However, it is also likely that there might have been adsorption in the long inlet tubing used (4 m) which affects the MARGA results. All these together with the rather low concentrations of NO₃⁻ increased the uncertainty of the results. However, these problems were discussed in detail and in the conclusions there are some recommendations to overcome these problems.

In general the manuscript is well structured and presents the results in 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. Minor remarks

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.atmos-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

meas-tech.net/6/231/2013/ doi:10.5194/amt-6-231-2013.)

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.

MU data was adjusted based on the biases in (external?) calibration standard using one concentration for example for nitrate $1.7 \mu\text{g m}^{-3}$. The measured ambient concentrations were however much lower and it is a bit questionable if the bias (%) was of the same magnitude.

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

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)?

p. 6 and p. 8: What was the material of the custom inertial separator inlet (cutoff $\approx 26 \mu\text{m}$) and the inlet cyclone (cutoff $2.5 \mu\text{m}$)?

p.16. r. 21: MARGA customized inlet had a cut-off of $\approx 6 \mu\text{m}$ (Should it be $26 \mu\text{m}$)?

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

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: $1.38 \pm 0.43 \mu\text{g}$. -> 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.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



and +3.5% to +10.7% for MU2.”

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

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 hight?

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?

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. . .)

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

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

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?

Figure 10: Units missing.

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

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper