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Atmospheric Measurement Techniques Discussions

Interactive comment on "Application of an online ion chromatography-based instrument for gradient flux measurements of speciated nitrogen and sulfur" *by* Ian C. Rumsey and John T. Walker

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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: This paper is a hybrid instrument/application description of the Applikon MARGA online IC system for the measurement of reactive gas and aerosol concentrations and fluxes (by AGM). The authors are among those who previously described the one sample box version of the instrument for the measurement of concentrations. Overall the paper is a good description of the technique which builds on the previous papers and extends them to include an assessment of the capability for measuring fluxes using the aerodynamic gradient method.

Response: Thank you.

Comment 2: Recommendations. The section on accuracy, which to some extent is a repeat of the work in the original MARGA description, would benefit from an extended assessment of the accuracy. All the tests published so far on the ECN annular denuder (GRAEGOR, MARGA) do not deal with real samples in all conditions and the uncertainty added by the sampling of a real matrix, i.e. the atmosphere. In this paper, liquid standard are used instead of stripping solution and the inlet effects, cross sensitivities to other species and any effects due to the stability of SJAC and denuder sampling efficiencies are not dealt with. This is a major issue for these type of techniques which the authors should address as they directly relate to the warrant one should give to interpretation of results derived from denuder instruments. There is at least one published cross-sensitivity (hydrolysis of N2O5) which is not mentioned in the paper and could not be tested for using the methods described in this manuscript. The flux measurement is built on the foundation of the analytical certainty of the wet chemistry including sjac and denuder systems and the authors should discuss the possibility of cross sensitivities with other molecules in the section on accuracy and be clear about what issues remain when using the MARGA instrument for the measurement of fluxes. This survey of possible interferences would be an really useful addition to the paper and would give added confidence in the results from such systems.

Response: Thank you for your comment. We have now added to the manuscript a section which describes the uncertainties not taken into account by the accuracy experiment in this study and the extent it may influence the results reported in this study. Included in this new section is a discussion of the N2O5 cross sensitivity and its potential influence on HNO3 fluxes. We acknowledge that the magnitude of this potential artifact has not been quantified in our study and therefore we will aim to quantify this artifact in future studies. The information that will be added to the accuracy methodology section of the manuscript is provided below.

"It is acknowledged that the liquid external standards used to determine accuracy do

not take into account all uncertainties associated with the MARGA measurement system. In this study, it is assumed that the performance of the WRD and SJAC for collecting gases and aerosols are similar to those reported by Keuken et al. (1988), Wyers et al. (1993) and Khylstov et al. (1995), respectively. The inlet associated with the MARGA sampling system may also affect measurement accuracy, particularly for "sticky" gases such as NH3 and HNO3. In this study, however, possible inlet effects were minimized by using a short length (30 cm) of PFA Teflon tubing. Cross-sensitivity of the WRD in measuring dinitrogen pentoxide (N2O5) as NO3- during the nighttime as reported by Phillips at al. (2013) may also affect the accuracy of NO3- measurements. In an analysis on the MARGA instrument, Phillips et al. (2013) determined that on average N2O5 contributed 17% of measured nighttime HNO3 at a sampling site near Frankfurt, Germany. The magnitude of N2O5 concentration varies for different geographic locations and is influenced by nitric oxide (NO) concentration, biogenic volatile organic compound (VOC) concentrations and air temperature (Phillips et al., 2013). During the period of study presented here, the influence of the artifact on HNO3 fluxes is likely small, as a result of the majority of flux occurring during the daytime owing to diurnal patterns in the momentum flux (see figure in supporting information) and also due to the HNO3 concentration, which is < 0.15 μg m-3 on average at night. Though the N2O5 artifact was not quantified in the current study, its potential importance for sites in the southeast U.S. invites future investigation."

The figure referred to in the above information added to the manuscript is provided below (figure 1 (figure S6 in supporting information)).

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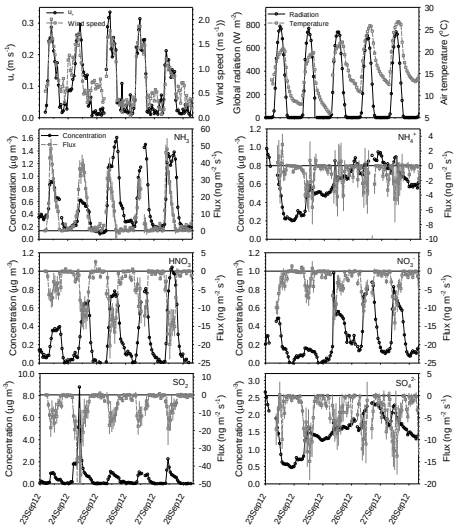

Figure 1. Example time series of meteorological variables, air concentrations, and fluxes. Fluxes also include flux error calculated from equation (4) in the main text. For plots of chemical species, concentrations and fluxes are represented by black circles and gray squares, respectively.

Fig. 1.