

Response to Comments from Reviewer # 2:

We sincerely thank the reviewer for helpful comments and suggestions. Point to point responses are shown below.

General comments:

(Q1) My major concerns are upon the assumption of collection of gaseous species. In sec 3.3.1, it was addressed that “because of the low diffusion coefficient of SO₂, the other acid gases (HNO₃, HONO and HCl) should be collected more efficiently and measured precisely with Na₂CO₃ solutions as absorptions in the GAC-IC system”. This assumption implies that solubility is the single factor controlling the collection efficiency. However, as shown in the HONO cases, there are indeed some other key factors in the system, photo-stability and chemical stability for instance. Thus, in expectation of to be cited as the major reference of this instrument, a detailed inter-comparison should be performed for each species in this study.

Response: For gas collection efficiency, diffusion coefficient and solubility are two key factors. The speed of gas diffusing to the surface of the WAD is primarily determined by the diffusion coefficient. Higher diffusion coefficients result in faster transport of gases. Among gaseous species measured in this study (SO₂, HNO₃, HONO and HCl), SO₂ has lower diffusion coefficient and solubility in water. Simon et al. (1993) has suggested that if collection efficiency for SO₂ is high, then high collection efficiency should be expected for other gases as well. In our study, a collection efficiency as high as 98% with Na₂CO₃ (25 μM) as the absorption solution was found for SO₂.

We agree with the reviewer that photo stability and chemical stability can influence HONO measurement. Considering high reactivity of HONO, in this study the inlet was covered by black material to block the sunlight and prevent the reaction of

$NO_2 + HV \xrightarrow{\text{Surface}} HONO$. The primary exposed surface in the WAD is wet by a film of liquid water, so the reaction of $NO_2 + H_2O \xrightarrow{\text{Surface}} HONO$ is not likely to happen in the WAD, but it may occur in the inlet.

Only SO_2 and HONO are inter-compared with other instruments in this study while other species are not compared due to the lack of instruments. We focus on the species that can be compared and we will perform comparison tests on the measurement of HNO_3 , HCl and NH_3 in the future whenever instruments are available. We have clearly stated that the measurements of these species as semi-quantitative in the revised manuscript.

(Q2) In sec 3.3.2, it was indicated that “The GAC-IC system measurement was about 10% higher than the LOPAP in the night which was primarily attributed to the 3-m long inlet tube connected in the GAC-IC system”. I’m confused that how the inlet loss resulting in higher levels of HONO measured in the GAC-IC system? It seems being opposite to general understandings.

(Q3) Moreover, the lower levels of HONO measured by GAC-IC during daytimes were attributed to O_3 -HONO reaction. However, the O_3 -HONO reaction could be still there during nighttimes. Actually, as the O_3 data of the campaigns are available, you can calculate this chemical sink to validate your argument.

Response: In fact, instead of inlet loss, we wish to state that a 10% higher GAC measurement at night than LOPAP (inlet gain) could be due to HONO produced from chemical reaction on the inner surface of the inlet between NO_2 and H_2O when RH was much higher (Su et al., 2008a; Svennson et al., 1987).

In this study, we originally assume the lower level of GAC-IC measurement is caused by O_3 -HONO reaction. Under this assumption, a larger difference of HONO measurement between GAC-IC and LOPAP should be associated with higher O_3 concentration, which is not seen in Figure 1, suggesting lower level of HONO

measured by GAC-IC during daytimes is not likely attributed to O₃-HONO reaction. We have modified this statement in the revised manuscript.

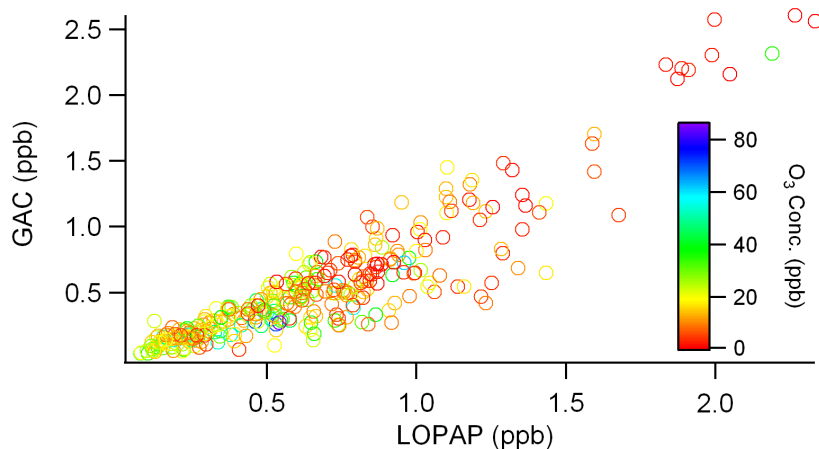


Fig.1. The inter-comparison between GAC-IC and LOPAP with color-coded according to O₃ concentration.

(Q4) The agreement between GAC-IC and filter-based measurements was good for sulfate, whereas significantly higher concentrations of nitrate and chloride were reported by GAC-IC. The authors argued that the differences were caused by evaporation loss of nitrate and chloride species during filter sampling processes. Besides that, I wonder if the GAC-IC measurements could include positive bias from the penetration of HNO₃ and HCl, in particular during daytimes.

Response: As stated in our response to Question 1 above, because the diffusion efficiency and solubility of HNO₃ and HCl are higher than those of SO₂, the collection efficiency of HNO₃ and HCl in the WAD should be equivalent or better than SO₂, which is about 98% with Na₂CO₃ (25 μM) as the absorption solution. In addition, SO₂ concentration (maximized at 43 ppb) is much higher than HNO₃ (the maximum and mean concentrations as 5.33 and 1.07 ppb, respectively, as can be seen in Table 2). Good comparison for sulfate between the GAC-IC and filter method indicates SO₂ with a high concentration does not penetrate the denuder. Therefore, the GAC-IC measurements for nitrate and chloride should not include positive bias from

the penetration of HNO₃ and HCl.

(Q5) The inter-comparison between GAC-IC and AMS looks good. However, given that there should be a substantial amount of aerosols existing in the size range of 1- 2.5 microns, the measurements of GAC-IC (PM2.5) are expected to be equal or larger than those of AMS (PM1). In this context, size distribution of each aerosol species is very important to complement the results presented in this manuscript. Otherwise, the current comparison could be unfair.

Response: We agree with the reviewer that size distribution of each aerosol species is important and helpful. Unfortunately, it is not available in this study. However, the species selected for comparison including sulfate, nitrate and ammonium are often enriched in PM₁. Therefore, a direct comparison between these two instruments could be made.

(Q6) Technical correction: Page 7761: “A Scanning Mobility Particle Sizer and a Condensation Particle Counter” should be “SMPS consisting of a DMA and a CPC”

Response: We appreciate this comment. It has been corrected in the revised manuscript.

References:

Simon, P. K. and Dasgupta, P. K.: Wet effluent denuder coupled liquid ion chromatography systems annular and parallel plate denuders, *Anal. Chem.*, 65, 1134-1139, 1993.

Su, H., Cheng, Y.F., Shao, M., Gao, D.F., Yu, Z.Y., Zeng, L.M., Slanina, J., Zhang, Y.H., Wiedensohler, A.: Nitrous acid (HONO) and its daytime sources at a rural site during the 2004 PRIDE-PRD experiment in China, *J. Geophys. Res.*, 113, D14312, doi: 10.1029/2007JD009060, 2008a.

Svensson, R., E. Ljungström, and O. Lindqvist: Kinetics of the reaction between nitrogen dioxide and water vapour, *Atmos. Environ.*, 21, 1529–1539, 1987.