Response to Comments from Reviewer #1:

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

General comments:

(Q1) Sections 2.1 and 3.1: Sampling inlet

The authors should pay more attention to the sampling inlet. In general, conductive or metal tubes should be used for aerosol sampling to avoid possible loss of particles due to electrostatic charges. On the other hand, Teflon or glass tubes (with very short residence time) should be used for the sampling of highly reactive gases to avoid chemical loss on the wall. These requirements make it difficult to use a common sampling inlet for aerosols and reactive gases. This point is very critical as the use of a common inlet is the basic concept of the GAC system.

Specifically, cares should be taken to avoid the loss of very sticky gases such as HONO, HNO3, and NH3. In general, quality of the measurements of these gases is often limited by the inlet design rather than the analyzer itself. I guess the 3-m inlet tube and 16.7 L/min sampling flow would not be an optimal condition for these gases.

Response: We agree with the reviewer that the sampling inlet and transport tubing play a very important role, especially when gas and particles are collected and measured at the same time, as with the GAC-IC. A Teflon-coated aluminum URG 2.5μm cut cyclone (electrically grounded) and Teflon transport tubing was used in our study. We felt this was a good choice for gas sampling in order to limit reactive gases wall loss. Ideally to minimize particle loss, conductive tubing should be used. However, particle loss in this study should not be significant based on the results of our inter-comparison between the GAC-IC and filter sampling system, where good correlation coefficients and a slope of 0.94 and 0.98 for sulfate and nitrate, respectively, were found.

We acknowledge that there may be sampling issues for specific gases. For example, the measurement of HONO may be impacted by this sampling inlet, as found by other authors (Su et al., 2008; Svennson et al., 1987). In this study, the inlet was covered by black material to block the sunlight to prevent the reaction of $NO_2 + HV \xrightarrow{Surface} HONO$. The primary exposed surface in the WAD is a film of liquid water where the reaction of $NO_2 + H_2O \xrightarrow{Surface} HONO$ does not likely happen, but this reaction may occur in the inlet. Because of the high reactivity of HONO, its sources and relevant heterogeneous reactions have large uncertainties and exact mechanisms remain unclear. The statement of uncertainty of our system for HONO measurement has been added in section 3.3.2 in the revised manuscript.

Because an independent comparison for HNO_3 measurement was not available, we only indicate in the revised manuscript that the measurement of HNO_3 is semi-quantitative. We also point out the sampling challenges by measuring gas plus particle simultaneously. Future work will include evaluating the performance of NH_3 and HNO_3 measurements through inter-comparison studies.

(Q2) Section 2.2.2: Aerosol collection efficiency

The evaluation of the aerosol collection efficiency is not straightforward and the results are very ambiguous. Why did the authors use polydisperse aerosol particles? The evaluation of the penetration rate and collection efficiency should be size-resolved. The authors can easily generate monodisperse aerosol particles and measure the number concentrations using their DMA and CPC, which makes the interpretation much clearer.

Response: We used poly-disperse aerosol to specifically test possible influence of particle concentration on collection efficiency (e.g., vapor depletion, etc.). High number concentration of mono-disperse particles at a flow rate of 16.7 L min^{-1} is difficult to generate, therefore poly-disperse aerosols are used. These tests were performed because ambient aerosols in China were characterized by high particle number and mass concentrations compared to the levels often found in western countries. The newly designed aerosol collector is an important improvement of the GAC-IC. By increasing the amount of steam generated and adding circulatory cooling water, more particles could be activated in the saturated environment and collected to avoid vapor depletion and loss of smaller particle activation. We have added the above information to clarify this in the second paragraph of section 2.2.2 in the revised manuscript.

(Q3) Sections 3.3.1 and 3.3.2: Inter-comparison of gaseous species

The GAC system might be able to provide the concentration of HCl, HONO, HNO3, SO2, and NH3. The inter-comparison for SO2 seems promising, but that for HONO seems problematic. Also, there is no inter-comparison for the other species. In the abstract the authors claim that the instrument is proved "highly reliable," but this statement is valid only for SO2.

Response: The reviewer is correct in that the inter-comparison of gaseous species has been done for SO_2 and HONO while it is not performed for other species due to the lack of relevant instruments to measure these other species. Thus in this manuscript we focus on SO_2 inter-comparison to assess that no pollutant gases penetrate the WAD and we consider measurements of other gases (HNO_3 and HCl) as semi quantitative at this point.

We discuss the validation of HNO_3 and HCl measurements as follows: 1) the collection efficiency of the two species by the WAD appears reliable (detailed discussion available in section 2.2.1); 2) these species can be precisely detected by the IC; 3) the spatial and diurnal variations of these two species are reasonable compared with nitrate and chloride. The above statements are summarized and included in the last paragraph of section 3.2 in the revised manuscript.

As the reviewer notes, the SO_2 comparison results are promising. As for the HONO, we have added following discussions in section 3.3.2 in the revised manuscript. Based on diurnal variation of HONO as seen in Figure 1b, good agreement between two instruments can be seen during the period of 15:00 to 7:00, then samples are grouped into a period with better agreement and a poorer one (15:00 to 7:00 with R^2 as 0.91 and 8:00 to 14:00 R^2 as 0.68 in Figure 1c and 1d) instead of simply classifying into day and night samples as in Figure 1a. At this time we do not have a good explanation for the 42% lower measurement by GAC during the period from 8:00-14:00. Therefore, it is likely that the difference during this period (8:00-14:00) is due to some heterogeneous reactions or interference contributed by daytime radiation on indoor measurements by GAC and outdoor measurement by LOPAP. So in this study, we consider the HONO measurement by GAC comparable with LOPAP from 15:00 to 7:00 (17 hours) and uncertain between 8:00 to 14:00 (7 hours). The above discussion and related statements have been included in section 3.3.2 of the revised manuscript.

Due to the lack of validation for NH_3 measurement in laboratory tests, the NH_3 data by the GAC-IC system are not presented and discussed in the current study. According to the reviewer's suggestion, we have removed the wording “highly reliable” from the revised manuscript.

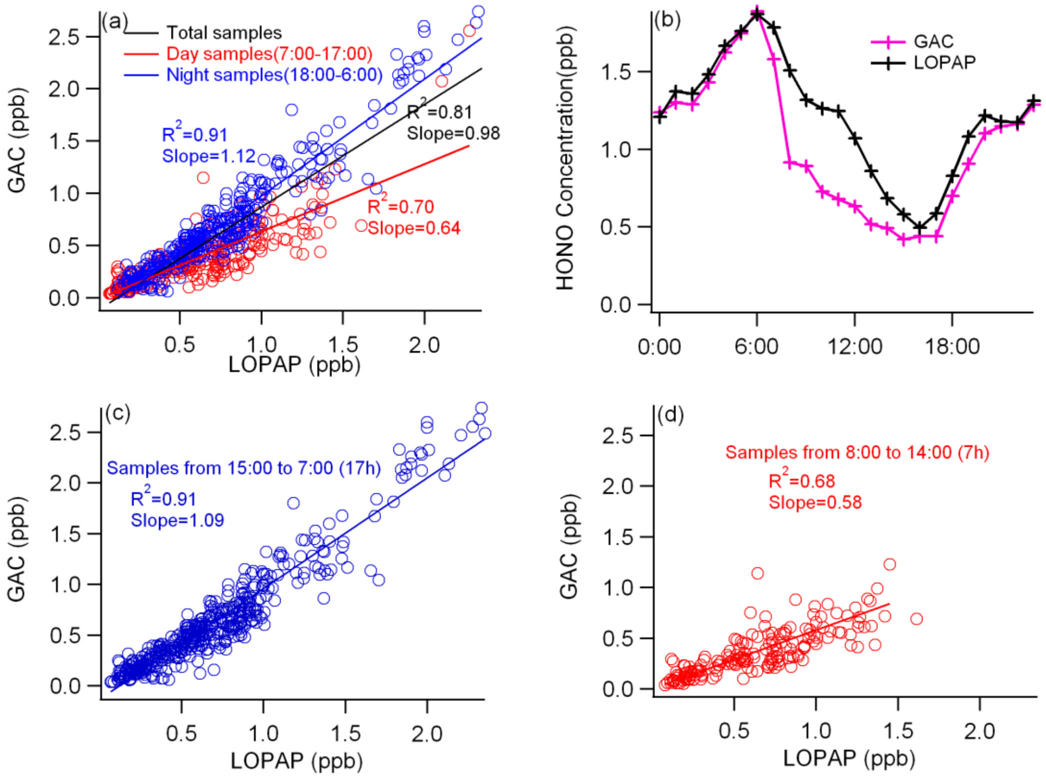

Fig.1 The inter-comparison between GAC-IC and LOPAP: (a) inter-comparison of day samples from 7:00 to 17:00 (11 hours) and night samples from 18:00 to 6:00 (13 hours); (b) diurnal variations of GAC-IC and LOPAP measurement; (c) inter-comparison of samples from 15:00 to 7:00 (17 hours); (d) inter-comparison of samples from 8:00 to 14:00 (7 hours).

(Q4) Section 3.3.4: Intercomparison of aerosol species

The intercomparison of aerosol species between GAC and AMS does not make sense to me. The cutoff diameters of the GAC and AMS are different, which introduces substantial uncertainties in the intercomparison. Furthermore, it is very confusing to discuss the quality of the AMS measurements (collection efficiency) based on this intercomparison. What was the relative humidity in the sample air for the AMS? What was the loss of particles in the Nafion tube? If the authors consider that the AMS measurements contain systematic errors, they should not use the data for the evaluation of the GAC system.

Response: We agree with the reviewer that it is hard to directly compare measurements of two instruments when cutoff size is different. However, the species we used for comparison between the GAC-IC and AMS such as sulfate, nitrate and ammonium are often enriched in PM_1. Therefore, a direct comparison between these two instruments can be made even though the cutoff size for the GAC-IC is 2.5 μm.

In this manuscript, we do not intend to evaluate the systematic error of AMS. The issue of collection efficiency (CE) influenced by RH for AMS is known and has been always considered in various studies. For example, Allan et al. (2004) have reported that the CE value depends on the relative humidity (RH) of the sampled air, which can vary from 0.5 at low RH to 1 at high RH. Takegawa et al. (2009) also applied a CE value as 1 under high RH. To minimize this impact, the nafion tube was applied as particle dryer in the inlet of AMS in our study. It is reasonable to compare results from two instruments at lower RH.

As can be seen in Figure 2 below (also Figure 13 in the revised manuscript), measurements by the GAC-IC system and AMS agree well when RH is below 50%. A less scattered plot and higher R^2 are achieved compared to the results using all data with RH up to 98%. The improved new R^2 from 0.81 to 0.94 and all data falling within the area between two regression lines with a slope of 1.5*original slope and original slope/1.5, respectively, suggest these species can be measured well by the GAC-IC system.

We have added above discussion and clarified these points in section 3.3.4 of the revised manuscript.

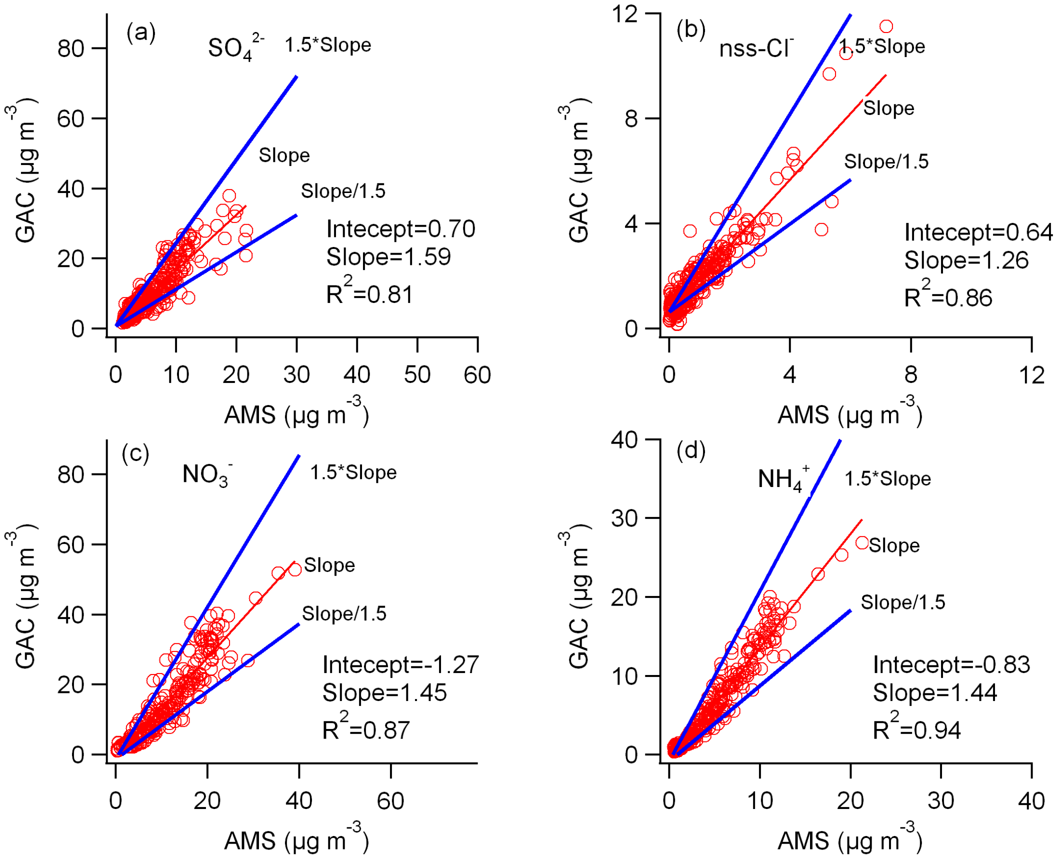

Fig.2. Inter-comparison between the GAC-IC system and AMS measured at RH below 50%. We use 1-hour average data for this comparison.

Other comments:

(Q1) Section 2.1: Aerosol trapper

The authors should present more details of the newly added components. I do not fully understand how they work. The "cycling cooling water" section should not be called "cyclone." The physical mechanism of a cyclone is totally different.

Response: We have added detailed description of the newly designed aerosol collector in the first paragraph of section 2.1 and removed the term “cyclone” in the revised manuscript. It has been described and modified as follows: “As shown in Figure 1, it has three glass components including an aerosol mixing chamber (100 mL), a coil aerosol cooler and an impactor aerosol trapper (contain cold water bath). Aerosol samples go into the collector through the “stream in” port, mixed with steam generated by ultra pure water (18.2 MΩ) at a flow rate of 1.0-1.2 mL $\min^{-1}$ under constant temperature of 120 °C. The stream goes through the aerosol chamber and the coil aerosol cooler where particles grow to droplets, which are finally collected by the impactor aerosol trapper (contain cold water bath). The collected water sample is pumped out of the trapper from the "sample out" port and the stream goes out from the "air out" port. There is circulating cooling water (around 10 °C) going through the outer shell of the coil aerosol cooler and the impactor aerosol trapper which accelerates the growth and condensation of droplets by lower the water saturation vapor pressure and increasing the degree of water saturation (RH)."

(Q2) Section 3.2: HNO3 and HCl

The authors claimed that the variations of HNO3 and HCl were controlled by the evaporation of nitrate and chloride. Is it true? Please check the budget.

Response: Good correlation between the GAC-IC and the filter measurements for HNO_3 and HCl was found for night samples while significant difference can be seen for day samples. Significant loss (about 70%) in filter measurement was estimated for nitrate and chloride based on calculation using samples collected during days with average temperature above 27 °C.

In this study, HNO_3 and nitrate exhibit totally reversed diurnal variation patterns, with 1-h average concentrations of HNO_3 and nitrate varying within approximately 2 ppb and 4.5 μg m^{-3} (1.6 ppb when evaporated), respectively. The level of this variation agrees well with the above estimate (70% loss or about 4.9 μg m^{-3}) due to high temperature. That is why we suggest the evaporation of nitrate and chloride as the main source of gaseous HNO_3 and HCl.

(Q3) Table 1: Why is the LOD of SO4 much higher than the other compounds?

Response: LOD for sulfate (0.16 μg m^{-3}) is calculated by three times signal to noise ratio. Compared to other species, sulfate has higher S/N ratio. Though the LOD of SO_4^{2-} is higher than other anions for these field deployments, it is not an issue since the ambient air SO_4^{2-} concentration was much higher (average and minimum ambient sulfate level as 12.37 and 0.47 μg m^{-3} in Kaiping).

(Q4) Table 3 provides no useful information and should be removed.

Response: In this study, a major objective is to show that the GAC-IC can work well under high aerosol loadings. We believe Table 3 provides useful information for the following reasons: 1) GAC-IC measurement shows high correlation with the filter method and the slopes of sulfate and nitrate between GAC and filter measurement are close to 1.0 , which is better than other studies listed in Table 3. This indicates that the GAC measures the same level as the filter method; 2) the good inter-comparison results between commercialized SJAC and the filter measurement in Beijing and Shanghai just include concentration data lower than 20 μg m^{-3} for sulfate and 15 μg m^{-3} for nitrate, while our study is carried out under much higher concentrations (<40 μg m^{-3} for sulfate and <30 μg m^{-3} for nitrate) than other studies listed in Table 3. This further proves that the GAC-IC can perform well under high aerosol loadings. Therefore, we prefer to leave Table 3 in the manuscript.

References:

Allan, J.D., Bower, K.N., Coe, H., Boudries, H., Jayne, J.T., Canagaratna, M.R., Millet, D.B., Goldstein, A.H., Quinn, P.K., Weber R.J., Worsnop, D.R.: Submicron aerosol composition at Trinidad Head, CA during ITCT 2K2, its relationship with gas phase volatile organic carbon and assessment of instrument performance, J. Geophys. Res, 109 (D23), D23S24, 2004.

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, 2008.

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

Takegawa, N., Miyakawa, T., Kuwata, M., Kondo, Y., Zhao, Y., Han, S., Kita, K., Miyazaki, Y., Deng, Z., Xiao, R. Hu, M., van Pinxteren, D., Herrmann, H., Hofzumahaus, A., Holland, F., Wahner, A., Blake, D. R., Sugimoto, N., and Zhu,T.:Variability of submicron aerosol observed at a rural site in beijing in the summer of 2006, J. Geophys. Res, 114, D00G05, doi:10.1029/2008JD010857, 2009.

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 (SO_2, HNO_3, HONO and HCl), SO_2 has lower diffusion coefficient and solubility in water. Simon et al. (1993) has suggested that if collection efficiency for SO_2 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 Na_2CO_3 (25 μM) as the absorption solution was found for SO_2.

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

$NO_2 + HV \xrightarrow{Surface} HONO$. The primary exposed surface in the WAD is wet by a film of liquid water, so the reaction of $NO_2 + H_2O \xrightarrow{Surface} HONO$ 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 O3-HONO reaction. However, the O3-HONO reaction could be still there during nighttimes. Actually, as the O3 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 O_3-HONO reaction. We have modified this statement in the revised manuscript.

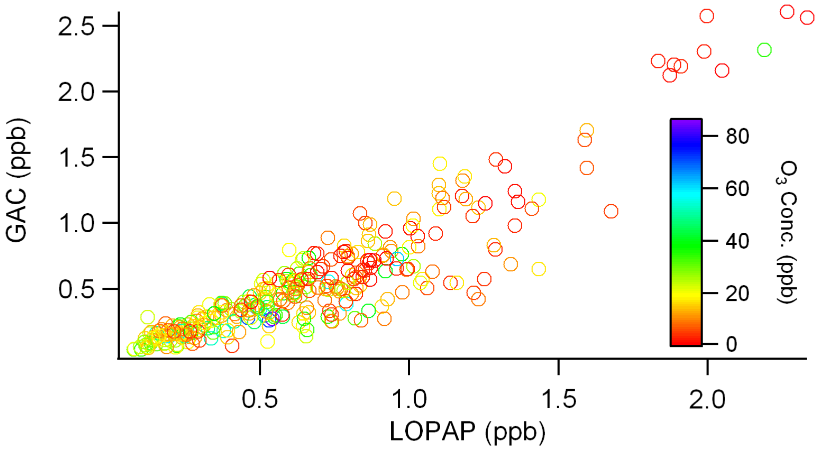

Fig.1. The inter-comparison between GAC-IC and LOPAP with color-coded according to O_3 concentration.

(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 HNO_3 and HCl are higher than those of SO_2, the collection efficiency of HNO_3 and HCl in the WAD should be equivalent or better than SO_2, which is about 98% with Na_2CO_3 (25 μM) as the absorption solution. In addition, SO_2 concentration (maximized at 43 ppb) is much higher than HNO_3 (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 SO_2 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 HNO_3 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 PM_1. 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.