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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of HNO_3 and N_2O_5 using Ion drift – Chemical Ionization Mass Spectrometry during the MCMA – 2006 Campaign" *by* J. Zheng et al.

J. Zheng et al.

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We have addressed the comments regarding writing style and grammar in the revised manuscript. The specific scientific comments are responded below.

1) “Introduction: It is…… is ID-CIMS the best technique for this problem?”

We agree with the referee that MCMA is not the biggest megacity at present; it should be stated as “one of the largest megacities in the world.”We have updated the emission data using the information published in the Mexico City Secretary of the Environment website; we have also added new references. The NOx emission is about 180,000 metric tons/year. Although the NOx emission was reduced from year

2000, the magnitude is still overwhelming and no comparable case can be found in the U.S. Lie et al. (2007) and Tie et al. (2007) suggested that the ozone production in the MCMA is under VOC-limited regime. The HNO3 data presented in our paper can be used to constrain model simulations and improve our understanding of the NOx and O3 chemistry in the MCMA. Regarding the introduction of HNO3 and N2O5 chemistry, we have added some detailed discussion of HNO3 heterogeneous reaction on the wet surface, which could lead to NO and HONO production. We have included possible heterogeneous processes on the surface of mineral dust (Hodzic et al., 2007) and soot (Karagulian and Rossi, 2007) that could remove HNO3 and N2O5 from the gas-phase. We have expanded the discussion on HNO3 and N2O5 chemistry to include physical processes.

Regarding the CIMS technique, we believe the ID-CIMS has three advantages over the traditional CIMS. First, the metal rings of the drift tube can act as Einzel lens to focus ions and improve instrument sensitivity. Second, the electric field inside the drift tube can guide the ion flight path and control its flight speed, thus the ion-molecule reaction can be more reliably calculated. Third, the electric field can break up water clusters inside the drift tube by introducing collisions with carrier gas molecules.

2) “Experimental……… as possible in their analysis.”

As the referee suggested, we agree to reduce the length of the experiment section. We have moved part of the experiment section into Appendix A, which describes the theoretical work to obtain reduced ionic mobility of the reagent ions. One of our objectives of this paper is to establish the working principle of the ID-CIMS during its first field deployment. Thus we provided a detailed description about its operation including theoretical works to determine the reduced mobility of the reagent ions. The measurement of N2O5 was an example of the advantage of the ID-CIMS over CIMS. N2O5 calibrations during field campaign were not practical. However the in-situ HNO3 calibration would give a good indication of the changes in the responses of the ID-

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CIMS to N2O5 in the field because both HNO3 and N2O5 measurements experienced the same changes in the operating conditions. The advantages mentioned above are also our motivation for the detailed discussion on the ID-CIMS operation including how to determine the reduced ion mobility when no measurements were available in the literature. We agree with the referee that the 12-ft inlet was not perfect for HNO3 measurements. However, the observation window was about 4-ft from the outside building wall and 8-ft from the hut ceiling. Thus surface effects might affect HNO3 concentration. The 12-ft inlet made it possible to sample air about 4-ft above the building surface. From laboratory tests, we found HNO3 would not permanently loss to the PFA tubing; however N2O5 could undergo heterogeneous reactions on the tubing surface. Thus we must use a shorter sample inlet for the N2O5 measurements. Even the memory effects might be more serious than we expected, we believe our conclusions based the HNO3 measurements were still valid. We also have reported 5-min averaged data in the final revision to minimize memory effect. As suggested by the referee, we have conducted further analysis on the HNO3 production from OH + NO2 reactions on March 20, when OH, NO2, and boundary layer height measurements were available. The results shows that heterogeneous reaction of HNO3 on dust surfaces is important during the MILAGRO campaign, leading to permanent removal of HNO3 to form non-volatile mineral nitrates such as Ca(NO3)2 (Querol et al., 2008; Fountoukis et al., 2007; Hodzic et al., 2007). With all supermicron aerosol nitrate considered and using a calculated dry deposition rate according to Fast et al. (2006), which is consistent with literature values (Myles et al., 2007; Pryor and Klemm, 2004), about 77% of HNO3 production can be accounted for. A gap of 23% is well within the experimental uncertainties.

3) “Results and discussion Two days of nitric acid data are discussed in detail…… I am sure that 5 minute data with detection limits of a few ppt would be valuable.”

We did find it was very common that gas-aerosol partitioning affected the aerosol nitrate and HNO3 concentrations during the MCMA 2006. Additional data have been

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presented in the revised manuscript. Regarding the N2O5 chemistry, we can only speculate the N2O5 flux through the boundary layer based on surface NOx observations. The nighttime surface O3 was routinely close to zero and meanwhile NO increased up to over 100 ppb. A large N2O5 source was not likely. A modeling work could support the speculation but it is beyond the scope of this work.

4) “Conclusions: The conclusions section should be much stronger if more detailed analyses of the data were performed. Bring the important findings of this analysis into this section.”

As suggested by the referee, we have added more discussion in the revised version, including supporting materials from other measurements. The conclusion has reflected these discussions.

5) The technical corrections have been fully considered in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4877, 2008.