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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) “Generally, too much information is provided on the instrument description and general ion molecule chemistry (eg calculation of collision rates), and not enough information is provided on the analysis of the observations. This paper needs to focus more on the observations, analysis thereof, and atmospheric implications, as this is the primary interest of the audience. The detailed instrumental description and calculation of collision ion-molecule collision rates, while important and needing to be documented, might better be suited to supplemental appendixes, or a separate work. The authors

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mention the use of NOx and O3 observations, but do not actually seem to use these except in the brief mention of O3 and NO concentrations, and in display in figure 9. It would be much more interesting if some further analysis were presented as to how much HNO3 was actually being produced from HO + NO2, and comparing this to the measured aerosol nitrate and HNO3. While there may not be OH measurements available from T0, there are OH measurements from T1, as well as from aircraft (C130 and DC8) which flew over the city on several occasions. From quick, back of the envelope calculations, this reviewer calculates significantly greater HNO3 production, than what is measured (HNO3 + aerosol nitrate), over the course of a day. This may imply that there are other important mechanisms in play aside from simple gas aerosol partitioning (ie, HNO3 loss – dry deposition of HNO3 and/or aerosol nitrate? transport?) Addressing changes in the boundary layer height over the course of a day, and how this affects the interpretation of the measurements should be included. Perhaps a simple normalization of the data to some inert tracer would be adequate, eg. CO.”

As suggested by the referee, we have moved the part of the experiment section describing the theoretical work to obtain reduced ionic mobility of the reagent ions into Appendix A. The purpose of a detailed instrument description is to establish the working principle of the ID-CIMS during its first field deployment.

To strengthen the analysis of the NOx and HNO3 chemistry during the MCMA-2006, we have included observation results of other species (NH3, O3, NOx, PBL height, and OH). More detailed HNO3 data have also been provided in the revised manuscript. The calculated HNO3 production rate from OH + NO2 reaction exceeded what was expected from the observed gaseous HNO3 and submicron aerosol nitrate. Heterogeneous reaction of HNO3 on dust surfaces has been shown to be important during MILAGRO, 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). Querol et al. (2008) estimate the fraction of total nitrate at T0 in the PM10 –

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PM2.5 range as ˜20% of the total nitrate, with a higher fraction in the early part of MILAGRO due to reduced precipitation and increased dust concentration. If the dust size distribution in Mexico is similar to that reported by Maring et al. (2003) and the dust reactivity is uniform across the dust size distribution, this size range would account for about ˜1/3 additional dust nitrate beyond that PM10-PM2.5 size range. 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. The above discussion has been included in the revision.

2) “The inlet configuration, in particular the inlet length, seems to be a significant issue to this reviewer.….. This reviewer suggests reporting the HNO3 concentrations on a longer time base (5 or 10 minutes), and being careful about making strong statements regarding HNO3 observations which are small (relative to the detection limit) $<$300 pptv (eg, the slow decay of HNO3 at night, as it is not clear that this is real).”

We appreciate the information provided by the referee. As suggested by the referee, we have reported our data in 5 min average to eliminate the memory effects. We have also considered the possibility of interference from memory effects when reporting low level HNO3 data.

3) “NH3 was not measured at the T0 super site, but it was measured at T1. The authors might mention this and state whether the NH3 observations at T1 are compatible with their assumptions about NH3 at T0. It may also strengthen the authors stated assumptions about NH3 to site the observed acidity of the aerosols as measured by the AMS (eg. fig 7, DeCarlo, et al, 2007).”

We have now added that the average NH3 concentration at T1 is 26.7  13.7 ppb from March 21 to 31, which is consistent with the NH3 level reported by Moya et al.

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(2004). The AMS measurements at T0 found that in the aerosol phase cations (NO3-, Cl-, and SO42-) were roughly 1.15 times of NH4+. Salcedo et al. (2006) and DeCarlo et al. (2007) found most of the time the aerosol was neutralized in and above Mexico City. Only periods with high SO2 and sulfate show a deficit of NH4+ with respect to that needed for full neutralization.

4) “While N2O5 may have been below the detection limits of the ID-CIMS (20 pptv for 10s integration period), this does not necessarily mean it is not important. Given the NOx, O3 observations, it is recommended the authors calculate with a simple model how much N2O5 one would expect at steady state, for several different assumptions about loss to surfaces, and use this as an estimate the importance of the N2O5 channel for HNO3 production, rather than the detection limit argument.”

We agree with the referee that it is true that even for N2O5 lower than 20 ppt, it still can play an important role in the nighttime NOx chemistry, given there are other sources and sinks of N2O5 at the same time. But nighttime NO on the surface was routinely higher than 100 ppb and no O3 was left. It was unlikely that N2O5 productions could proceed. The N2O5 observed on March 26 was a special case. The dark cloud coverage in the late afternoon and cooler weather (15C) after the shower made it possible for N2O5 to survive.

5) “HNO3 comparison: The comparison of the two instruments for HNO3 $<$ 1 ppbv is really not very convincing that these instruments are measuring the same thing. There seems to be a scatter of about +-400 pptv. What is the detection limit of the ICMS for its 2 hr integration period? The authors state that the intercept is well below the ID-CIMS detection limit (100 pptv for 10 s integration period). How was this detection limit estimated? If the detection limit is simply governed by the number of product ions reaching the detector, then averaging for 2 hour intervals should give a significantly lower detection limit, much lower than the intercept (46 pptv). If the detection limit, or perhaps ’uncertainty’ is a better term, is dominated by other things, eg background uncertainty, than this should be stated as such, and

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one might not then expect the detection limit to decrease substantially with averaging time. There almost seem to be two relationships in the scatter plot for the comparison, one which falls mainly below the line, and one which falls mainly above the line. If the authors were to consider each group separately would there by any characteristic which groups the points (ie different time periods? Or, one set is composed of points for the ’upslope’ of the HNO3 diurnal peak, and the other is the ’downslope’?). This reviewer has encountered similar patterns in scatter plots previously, and in most cases the cause was due to differences in instrumental response time.”

More detailed information about the ICMS has been provided in the revised manuscript including its inlet setup. The DL of the ID-CIMS was based on three times of the standard deviation of the baseline signal. The DL was 100 ppt and 38 ppt for 10-s and 5-min integration time, respectively. The DL of the ICMS is 0.06 ppb. We have added error bars to the ID-CIMS HNO3 data in Fig. 12, which can indicate the variation of HNO3 during the period of average. The error bars can account for the difference in response time between the two instruments, i.e. higher level of variation indicates faster changing of HNO3, which was easier to be captured by the ID-CIMS. Also, the variation of HNO3 affected the correlation more significantly at low concentration data points than at high concentration data points.

6) “What is the composition of the dilution stream (20-150 slpm) for the calibration sequences? Is it N2, or ambient air? Have you tested whether or not this ion chemistry has a water vapor dependence on the sensitivity? This reviewer asks because product ions formed through a clustering mechanism often show a high dependence on [H2O] in the flow tube. Were calibrations conducted in the while in the field? If so, how often?”

The dilution flow used was filtered ambient air. We did not find the ion chemistry depended on water vapor. We did not observe any water clusters either. HNO3 calibrations were conducted in the laboratory and the field (about once every 2 days), but

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N2O5 was only calibrated in the laboratory.

7) “Does all of the SF6- get titrated to SiF5-, or is there still SF6- in the mass spectrum? Have you considered NO3-.HNO3 as a possible interference to your monitoring of the reagent ion at m/z 125? What is the typical ratio of SiF5-.HNO3/ SiF5- for say 10 ppbv of ambient HNO3, under the field campaign conditions? Does SiF5- react with water? If so, is monitoring of SiF5-.H2O needed to account for partitioning of the regent ion to the water cluster under humidity changes (ie does SiF5-.H2O react with HNO3?)? What are typical values for V2 and V3? What is the typical reaction time (drift time)? Is this operation in the kinetic limit or approaching equilibrium, for the HNO3 + SiF5- system?”

The SF6- flow was controlled by a mass flow controller and the magnitude of SF6- peak was maintained below 2% of the SiF5- signal, which is about 1.6 million CPS. The 30SiF5- was about 3% of the 28SiF5- signal thus NO3-HNO3 was negligible. The typical ratio between SiF5-HNO3/SiF5- for 10 ppb HNO3 is 1.3410-3. SiF5- forms weak cluster ions with water. However, we did not observe any water clusters in the mass spectrum. This might be explained by the electric field inside the drift tube (3.2 V/cm at 3 torr corresponding to a value of 3.3 Td), which can break up weakly bounded water clusters. The typical values of V2 and V3 were -32 V and -3 V, respectively. The typical reaction time inside the drift tube was 2.6 ms and the reaction was in the kinetic limit.

8) “Backgrounds: Another way to get a sense of the instrument response is by looking at changes during the background collection. Where, physically, was the nylon filter, used for backgrounds? Was it at the ambient end of the 12 foot tube or at the instrument end? If it was at the ambient end, this would give the reader a better feeling for the response of the 12 foot inlet. If it was at the instrument end, it only tells you about the response downstream from the filter. The zero shown in figure 6 at 13 hrs seems significantly less responsive than the other zeros. Is there a known reason for this?”

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We compared the results between positioning the nylon filter in the front of the inlet and in the front of the drift tube. We found they were comparable. Because the nylon filter had to be manually installed in front of the inlet, it was not a safe practice to climb up the hut ceiling (10-ft above roof top) and stand up there. After several tests, we decided to install the filter in the front of the drift tube during background checks. Again, the inlet memory effect might be more serious than what we expected. We have reported 5 min average data. Regarding the “zero shown in Fig. 6 at 13 hrs”, it was most likely due to a sluggish switch between the inlet and the filter.

9) “Pg 4879, lns 26-28: Do the authors mean through an HNO3 photolysis mechanism which recycles NOx? Is there a reference supporting this statement? Pg 4882, ln 24: This formula is an approximation which is only valid while operating in the kinetic limit (ie. R- $>>$ P-). The authors should either state this, or write the full rate equation.”

We have included detailed photolysis mechanism in the paper. The ion-molecule reaction was in kinetic limit (R-$>>$P-).

10) “Pg 4883, lns 22-23: This line is somewhat confusing. This reviewer assumes the author means that the quadrupole is tuned alternately (hopping) between masses 125 and 186, as opposed to both masses being tuned continuously, which would require two quadrupoles, and two detectors. Did the mass cycle consist only of 2 masses, or were more masses monitored in the hopping cycle? What was the total length of the mass cycle?”

Mass 125 and 186 were measured in cycles. The integration time was 50 ms and 9 s, respectively. Each cycle was about 10 s.

11) “Pg 4885, line 15-17: It is not clear to this reviewer that this sentence is true. The parameters may vary with temperature, and it is not stated that the drift tube was temperature controlled. The parameters may also vary with water vapor (ie changing reagent ions), which was not addressed either. Pg 4888, lns 13-24: Perhaps

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the authors could include a brief description of the ICMS inlet for comparison purposes, size, length, residence time, material, etc.”

We believe the ion-molecule reaction was collision limited and the ion flight speed was strongly affected by the electric field. Nevertheless, we do think we should regulate the temperature of the drift tube region in the future work. The ICMS inlet has been described in the revised manuscript.

12) “Pg 4890, lns 5-8: Quantify this statement further using NOx measurements, and assumptions, or measurements about OH. Pg 4890, lns 14-15: Given the high NOx and intense photochemistry, do the HNO3 measurements taken with the aerosol measurements balance the HNO3 production? Conclusions: It is not clear to this reviewer that there are not other important processes playing a part in the observed nitrate/HNO3 concentrations, including dry deposition and transport.”

A further discussion regarding the HNO3 production and loss processes has been added in the revised paper. OH and boundary height measurements have been used to estimate the HNO3 budget in MCMA. The conclusion section has been revised accordingly.

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