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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.

Anonymous Referee #1

Received and published: 25 April 2008

General comments:

This is an interesting report of HNO3 observations and lack of N2O5 observations made during the 2006 campaign in Mexico City at the T0 super site. Upon completion of appropriate modifications and clarifications and corrections, this reviewer feels that the information presented in this manuscript is unique and interesting and should be published in ACP.

In general the phasing and language of this manuscript needs to be cleaned up. Perhaps one of the co-authors can proofread the manuscript for grammatical corrections. This reviewer will touch on some, but will not get them all.

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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 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.

Specific comments:

The inlet configuration, in particular the inlet length, seems to be a significant issue to this reviewer. From the reviewer’s experience there seem to be several time constants associated with the overall instrumental response to HNO3, not all of which are apparent from the response test shown in figure 4: 1) inlet and drift tube residence; 2) wall

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equilibration; 3) diffusion into and out of inlet material. The inlet response test shown by the authors captures 1 and part of 2, in the opinion of this reviewer. The wall equilibration time is dependent on flow rate, wall material, temperature, and water vapor. The mass accommodation of HNO3 on the inlet wall can be significant, and changes with temperature and water vapor concentration. Diffusion into and out of the wall material depends on the temperature, the wall material, and the wall thickness. This time constant tends to be much longer than 1 and 2. The inlet test shown in figure 4 has a maximum concentration of 40 ppbv HNO3 and decays to less than 4 ppbv in about 12 seconds. While this may seem quite good, this reviewer's guess is that the time constant for moving from 1 ppbv to 100 pptv will not scale, i.e. it will take much longer. The reviewer interprets the concentration dependence of the response time in terms of a shift from the domination of processes 1 and 2 at high HNO3 concentrations to processes 2 and 3 at lower HNO3 concentrations. The ambient HNO3 concentrations (0 pptv - 3 ppbv) for this experiment lie at the lower end of this scale, where processes 2 and 3 can be important. 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).

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).

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

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HNO3 production, rather than the detection limit argument.

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 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.

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?

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?

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If so, is monitoring of $SiF_5^-.H_2O$ needed to account for partitioning of the regent ion to the water cluster under humidity changes (ie does $SiF_5^-.H_2O$ react with HNO_3?)?

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 HNO_3 + SiF_5^- system?

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?

Pg 4879, lns 26-28: Do the authors mean through an HNO_3 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.

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?

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

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reagent ions), which was not addressed either.

Pg 4888, lns 13-24: Perhaps the authors could include a brief description of the ICMS inlet for comparison purposes, size, length, residence time, material, etc.

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.

Technical comments:

Pg. 4880, ln 10: Rephase: eg… ’N2O5 compared to NO3 is relatively unreactive … and can undergo…’. ln 12 and following: ’in-situ’ write as ’in situ’ in italics. Pg. 4881, lns 3-10: This paragraph seems out of place. Perhaps a better location would be after the last paragraph on pg. 4879. Pg. 4882, lns 20-25: remove the ’+or-’ and replace with ’-’. Pg 4883, ln 11: ’similarly’ should be ’similar’. Pg 4887, ln 1: remove ’only’. ln 2: remove ’the plots of the’. Lns 15-16: change ’had been proved’ to ’has been shown’. Pg 4888, ln 1-2: change ’well-fixed by’ to ’fit with’; remove ’showing that the inlet had little memory effect’. Pg 4890, ln 9-11: This sentence needs to be rephrased. Lns 12-15 Rephase, considering above comments. Pg 4892, ln 19: Change ’on’ to ’at’. Pg 4893, ln 8: Change to ’Although the ID-CIMS measures the sum of NO3 and N2O5 as NO3- …’

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