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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 #3

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General Comments: This paper describes results of measurements of nitric acid and N2O5 using the technique of ion drift – chemical ionization mass spectrometry (ID-CIMS) during the 2006 Mexico City Metropolitan Area (MCMA) field campaign. Interesting data is presented in this paper that could be valuable in understanding NOx chemistry within the Mexico City basin. The analysis of the data is weak, however, and needs to be much more strongly tied to other measurements, of which there are many, and to detailed modeling to be of any real value. I recommend significantly reducing the ID-CIMS section (2.1), and expanding the analysis of the results.

Specific Comments: 1. Introduction: It is stated that MCMA is

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the biggest megacity. This is incorrect at present, and changing rapidly. Please see the follow for discussions of megacity rankings: (1) http://www.dailytimes.com.pk/default.asp?page=2008%5C02%5C23%5Cstory_23-2-2008_pg12_9 (2) ‘Evaluation of emissions and air quality in megacities’ that appeared in the journal ‘Atmospheric Environment’ (2008 vol:42 iss:7) ; (3) http://en.wikipedia.org/wiki/Megacity ; The description of the emissions of MCMA appears to use data from Molina and Molina, 2002, and are also likely out of date. Please use up-to-date emissions, and at least in the case of NOx emissions, describe how they are relevant to this paper. Perhaps compare them to other cities that have been studied extensively. The description of the atmospheric chemistry of nitric acid and N2O5 (pp middle 4879- middle 4880) is quite brief. I recommend expanding this to include loss of nitric and N2O5 on aerosols, especially since aerosol nitrate is discussed later in the paper. Also, discuss the roles of dilution of emissions by background air, the changing height of the boundary layer, and the possible role of direct emissions of nitric acid. This is where some detailed modeling and perhaps a diagram of HNO3 and N2O5 chemistry and physical processes would be useful. Next the variety of available techniques is discussed. It mentions that CIMS has several advantages, but doesn’t say how ID-CIMS fits into the picture. Do conventional CIMS and ID-CIMS have the same advantages and disadvantages? In other words, is ID-CIMS the best technique for this problem? 2. Experimental Next 4 pages (4881-4885) are devoted to a partial description of the instrument and the method. While I appreciate the value of proper operation and assessment of instrument operation, this is perhaps too much instrument discussion at the expense of data analysis. In particular, the discussion of details of ion mobility and the ab initio ion-molecule parameters could be left out or shortened greatly, since calibrations of the instrument response are used (section 2.3). While it is interesting that the calibrations and the calculations agree within a factor of 2, this could be stated without all the detail. Refer to another paper for the details. In section 2.4 the instrumental setup and inlet characterization are described. What is a red flag for me is length of

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the inlet (12 feet) and residence time (0.4 s). Nitric acid is known to be very difficult to sample. Why didn’t you use the short inlet that you used for N2O5? Why didn’t you use a narrow diameter inlet tube to reduce the residence time? It is stated (top of page 4888) that memory effects are not a problem, but I don’t follow from the data taken and the fitting done to that conclusion. It appears to me that an inlet with a 0.4 s residence time that has a decay lifetime of 5 seconds has a serious inlet memory problem! At the end of this section, other measurements are mentioned, but I believe there were much more species measured that there at the T0 site during MCMA 2006. The authors should make use of as much of the chemical (OH, NO2 and others) and physical data (e.g. boundary layer height, wind speed) as possible in their analysis. 3. Results and discussion Two days of nitric acid data are discussed in detail that supposedly represent a polluted and a relatively clean data. Why not show all of the data? Near the end, there is a jump (it appears to me) to the conclusion that gas to particle partitioning controls the nitric acid and aerosol nitrate behavior. I don’t see how this conclusion could be reached from the observations shown. Is there some further analysis you performed, but didn’t discuss? It is mentioned that N2O5 observations are mostly below the detection limit and therefore cannot be important to NOx chemistry in MCMA. This is definitely not necessarily the case! There could be large flux through N2O5 (large source and large sink) that could influence gas phase nitric acid and aerosol nitrate and still remain below the instrument detection limit. This needs to be assessed through some kind of modeling (it could be quite simple). Also, why not average the data beyond 10 s to reduce the detection limit. I am sure that 5 minute data with detection limits of a few ppt would be valuable. 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.

Technical Corrections: While the English usage is not bad, there remain many errors. After the revisions, I suggest the author seek help from the co-authors and perhaps others in the home institution in correcting typos and grammar usage errors. Page 4878, abstract, line 2. Probably should include “gas-phase” be-

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fore HNO3 to make it clear that these are observations of gas-phase nitric acid. Line 15. Suggest “N2O5 was found to be below the detection limit…” Lines 20-21. Suggest “…produced from the reaction of OH with NO2 and was regulated by gas to particle partitioning…” Page 4878, introduction, line 25-26. Suggest “…(MCMA), one of largest megacities in the world at present, has suffered from very poor air quality, particularly as related to ozone and particulate matter…” Page 4879, line 1. Suggest “As the home of greater than 20 million residents…” Page 4879, line11. Suggest “…higher than 110 ppb for over 80% of all days, and a peak O3 concentration of frequently (more than **10%** of all days) more than 300 ppb…” [It would be good to describe the situation in 2006 as well.] Page 4879, line18. Suggest “…in the MCMA is one of the critical pieces of information that is required to develop effective O3 control…” Page 4879, line 21. Suggest “NO2 + OH + M → HNO3 + M (1)” Page 4879, line 23. Suggest “…deposition is considered to be an irreversible sink for NOx…” Page 4879, line29. Expand the discussion to describe how long range transport of HNO3 can contribute to O3 production (requires process to convert HNO3 to NOx). Page 4880, line 1. Suggest “During the nighttime, NOx will react with to form the nitrate radical…” [It isn’t titration since that requires addition of NO equal in amount to the initial O3, which virtually never happens.] Page 4880, line 5. Move reaction 5 to below the text where it is discussed (after line 12). Page 4880, line 7. The equilibrium coefficient as written is incorrect. It should be 3.0x10-27exp(10990/T) [which formula was used for Figure 8?] Page 4880, line 10. Suggest “Compared with NO3, N2O5 is relatively unreactive …” Page 4880, line 12. It says that in situ observations of HNO3 and N2O5 are indispensible, but this paragraph doesn’t really tell me why. Page 4880, line 16-18. Suggest “…including nylon filter (Anlauf et al., 1988), mist chamber (Talbot et al., 1990), denuder (perrino et al., 1990; Simon et al., 1995), luminal (Hering et al., 1988), and chemical…” Page

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4880, line 25-26. Suggest “…have been performed by cavity ring-down spectroscopy (CRDS) (Brown et al., 2002) and CIMS (Huey et al., 1995).” Page 4881, line 1. Suggest “…N2O5 concentrations range from a few ppt…” Page 4881, line 3. Suggest “…have been conducted within the MCMA, most recently in 2002, 2003 and 2006.” Page 4881, line 5. Suggest “…campaigns were to fully characterize the current air quality, to investigate the underlying chemical…” Page 4881, line 9. Suggest “…campaign using a recently developed…” and “…technique in its first field deployment.” Page 4881, lines 17 -21. The permeation device is explained, by the reason for the glass beads is not. Page 4881, line 21. Suggest “…to produce the ions;” Page 4881, line 26. Suggest “…the reagent ions are produced…” Page 4882, line 11. Should be “Varian VT-551”. Page 4882, line13. “…ambient air into the inlet, one liter of which is drawn into the drift tube…” Page 4882, line 14. Suggest “A flow of N2 carrying the reagent ions mixes with the air sample within the drift tube…” Page 4882, line 18. Suggest “…in that it enables quantification of neutral species…” Page 4882, line 23. Suggest “The relationship between the ion signals, the ion-molecule rate coefficient, the initial analyte concentration, and the reaction time, ∆t, is given by:” Page 4883, lines 9-10. In the atmospheric sciences community, pressure is usually given by a capital letter P. Page 4883, line 11. “The ion chemistry use to detect HNO3 is similar to that described…” Page 4883, line 8-9. “…doped with ˜0.1% SF6 flows through the ion source region, where an electron attaches to the SF6.” Page 4883, equations 11-12. Move equation 11 after line 19, and equation 12 after line 21 (after the chemistry is discussed. Page 4883, line 21. Suggest “During the field campaign, the count rates of the reagent ion (corresponding to the most abundant isotope at m/e=125, 30SiF-5) and the product ion…” Page 4884, line 1. Suggest “N2O5 is detected using the I- reagent ion…”

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Page 4884, equation 14. Move equation 14 below line 6. Page 4884, line 17. “…we performed ab initio calculations…” Page 4885, line 2. Suggest adding a reference for the model here. Page 4885, line 9. Are there similar systems for which measured ion-molecule data exist to compare with your model? That would give the reader an idea of the accuracy of the calculations. Page 4885, line 11. The inclusion of “in principle” makes it sound like the technique doesn’t work. I think you mean that the technique can determine concentrations without calibrations. I am very skeptical of this, and indeed data presented later in this paper show this is not the case. As I indicated above, since you calibrate, the calculations are uneccesary! Page 4885, line 19. Suggest “…is temperature controlled at 40.0 °C.” Page 4885, line 22. Please indicate the range of concentrations used for calibration. Also, suggest “….tube in which it is mixed with a 20 to 150 slpm dilution flow.” Page 4886, line 26. Is there interference from HNO3 in the N2O5 determination by UV absorption? If so, you should indicate how much it could be, and what steps were taken to minimize it. Page 4887, line 1. Suggest “…and find that less than 6%...” Page 4887, line 5. Suggest “…are performed once every few hours…” Page 4887, line 6. Suggest “…air flow through a two-inch nylon filter.” Page 4887, line 8. Suggest “…through a 12-inch long heated metal tube.” Page 4887, line 9. Suggest “…integration times are estimated at 100 ppt and 20 ppt, respectively.” What are these detection limits based on? Analysis of the base line at the 2-sigma (or other) level? Please give some indication as to how you arrived at these detection limits. Also, indicate the detection limits at some longer integration times (say 1 minute and 5 minutes). Page 4887, line 15. Suggest “…cluster of buildings with similar height.” And “…which had been proven to…” Page 4887, line 17. Suggest “…minimize surface effects, ambient air…” Page 4887, line 18. Why was the sampling line so long? Why did you use such a large diameter tubing? Why not pull the large flow through 3/8” o.d. tubing, which

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would result in a residence time of only a few milliseconds? Page 4887, line 20. Qualify “…dry and relatively cold.” Give the average %RH and maximum and minimum temperature. Compare with climatological averages. Page 4887, line 28. Suggest “…and the HNO3 signal decreased…” Page 4888, line 1. Suggest “…signal was well-fitted by…” Page 4888, line 3-4. Suggest the following to correct the English, but I am not sure I agree with the conclusion: “…data points is less than 20% if data is collected every 9 s.” Page 4888, line 9. Suggest “This version of the AMS was equipped …” Page 4888, line 11. Suggest “…about the AMS are described by DeCarlo et al. (2006).” Page 4888, line 17. Suggest “…to remove the gas phase species.” Page 4888, line 19. I don’t know what a “cooled maze” is. Page 4888, line 27-28. “… were 0.2 ppb for both species…” and “…at 1-min intervals.” I don’t think the Thermo Scientific can do 0.2 ppb O3 in 1-minute. I think it is more like 1 ppb in 1-minute. Page 4889, line 5. Suggest “… to 17 March were not possible.” Page 4889, line 6. Suggest “… to the N2O5 measurement mode.” Page 4889, line 8. The word “diurnal” normally means over a full 24-hour cycle in atmospheric measurements, although technically it can mean daytime measurements. It is stated that the day was “sunny and hazy”. Do you have supporting data (e.g. UV radiation measurements)? Page 4889, line 9. Suggest “Due to its production from photochemical sources, HNO3 starts to accumulate after sunrise.” Suggest showing sunrise and sunset on the figure unless UV flux or j-value data are included. Page 4889, line 11. Suggest “After that, it steadily increased, reaching values near 3 ppb at 2:00 p.m, when photochemical activity was near its maximum.” Again supporting data (like the OH concentration) would be helpful to see when photochemical activity maximizes. Page 4889, line 13. Suggest “… HNO3 remained at peak levels, and started to decrease sharply after about 4:00 p.m.” Page 4889, line 16. Suggest “…

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other HNO3 sources present.” Page 4889, line 17. Suggest “… no detectable N2O5 was present ($<$ 20 pptv).” Page 4889, line 21. Suggest “… when HNO3 production was expected to be maximum.” Page 4889, line 24. Suggest “Similar to the previous day’s observations, values near 300 pptv HNO3 were still observed at about 6:30 p.m.” Page 4889, line 25. Suggest “Again, when the ID-CIMS…” Page 4890, line 2. Suggest “…and reached a maximum value of…” Page 4890, line 7. Suggest “… given the large NOx emissions in the MCMA…” Page 4890, line 9-11. N2O5 could be at low levels and still be an important HNO3 source, depending on the rate of production and the rate of conversion to HNO3. Some sample calculations might be useful here, or perhaps a graph showing a range of assumptions. Page 4890, line 12. I think you need to be more rigorous before you state that “It is evident that gas-phase chemistry alone could not explain the observed slow rise in the HNO3…” Perhaps a figure that shows what HNO3 would be expected to do based on the observed OH and NO2 values would be convincing. Page 4890, line 26. Suggest “… was expected to be a solid.” Page 4890, line 27. Suggest “… High ammonia (NH3) concentrations ($>$ 35 ppbv in the early morning) were reported…” Page 4891, line 3. Suggest “… inside the MCMA increased since 2003.” Page 4891, line 14. Suggest “… there appeared to be a good correlation…” Page 4891, line 21. Suggest “…partitioning hence likely accounts for the…” Page 4892, line 2. Suggest “This probably explains the difference…” Page 4892, line 19. Suggest “…nighttime chemistry at the surface.” Page 4892, line 24. Suggest “…and the y-intercept was much smaller than the detection limit of either instrument.” Page 4894, line 18. Suggest “The authors are grateful…” Page 4900. Suggest “Varian VT-551” Page 4901, Suggest “Plot of calculated versus volumetrically…”

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