Atmos. Chem. Phys. Discuss., 8, S2960–S2963, 2008
www.atmos-chem-phys-discuss.net/8/S2960/2008/

Atmospheric
Chemistry
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Discussions

# *Interactive comment on* “On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City” *by* C. J. Hennigan et al.

**C. J. Hennigan et al.**

Received and published: 23 May 2008

Author Response to Anonymous Referee 1

We would like to thank the Referee for the detailed and insightful review.

Comment 1: **8220;8230;Entrained air presumably has low hydrocarbon concentrations which should drive semivolatiles from the aerosol to gas phase. Thus the authors conclusion appears reasonable. However, I’m not sure that it is justified by the data; I don’t think that the fact that there is a very good correlation between WSOC and $NH_4NO_3$ automatically rules in favor of a 1/3 - 2/3 split for both species. Part of the correlation is generated in the growth phase. Part is due to dilution which (may) act on both compounds similarly. Additional correla-**

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**tion will be generated because the lifting boundary layer which causes dilution, also changes the thermodynamics in a way that favors evaporation of $NH_4NO_3$.**

We agree with the Referee's comments, which are similarly expressed by Referee 2. Though the high correlation between WSOC and $NO_3^-$ is compelling, it is not enough to conclude that WSOC experienced volatile losses equal to $NO_3^-$. So, we have substantially revised our treatment of WSOC to be more quantitative and feel that the changes now provide adequate support for the stated conclusions. To do so, we have used available aircraft data from 3/29 to estimate the aloft WSOC concentration. (A similar measurement of WSOC was made on the NSF C-130, by our research group, during MIRAGE). Along with the surface data, this allows us to actually estimate photochemical production, and also dilution/evaporation losses. These changes are reflected in substantial revisions of both WSOC (formation/loss) sections.

Specific Comment 1: **P 4816: Thermodynamic model to determine partitioning of nitrate between gas and aerosol phase: The complete partitioning of $HNO_3$ into the gas phase is justified only by mentioning low T, high RH, and excess ammonia gas, with a reference to Fountoukis et al., (2007). Additional information would be useful. It is not even mentioned in this paper that gas phase $HNO_3$ (by difference) and $NH_3$ measurements were made at the surface site.**

We have clarified this with additions to the 'Methods' section. We have noted that $NH_3$ (g) was measured and that its concentrations were high. However, we have not explicitly used the $HNO_3$ (g) data. We do not go into further details since it is covered in Fountoukis et al. [2007] and our goal is to maintain a focus on SOA.

Specific Comment 2: **p 4816, Eq. (2) It is concluded from Eq. 2 that "75% of the observed nitrate concentration increase was due to secondary photochemical production while approximately 25% was due to entrainment from the free troposphere". I suspect that the error bars on these numbers are quite high. OH is difficult to measure and NO2 is calculated rather than observed. A positive**

**contribution to the time rate of change of aerosol nitrate implies that the concentration of nitrate aloft (free troposphere) is greater than at the surface. The aloft region is at an altitude below 1 km and presumably contains pollutants from the previous days boundary layer. My sense of the errors in Fig 2 is that it is equally likely that the entrainment term is negative. Fortunately, the entrainment; chemical production numbers do not impact this papers main points.**

We agree, and have added a discussion of the assumptions and uncertainties associated with estimating nitric acid production in our analysis (New ’Model Assumptions’ section). Furthermore, we have compared the model predicted $NO_3{}^-$ aloft, using the predicted $HNO_3$ production, to the nitrate observed aloft from the C-130. We note that differences could be due to the $HNO_3$ production rate and give ranges in the production and dilution rates of $NO_3{}^-$ based on these two methods.

Specific Comment 3: **P 4818 100 ppb CO and 6500 ppm $H_2O$ aloft. It would help the reader to know what the altitude range is for entrainment between 11:00 and 12:45. I assume that at this time of day, boundary layer heights are greater and the free troposphere is cleaner than determined from Eq. 2. There were balloons and sondes at T1. Is there data to back up the assumed CO and water vapor concentrations on March 29?** We have added more details on the BL expansion to the text. Additionally, we have used aircraft data from 3/29/2006 to estimate the aloft water vapor mixing ratio. Analysis using CO has been deleted.

Specific Comment 4: **P4820, lines 11-14. The 20% of WSOC apportioned back to the gas phase should be explained as the ratio of 0.9 $\mu$g m$^{-3}$ lost to peak (about 5) $\mu$g m$^{-3}$ WSOC.**

We have addressed this comment with our revision of the WSOC analyses (see Comment 1 above).

References:

Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., VanReken, T., Fischer, M., Matías, E., Moya, M., Farmer, D., Cohen, R. C., Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006, *Atmos. Chem. Phys. Dis.*, 7, 9203-9233, 2007.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4811, 2008.

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