Atmos. Chem. Phys. Discuss., 8, S2966–S2971, 2008
www.atmos-chem-phys-discuss.net/8/S2966/2008/


Atmospheric Chemistry and Physics 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 2

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

Comment 1: **What is happening in the afternoon, do these species correlate as well? It is a little disappointing to see these analysis performed on such a short time period (3 days), knowing that authors dispose of about 1 month of data. I suggest that a scatter plot WSOC vs. nitrate for the whole month of March be added in the paper, and these correlations further discussed (the influence of biomass emissions can be screened using acetonitrile tracer). Other periods throughout the month were characterized by factors which would complicate the**

**analysis (e.g., high dust, biomass burning contributions).**

We chose only this three-day period for our analysis for several reasons: 1. Lowest contribution from biomass burning (see Stone et al. [2008], and Comment 4, below). 2. Consistent meteorology and pollutant profiles each day. 3. Highest nitrate concentrations for the entire study. We feel that focusing on a three-day period with the best data for our analysis makes a stronger scientific case than a more complex but broader analysis.

**I am not fully satisfied by statistical indicators presented in the paper. What is the statistical power here? Do the authors believe that the sample sizes are sufficiently large to believe these correlations are accurate? The confidence intervals should be calculated for $R^2$'s, which I believe should be very wide because N is so small;even if authors can establish that WSOC and nitrates are highly correlated, it does not systematically imply that they have the same "sources and atmospheric processing" (p.4819, l.15) and that "the volatility of WSOC is similar to that of nitrate (p.4820, l.8)" Therefore, I think that a further discussion on the WSOC behavior is needed to justify the evaporation of SOA components.**

We agree with the Referee's comments, which are similarly expressed by Referee #1. Though the high correlation between WSOC and nitrate is compelling, it is not enough to conclude that WSOC experienced volatile losses equal to nitrate. 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 our aircraft data from 3/29 to estimate the aloft WSOC concentration. With BL data, this allows us to estimate photochemical production, and also dilution/evaporation losses. These changes are reflected in revisions of both WSOC sections. (Also, see the discussion to reviewer 1's first comment).

**Also, the afternoon peak should be discussed in the paper.**

We recognize that the peak in WSOC and nitrate concentrations following the noon-



ACPD

8, S2966–S2971, 2008



time concentration decrease may be interesting and may merit future analysis. We plan to do this in the future. However, for the present analysis, we have chosen to include only the initial AM concentration increases and subsequent losses to maintain a clear focus to this paper. Meteorological data suggests that this afternoon peak may be more due to transport than local processes, but this will require further investigation.

**Finally, as the study is also based on the assumption that ISORROPIA-II model reproduces correctly the gas-aerosol partitioning of inorganic, a discussion on the accuracy of the predicted nitrate concentrations and aerosol water content should be presented in the paper, even if the paper of Fountoukis et al., 2007 is referenced here.**

Discussion of ISORROPIA's accuracy (with reference to Fountoukis et al. [2007]) has been included. We added (in 'Methods' section, 3rd paragraph): "Application of the model in Mexico City during the MILAGRO study produced predictions that agreed with measured concentrations within 20% [Fountoukis et al., 2007]."

Comment 2: **Could authors give an estimate of the accuracy expected for the box model results, and its variability during the day?**

Accuracy of box model results has been provided. The following has been added (to 'Methods' section, last paragraph): "The mean uncertainty in the box model results, due to uncertainty in BL height measurements and in the measured pollutant concentrations, was estimated to be 35%."

**I suggest that values used for the PBL height be indicated in the paper. An additional plot including PBL height, wind speed and acetonitrile concentrations could be added in the manuscript.**

PBL heights have been added to the paper, and wind speeds have been added to Figure 1. We have not added acetonitrile data since we clearly state that biomass burning impacts were minimal for the three days analyzed based on the measurements



ACPD

8, S2966–S2971, 2008



of levoglucosan at the site and reported in Stone et al. [2008]. We do note ('Methods' section, 2nd paragraph) the low correlation ($R^2$ = 0.18) between WSOC and acetonitrile for 3/27-3/29.

**Does the term 'entrainment from the free troposphere' account for aerosols contained in the residual layer (from previous day) that mixes during early morning with newly emitted/formed particles?**

We use measurements of the BL height measured by Shaw et al. [2007] via Wind Profiler Radar as the definition of the delineation between the well mixed BL below and the isolated air masses above. As we note, the aircraft measurements of water vapor are consistent with the BL heights and confirm this clear delineation. We do not attempt to delineate residual layers from other layers above; the analysis is based on observations.

**On page 4816, what values are used for $NO_3^-$ concentrations aloft?**

Nitrate concentration aloft has been added to the paper. Box model analysis predicted an aloft nitrate concentration of 6.4 $\mu$g m$^{-3}$. We then compare this value to observations on the C-130 ('$NH_4NO_3$ Formation' section, paragraphs 1 2).

**In the section 'Nitrate loss', what is the form of the Eq. (2) after all new assumptions are considered (photochemical production and entrainment are neglected)? I do not understand how the 66% dilution and 34% evaporation terms have been computed. This part needs to be explained more clearly, and the new form for the Eq. (2) clearly written.**

The 'Nitrate Loss' section has been revised to explain the calculation more clearly.

**Authors assume aloft CO and water vapor concentrations of 100ppb and 6500ppm, where do these values come from?**

We have used aircraft measurements of water vapor from 3/29/2006 to estimate the aloft water vapor mixing ratio during these three days. Analysis using CO has been



ACPD
8, S2966–S2971, 2008

deleted.

Comment 3: **I suggest that the description of the box modeling approach and the ISORROPIA II model be included in the 'Methods' section.**

Done

Comment 4: **In section 3.3, could authors give acetonitrile values that are typical for biomass and anthropogenic air masses? I think that a time series of acetonitrile (see comment 2) is needed in order to convince us that WSOC are from anthropogenic origin.**

See response to second Comment 2 above. We do not add acetonitrile to Figure 1. Instead, we reference Stone et al. [2008] ('Methods' section, 2nd paragraph): "Stone et al. [2008] applied a chemical mass balance model to source apportion particle OC at T1 and attributed less than 10% of total OC to wood smoke for the 3/27-3/29 period." The Stone analysis is based on 12 and/or 24 hour averages. We have also added that, based on higher time resolution data (average over minutes), there is no correlation ($R^2$ = 0.18) between acetonitrile and WSOC on these three days. This should be sufficient to clearly demonstrate that there is very little influence from biomass burning on WSOC during these three days.

**Figure 3: Please include the number of data used to compute correlation coefficients.**

Done

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.

Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J., Schauer, J.



ACPD

8, S2966–S2971, 2008

J., Source apportionment of fine organic aerosol in Mexico City during the MILAGRO Experiment 2006, *Atmos. Chem. Phys.*, 8, 1249-1259, 2008.

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



ACPD

8, S2966–S2971, 2008