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Comment

***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.***

**Anonymous Referee #2**

Received and published: 1 May 2008

This paper investigates the volatility of secondary organic aerosol (SOA) components measured downwind of Mexico City during the MILAGRO field experiment. This is an important topic as the gas-aerosol partitioning of semi-volatile compounds largely determines the chemical composition of atmospheric particles, as well as their hygroscopic and optical properties. While the absorption of semi-volatile material into the inorganic aerosol phase (mainly ammonium nitrates) is fairly well constrained from thermodynamic modeling, the partitioning into the organic/aqueous aerosol phase (SOA) require better characterization that cannot be achieved from sole chamber measurements. In this study, analyses of diurnal variability of ambient water soluble organic aerosols (WSOC) provide valuable insights into the semi-volatile nature of SOA. As-

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suming the similar formation and partitioning behavior as for ammonium nitrate component, authors estimate that 1/3 of WSOC produced in the early morning in Mexico City are semi-volatile and desorb back to the gas phase around noon suggesting the presence of non-acidic secondary organic aerosols. Although I recognize the importance of these results, I am not completely convinced by the methodology and assumptions used to derive these conclusions, and would like to see the following comments addressed prior to the publication:

**Comment1:**

The main conclusion on the semi-volatile nature of SOA is based on the assumption that WSOC and nitrates are highly correlated and therefore undergo the same chemical and dynamical processing in the boundary layer.

First, 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. Also, 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).

Second, 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)'. I agree that the mixing in the PBL should affect in the same way both WSOC and nitrate species however it is less obvious that the chemical production and thermodynamic equilibrium act the same. The figure 1a shows that nitrate concentra-

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tions drop by 82% (14.9 ug/m<sup>3</sup>) between 11am and 12:45pm on March 27, and this decrease is attributed for 2/3 (9.8 ug/m<sup>3</sup>=54%) to the enhanced PBL dilution and 1/3 (5.1 ug/m<sup>3</sup>=28%) to particle evaporation. For WSOC we know that they are following the same decrease due to PBL mixing, which explains the decrease of 54% in concentrations, and if WSOC were evaporating in a similar way to nitrate we should observe an additional 28% decrease, which will correspond to a total decrease of 4 ug/m<sup>3</sup> in WSOC concentrations, which is not observed from the data (decrease of only 2.9 ug/m<sup>3</sup>).

Species	11am	12:45pm	Drop in conc	Drop in conc	Drop (PBL)	Drop (evap)
Nitrate	16.9 ug/m <sup>3</sup>	2 ug/m <sup>3</sup>	14.9 ug/m <sup>3</sup>	82%	54%	28%
WSOC	4.9 ug/m <sup>3</sup>	2 ug/m <sup>3</sup>	2.9 ug/m <sup>3</sup>	59%	54% the same	<b>only 5%</b>

Based on these remarks, I am not convinced that WSOC evaporates as much as nitrate.

Also, we know that evaporation of ammonium nitrate is temperature and humidity dependent, and that the increase of T will conduce to its evaporation. From figure 1 we can see that both concentrations of nitrate and WSOC start decreasing at the same time (11am), probably first due to the PBL rise until 12pm, and then we can see that only nitrate continues to decrease further until 12:45pm while WSOC concentrations start to increase again. The nitrate decrease between 12 and 12:45pm coincides with the rise of Temperature from 19-23 degrees, indicates that it evaporates most likely. We do not see that same behavior for WSOC as clearly as for nitrate from plots presented on Fig1.

Therefore, I think that a further discussion on the WSOC behavior is needed to justify the evaporation of SOA components. Additional days could be analyzed in order to see if the conclusions are consistent. Also, the afternoon peak should be discussed in the

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paper.

Finally, as the study is also based on the assumption that ISORROPIAII 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.

### **Comment 2:**

I would like to come back to the box modeling approach and the assumptions used in this study. In order to represent the temporal variability of nitrate concentrations, authors estimate the production and loss fluxes. Advection and dry/wet deposition are neglected and 90% of total nitrate ( $\text{HNO}_3 + \text{NO}_3$ ) is assumed to contribute to particulate nitrate production. Could authors give an estimate of the accuracy expected for the box model results, and its variability during the day?

Also, 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.

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?

On page 4816, what values are used for  $\text{NO}_3$  concentrations aloft?

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.

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

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**Comment 3:**

In the 'Methods' section the authors only present the data used in this study. The description of the methodology is mixed with the description of the results under the 'Results and discussion' sections, which make it difficult to follow. I suggest that the description of the box modeling approach and the ISORROPIA II model be included in the 'Methods' section.

**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.

**Figure 3**, please include the number of data used to compute correlation coefficients.

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