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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.

Anonymous Referee #1

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Review of "On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City" by Hennigan et al for Atmos. Phys. Chem. Discuss

In view of the order of magnitude discrepancies between some observed and calculated organic aerosol concentrations, this paper addresses an extremely important question – What is the fate of semivolatile organic aerosol? This paper presents what may be the first field evidence that a portion of the semivolatile aerosols evaporate. From smog chamber experiments, one would expect this to be the case – but from the field measurements showing an excess amount of organic aerosol one

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would expect it not to be. This is an interesting problem which the authors have attacked in an ingenious manner. The conclusion is reached that 1/3 of the organic aerosol formed in the morning evaporates around noon, during the period where there is rapid boundary layer growth. 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.

This paper address what happens to WSOC during the early afternoon by comparing its time dependence to that of NH4NO3. By a combination of thermodynamic modeling and time series observations of boundary layer height and surface NH4NO3 concentrations, it is determined that 1/3 of the NH4NO3 concentration decrease is due to evaporation and 2/3 to dilution in the growing boundary layer (11:00 – 12:45). I am troubled by the next step in the analysis. WSOC and NH4NO3 concentrations are correlated (r2=0.88) during the time period from 8:00 to 12:45. On this basis it is estimated that the decrease in WSOC between 11:00 and 12:45 is due 1/3 to evaporation and 2/3 to dilution, i.e. the same proportions as for NH4NO3. However, the fractional decrease in WSOC and NH4NO3 are different, 58% and 82%, respectively. The percent decrease in NH4NO3 due to dilution is 82% times 2/3 = 54%, which is almost identical to the decrease in WSOC. I don't think that the fact that there is a very good correlation between WSOC and NH4NO3 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 correlation will be generated because the lifting boundary layer which causes dilution, also changes the thermodynamics in a way that favors evaporation of NH4NO3.

I don't know whether my argument is fully correct but I would like to see it addressed in a revised paper.

Specific comments

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P 4816: Thermodynamic model to determine partitioning of nitrate between gas and aerosol phase: The complete partitioning of HNO3 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 HNO3 (by difference) and NH3 measurements were made at the surface site.

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.

P 4818 100 ppb CO and 6500 ppm H2O 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?

P4820 lines 11 – 14. The 20% of WSOC apportioned back to the gas phase should be explained as the ratio of 0.9 ug m3 lost to peak (about 5) ug m3 WSOC.

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

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