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Atmospheric
Chemistry
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Discussions

Interactive comment on “Gas/particle partitioning of water-soluble organic aerosol in Atlanta” *by* C. J. Hennigan et al.

Anonymous Referee #1

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The authors present measurements of waters-soluble organic carbon in both the particle (p) and gas phase (g) over 4.5 months in summer 2007 in Atlanta. Based on this huge data set, they correlate the WSOC(p) concentration as well as the partitioning ratio Fp (=WSOC(p)/(total WSOC) and the concentration ratio (p/g) to various ambient parameters such as relative humidity, temperature, NOx and ozone levels. While previous studies of organic partitioning only focused on selected species (groups), the current approach gives an overall idea of the total WSOC budget and important parameters that affect its partitioning. This approach is certainly highly useful and complementary to prior SOA studies in order to understand SOA formation, even though it only provides little information of the chemical processes and speciation of individual compounds. Thus, this study is of high interest to understand SOA formation and falls

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into the scope of Atmospheric Chemistry and Physics. I have a some thought and comments that should be considered before publication.

General comments Section 3.1: Do you have any means to compare also the total masses instead of just the carbon mass of WSOC? The comparison of the slopes of WSOC(p)/(g) to WS organic mass (p)/(g) would give information on the oxidation state of WSOC.

Section 3.2.2. What value for the Henry's Law constant would be required to explain the observed partitioning? Such a value should be easy to derive based on the measured WSOC(p), WSOC(g) and calculated aerosol water content. Is it in the order of magnitude as suggested by lab studies by e.g., Kroll et al., 2005; Volkamer et al., 2008, who observed KH $>$ 10(7) M atm-1.

Section 3.2. and Fig 6: What 'average inorganic aerosol composition' is assumed here? How would the water mass change if also the uptake of water by WSOC would be considered? (Some comments should be added in the text).

p. 647, l. 7 ff: The main products of terpene oxidation are less water-soluble (e.g., pinonaldehyde) than those of isoprene (some of its major oxidation products are glyoxal and methylglyoxal). This might be the reason of the different dependencies on liquid water. Something about these facts should be added in order to clarify that the lab studies are not contradictory. Section 3.2.3: It is actually not the absolute NOx level but the ratio of organic C/NOx that determines the fate of RO/RO2 radicals. How does Fig. 7b change if you plot Fp vs the NOx/WSOC(g) ratio?

p. 648, l. 25ff: Can you perform an estimate of how much sesquiterpenes could contribute to total SOA (e.g., product of emission flux and SOA yield)? I assume that despite their high yields, the absolute SOA mass would be small as compared to monoterpenes and isoprene.

p. 649, l. 1ff: It is true that under high NOx conditions the formation of aldehyde compounds is favored. However, they are more water-soluble (e.g., glyoxal) than the low-volatility hydroperoxides. Thus, should not be expected that you also see an increased SOA mass at high NOx conditions and high RH since water-soluble products are readily taken up and eventually even oxidized to other species (e.g., Ervens et al., 2008)?

p. 649, l. 16: As for NOx, also the absolute ozone level might not be the key parameter but the ratio of WSOC/ozone. Is there any correlation of these concentrations?

p. 653, l. 7ff: The conclusion that the combination of (i) the presence of liquid water and (ii) the subsequent reaction with WSOC(p) leads to enhanced SOA formation. Indeed it is in agreement with recent laboratory studies. In such lab studies, however, no consistent conclusion can be drawn about the (ir)reversibility of such heterogeneous reactions. Do you have evidence about that from your measurements? E.g., have you encountered periods of high RH followed by low RH where the total WSOC(p) was higher than in periods in the opposite order? (This could be a hint of irreversibility).

Section 3.3: These considerations of controlling SOA formation by the means of NOx are highly useful. However, by changing the NOx level the yields of biogenic and anthropogenic precursors would change with opposite signs. So, could you comment on what would be expected in terms of the anthropogenic vs biogenic SOA fraction by controlling NOx levels?

Specific comments p. 636; l. 18/19: What is meant here by ’phase state’?

p. 646, l. 24: What is meant here by ’water uptake’? Uptake of water or uptake by water?

p. 650, l. 2: An absorbing medium always implies a volume process (as opposed to adsorption that occurs on a surface).

p. p. 655, l. 22: I think it is misleading to say that there is ’no net dependence on temperature’. There is ’no net effect’ since in reality there are two effects (with opposite signs)

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that obviously just cancel each other (higher emission rates and less partitioning due to higher volatility).

Fig. 1: Why does the regression line has an intercept? It implies that WSOC(g) could become zero. I think it would be more reasonable to force it through the origin which would also be consistent with your approach in Figs. 8b and 9b.

Fig. 7: The dimension of x-axis seems odd. Replace it by (ppb). Strictly speaking, ppm (or ppb) is not a concentration but a mixing ratio. This should be replaced in the legend and text.

Fig. 9b. Could this figure be combine with Fig. 8b? It might be nice to see in one plot the average as well as the individual RH regimes.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 635, 2009.