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Atmospheric
Chemistry
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Discussions

Interactive comment on "Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies" *by* B. Ervens et al.

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We thank the reviewer for his/her careful comments on our manuscript that will help to clarify several sections. We address the comments in detail below. In addition, we have modified text at a few places in order to improve readability and added some references that came to our attention after submission of the first version of the manuscript in order to give a more complete review of the most recent literature related aqSOA formation.

General reviewer comment: Review of Ervens et al. "Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies." In this paper the authors review the literature on aqueous phase

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organic reactions. In addition to secondary organic aerosol (SOA) formed from the gas/particle partitioning of semi volatile organic compounds (gasSOA), the authors point out the potential importance of SOA formation in cloud droplets and aqueous aerosol particle(aqSOA) in the atmosphere. The paper is well written and provides excellent basis for future works on this important topic. This paper should be published in Atmospheric Chemistry and Physics. I only have a few minor comments.

Specific comments:

1) Page 22318, line 25, “In East Asia, SOA predictions were low by 50% for the boundary layer but low by a factor 10–100 in the free troposphere (Heald et al., 2005), suggesting a role for aqSOA formation through cloud processing.” Can the authors elaborate this point?

Response: In the study by Heald et al. (2005) several possibilities are discussed that could explain the large discrepancies between observed and predicted OC aloft (e.g., halogen-mediated processes, cloud processing). All of these mechanisms represent sustained SOA formation processes in ageing air masses that is not included in models. In order to make this clear we added “. . .suggesting a role for aqSOA formation through cloud processing as a mechanism of sustained SOA formation away from emission sources.”

2) Page 22325, line 14, “In Atlanta, the fraction of total WSOC (gas+particulate) that is present in particles (Fp) increases sharply at high RH, suggesting a positive correlation with aerosol water (Fig. 2a, b)”. Do the authors refer to Fig. 2a, c?

Response: The reviewer is right. We have changed it in the revised manuscript and refer to Fig 2a,c.

3) Page 22325, line 16, “No relationship was readily observed between Fp and particle organic mass (Fig. 2c), which would be expected from the gasSOA formation route...” Do the authors refer to Fig. 2b?

Response: The reviewer is right. We have changed it in the revised manuscript and refer to Fig 2b.

4) Page 22325, line 20, “This peak in Fp coincides with particulate nitrate and thus the formation of both particulate components might be initiated by HONO.” Can the authors elaborate this point?

Response: HONO accumulates during the night and is quickly photolysed upon sunrise (e.g., Seinfeld and Pandis, 1998). Its photolysis represents an important morning OH source. The presence of OH is crucial to SOA formation as it is required for the oxidation of SOA precursors to form lower volatility and/or water-soluble products. At the same time NO is formed from HONO photolysis which can be further oxidized and thus represents a source of nitrate. We extended the text to clarify this “. . . might be initiated by HONO as this acts both as precursor of the OH radical and NO. Whereas the former is a crucial oxidant to form SOA, the latter becomes further oxidized to HNO3 that might partition to the particle phase.”

5) 3.4.2 Correlations of WSOC with RH (page 22325). The authors discussed that the increase in particle-phase water-soluble organic carbon (WSOCp) at high RH may point to aqSOA formation. Fig. 2a shows the averaged diurnal evolution of temperature, RH and Fp in Atlanta. In this figure, the Fp had a peak in the afternoon when the RH was low. The time evolution data of Fp and RH do not agree with the positive correlation between Fp and RH (Fig. 2c). I assume Fig. 2a shows the representative data. Can the authors explain this?

Response: The reviewer’s point is valid. We only showed overall results from an analysis that included all data. A more detailed analysis demonstrates that during drier afternoon periods in Atlanta, Fp can be correlated with OC, as seen in LA. This more detailed analysis is part of a larger manuscript focused on contrasting LA and Atlanta that will soon be submitted (Zhang et al., 2011, in preparation). We have modified the text (first paragraph in section 3.4.2) to include this point:

“The observed increase in particle-phase water-soluble organic carbon (WSOCp) at high RH may also point to aqSOA formation. In Atlanta, the fraction of total WSOC (gas + particulate) that is present in particles (Fp) increases sharply at high RH (>70%), suggesting a positive correlation with aerosol water (Fig. 2, a, c). No relationship was readily observed between Fp and particle organic mass (Fig. 2b) when all data were analyzed together, which would be expected from the gasSOA formation route since gasSOA forms through partitioning of semivolatile species into particulate organic matter (Hennigan et al., 2008a, b, 2009). However, during drier periods (<70%), which often occur in the afternoon (Fig 2a), there is evidence for gasSOA since Fp shows a correlation to OC (Zhang et al, manuscript in preparation), thus there is evidence that both aqSOA and gasSOA are occuring in Atlanta, possibility at different times of the day. The morning peak in Fp coincides with particulate nitrate and thus the formation of both particulate components might be initiated by HONO as it acts both as precursor of the OH radical and NO. Whereas the former is a crucial oxidant to form SOA, the latter becomes further oxidized to HNO3 that might partition to the particle phase.”

6) Page 22326, line 26, “The increase of the O/C ratio with RH (Fig. 2e) suggests that not only oxygen is added to preexisting molecules. . .” The data look scattered in Fig. 2e. A positive correlation between the O/C ratio and RH is not clear.

Response: We agree that the trend of increasing O/C with RH is not clearly obvious in Figure 2e. Even though the line does represent the linear correlation through the points, it has a poor correlation coefficient. However, in the revised manuscript we have left it in the figure but describe more clearly that such an increasing trend of O/C with RH would be the trend if indeed aqSOA is added to preexisting aerosol as a function of available aerosol water. In addition, we have modified Figure 2e and marked all data points that were recorded during day time and expanded the text:

“The data in Figure 2e might suggest the expected trend with lowest O/C ratios at the lowest RH even though the linear correlation coefficient is not high. Since the amount of aqSOA and thus the overall O/C ratios of the total OA mass depend on the intensity of photochemistry, the highest values can be seen around noon (Fig. 2d). In order to emphasize this correlation, data points that were recorded during the day (∼6 am – ∼6 pm) are marked by small red points in Figure 2e. It is obvious that these points show higher O/C ratios and a better correlation with RH and thus might point to photochemically formed aqSOA products in the aqueous aerosol phase. It should be noted that it is not RH but rather the amount of aerosol water (i.e., a combination of RH and the amount of hygroscopic aerosol mass) that will determine the size of the 'aqueous phase reactor' where aqSOA formation can take place. This caveat might explain some of the scatter in Figure 2e."

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22301, 2011.

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