

Responses to Referee 2:

The authors thank the reviewer for her/his constructive and helpful comments. We have modified our manuscript according to the reviewer's comments and changes of the text and figures are marked in red in this response letter and in the manuscript.

The authors present analysis of SP-AMS data combined with modelled data on the boundary layer height and supporting data of aerosol size distribution measurements. Their main finding is that sulfate aerosol mass concentration behaves differently than the organic aerosol during NPF event times: the sulfate concentration decreases less than the organic aerosol, and the same type of behaviour can be found for LVOOA with respect to SVOOA.

There are two main explanations for this observation: either it is a) a mixing effect of the PBL and the residual layer, with two different types of aerosols mixing, or b) there is formation of sulphate/LVOOA aerosol during the same period. The authors study explanation b) by exploring the possibility of low- or nonvolatile vapors condensing on the existing aerosol and comparing the resulting aerosol mass to the observed one. Based on the discrepancy of the thus computed aerosol mass and the observations, the authors then conclude that the condensation of sulphuric acid cannot explain the sulphate time evolution and the sulphate aerosol is entrained from the residual layer. Similar results and conclusions are obtained for LVOOA aerosol.

This result is an interesting and important one, and the paper is well written and very well suited for ACP. I suggest that the paper is published, but I think that the conclusions could be supported more strongly by some additional discussion of the possible origin and composition of the entrained aerosol and the mixing process:

Answer: we thank the referee for the nice summary of the manuscript and positive recommendation for possible publication.

1. *Firstly, what is the origin of the sulphate aerosol in the residual layer? Can its composition be estimated? (even approximately, e.g. amount/fraction of sulphate, LVOOA, SVOOA in the residual layer could be back-calculated from the data quite easily, I think).*

Answer:

The origin of sulfate rich aerosol in the residual layer is likely related to the cloud processing of aerosols as a significant fraction of sulphate is formed in clouds (Ervens et al., 2011). It is also possible that sulphate rich aerosol has entrained from free troposphere. In addition, e.g. Sorooshian et al. (2010) and Hao et al. (2013) reported increased oxidation level of cloud residual particles suggesting that cloud processing of organics would lead to compounds having elevated O:C ratio. As suggested by the reviewer, we conducted the back-calculated approximation of aerosol chemical composition in the residual layer based on the comparison between our measurement and dilution modelling results. In the calculation we assumed that the partitioning of organic vapors is negligible, and the ammonium and nitrate were excluded in the analysis. On average, the aerosol mass in the residual layer was roughly comprised of $62.6 \pm 16.6\%$ SO_4 , $35.6 \pm 15.4\%$ LVOOA and $1.8 \pm 7.1\%$ SVOOA in the four studied events, in a distinct contrast to aerosol chemical composition of $24.3 \pm 11.6\%$ SO_4 , $17.2 \pm 0.1\%$ LVOOA and $58.5 \pm 0.1\%$ SVOOA in the stable surface boundary layer before PBL dilution was initiated.

We have added discussion in Page 9 that “**Additionally, we conducted the back-calculated approximation of aerosol chemical composition in the residual layer based on the comparison between our measurement and dilution modelling results. In the calculation we assumed that the partitioning of organic vapors is negligible, and the ammonium and nitrate were excluded in the analysis. Hence, only Org and SO_4 aerosol were included in the analysis. On average, the approximated aerosol mass in the residual layer was comprised of $62.6 \pm 16.6\%$ SO_4 , $35.6 \pm 15.4\%$ LVOOA and $1.8 \pm 7.1\%$ SVOOA in the four studied events, in a distinct contrast to aerosol chemical composition of $24.3 \pm 11.6\%$ SO_4 , $17.2 \pm 0.1\%$ LVOOA and $58.5 \pm 0.1\%$ SVOOA in the stable surface boundary layer before PBL dilution**

was initiated. The origin of sulfate rich aerosol in the residual layer is likely related to the cloud processing of aerosols as a significant fraction of sulphate is formed in clouds (Ervens et al., 2011). It is also possible that sulphate rich aerosol has entrained from free troposphere. In addition, e.g. Sorooshian et al. (2010) and Hao et al. (2013) reported increased oxidation level of cloud residual particles suggesting that cloud processing of organics would lead to compounds having elevated O:C ratio.”

2. *Secondly, is there any indication of an external mixture when the mixing is occurring? In the case of a mixing, I guess there would be two different modes of aerosol (the entrained, sulphate-dominated mode and the PBL mode with less sulphate), while in the case of sulphuric acid condensing, the sulphate should be evenly distributed over the pre-existing aerosol. Is there any data available to test this assumption (e.g. the size information in the SP-AMS)?*

Answer:

This is a very interesting point. Unfortunately, the AMS signal was very low and hence also very noisy after the PBL dilution (total organic concentration app. 0.3 $\mu\text{g}/\text{m}^3$) preventing us to analyze reliable changes in size-dependent composition before and after the PBL mixing (see Fig. C1). In addition, as it seems based on our results that the particle population entrained from residual layer is dominating the aerosol mass after the dilution, distinguishing the two population from AMS size resolved composition would require very good data quality. Hence, we didn't add the size information in the revised manuscript.

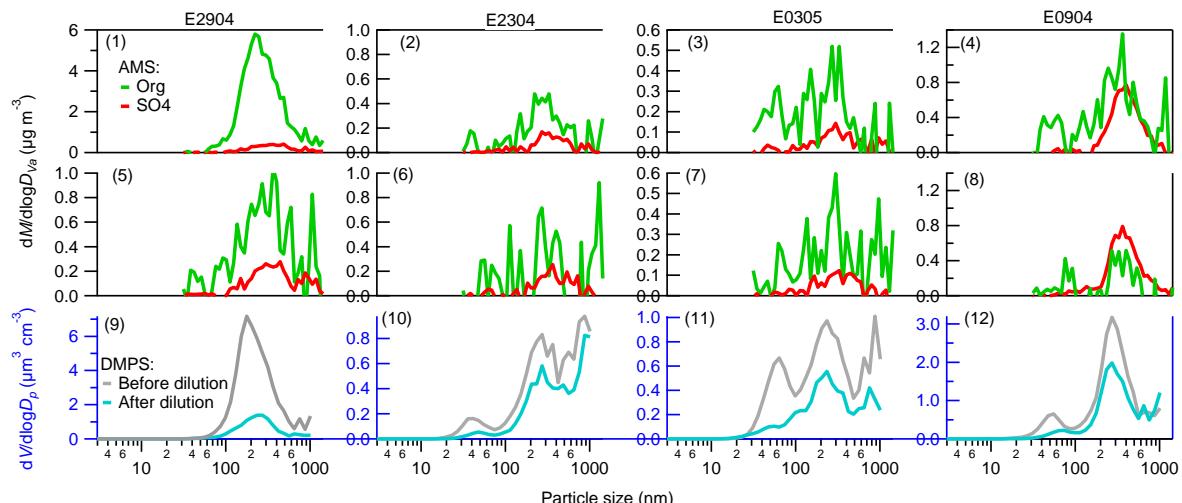


Fig. C1 Size distributions of aerosol particles before and after PBL dilution mixing in four events. The time periods defined as before dilution and after dilution were tabulated in table S1. Panels (1)-(4): aerosol mass size distributions of Org and SO_4 before dilution by AMS; (2)-(8): aerosol mass size distributions of Org and SO_4 after dilution by AMS; (9)-(12): aerosol volume size distribution by DMPS. Note that AMS measures vacuum aerodynamic diameter and DMPS measures mobility diameter of aerosol particles.

Table S1 Time periods defined as before and after PBL dilution mixing.

Events	Before dilution	After dilution
E2904	3:14-4:44	9:00-9:50
E0305	4:03-5:58	9:34-12:00
E2304	3:14-6:05	9:10-10:06
E0904	2:05-4:20	9:57-11:42

Below are also some more minor comments:

P7 l22: If the DF is defined as in Eq. 2, then the initial concentration should be multiplied and not divided by the DF. (Typo?)

Answer:

The reviewer is correct. It was a typo in the manuscript and we have fixed it.

P8 l6: It seems that the mass_SA depends strongly on the CS_SA; if I understand correctly, the SA concentration estimate from the proxy is also depending on CS_SA, and therefore the uncertainty in Eq. (3) is proportional to CS^2. I think it would be interesting to compute the uncertainty in this, and also indicate the range of uncertainty in the figures.

Answer:

The estimation of SA proxy is a function of dry size CS and relative humidity $(CS_{dry} \times RH)^{-0.13}$, as indicated in Eq. 11 in Mikkonen et al (2012), whereas CS_{SA} for mass_SA is corrected by RH. Thus, defining the uncertainty of condensated sulfuric acid in Eq. (3) is not as straightforward as the reviewer suggested.

To make estimate for uncertainty of condensated SA by applying equation of $\int_0^t CS \times SA$ in Eq.(3), we applied a formula from Farrance & Frenkel (2012):

$$y = x_1 \times x_2 \quad (C1)$$

$$\left(\frac{u(y)}{y}\right)^2 = \left[\left(\frac{u(x_1)}{x_1}\right)^2 + \left(\frac{u(x_2)}{x_2}\right)^2\right] \quad (C2)$$

where $u(y)$ refers to uncertainty for variable y , $u(x_1)$ and $u(x_2)$ are uncertainties for variable x .

By applying Eqs (C1) and (C2) to our case, we obtain:

$$SD_{CS \times SA}^2 = \left[\left(\frac{SD_{CS}}{CS}\right)^2 + \left(\frac{SD_{SA}}{SA}\right)^2 \right] \times (CS \times SA)^2 \quad (C3)$$

where SD_{CS} and SD_{SA} represent the uncertainties for condensation sink and sulfuric acid, $SD_{CS \times SA}$ is the uncertainty of multiplied CS by SA.

In the calculation, we estimated an uncertainty value of 40% for SA and 20% for CS. The uncertainty for $CS \times SA$ is about 44.7% based on Eq. (C3). We took a 1.6 times of this value as an upper boundary and 0.4 times as a bottom boundary. The uncertainty range for condensated SA in Eq.(3) of the manuscript roughly is 17.9% -71.5%. However, because of the difficulties in estimating the SA proxy and CS uncertainties, we did not include these results in the manuscript.

P9, l26: as it was just mentioned that [HOM] measurements were not quantitative, how was the concentration determined here?

Answer:

It should be noted that x-axis of the Fig. 5 doesn't represent the quantitative HOM concentration, but rather the relative change in the HOM concentration during the growth period. Hence, we did not attempt to determine any absolute concentration. We have now brought this up now more clearly in the manuscript text.

We have added a sentence in Line 31, Page 9: “**It should be noted that x-axis of the Fig. 5 doesn't represent the quantitative HOM concentration, but rather the relative change in the HOM concentration during the growth period.**”

We also changed the legend of x-axis in Fig. 5 to “**Estimated cumulative HOM condensation (a.u.)**”.

p10, line 3: as the calculation is done assuming a non-volatile HOM, but then the statement says that HOM contributes to semi-volatile aerosol; could this be elaborated on as this seems contradictory?

Answer:

We thank the reviewer for the good comment. The volatility bins of AMS-PMF-derived LVOOA and SVOOA component vary a lot. For example, the PMF SVOOA consisted of 50% SVOA ($C^* = 1-100 \mu\text{g m}^{-3}$), 42% LVOA ($C^* = 10^{-1}-10^{-3} \mu\text{g m}^{-3}$) and 6 % ELVOC ($C^* \leq 10^{-4} \mu\text{g m}^{-3}$) in Paris (Paciga et al., 2016). A study conducted in Hyytiälä in 2014 showed a poor correlation of AMS PMF-SVOOA to VTDMA-derived SVOA ($r^2=0.16$) (Hong et al., 2017), which could indicate a wide range of volatility bins of PMF-SVOOA. Thus, it is still possible that HOMs contributes to both PMF-SVOOA and LVOOA.

References:

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069-11102, 2011.

Farrance, I. and Frenkel, R.: Uncertainty of Measurement: A review of the rules for calculating uncertainty components through functional relationships, *The Clinical biochemist. Reviews*, 33(2), 49-75, 2012.

Hao, L., Romakkaniemi, S., Kortelainen, A., Jaatinen, A., Portin, H., Miettinen, P., Komppula, M., Leskinen, A., Virtanen, A., Smith, J.N., Sueper, D., Worsnop, D.R., Lehtinen, K.E.J., and Laaksonen, A.: Aerosol Chemical Composition in Cloud Events by High Resolution Time-of-Flight Aerosol Mass Spectrometry. *Environ. Sci. Technol.*, 47, 2645-2653, 2013.

Hong, J., Äijälä, M., Häme, S. A. K., Hao, L., Duplissy, J., Heikkinen, L. M., Nie, W., Mikkilä, J., Kulmala, M., Prisle, N. L., Virtanen, A., Ehn, M., Paasonen, P., Worsnop, D. R., Riipinen, I., Petäjä, T., and Kerminen, V.-M.: Estimates of the organic aerosol volatility in a boreal forest using two independent methods, *Atmos. Chem. Phys.*, 17, 4387-4399, <https://doi.org/10.5194/acp-17-4387-2017>, 2017.

Mikkonen, S., Romakkaniemi, S., Smith, J. N., Korhonen, H., Petäjä, T., Plass-Duelmer, C., Boy, M., McMurry, P. H., Lehtinen, K. E. J., Joutsensaari, J., Hamed, A., Mauldin III, R. L., Birmili, W., Spindler, G., Arnold, F., Kulmala, M., and Laaksonen, A.: A statistical proxy for sulphuric acid concentration, *Atmos. Chem. Phys.*, 11, 11319-11334, 2011.

Paciga, A., Karnezi, E., Kostenidou, E., Hildebrandt, L., Psichoudaki, M., Engelhart, G. J., Lee, B.-H., Crippa, M., Prévôt, A. S. H., Baltensperger, U., and Pandis, S. N.: Volatility of organic aerosol and its components in the megacity of Paris, *Atmos. Chem. Phys.*, 16, 2013-2023, <https://doi.org/10.5194/acp-16-2013-2016>, 2016.

Sorooshian, A., Murphy, S. M., Hersey, S., Bahreini, R., Jonsson, H., Flagan, R. C., Seinfeld, J. H.: Constraining the contribution of organic acids and AMS m/z 44 to the organic aerosol budget: On the importance of meteorology, aerosol hygroscopicity, and region, *Geophys. Res. Lett.*, 37, L21807, DOI: 10.1029/2010GL044951, 2010.