

Responses to Referee 1:

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 manuscript by Hao et al. investigated the effects of boundary layer dynamics and chemistry on aerosol composition during new particle formation (NPF) periods in Finland. The authors found that sulfate showed a much slower decrease than organics as a result of rising boundary layer during before the NPF period, which was likely due to the mix of residual layer with new boundary layer. During the growth period, they found the simultaneous increases in semi-volatile OOA and highly oxygenated organic molecules, suggesting a link between them. This manuscript is overall well written and I recommend it for publication after addressing the following comments.

We thank the referee for her/his positive comment on our manuscript.

1. The interpretation of slower decrease in sulfate than organics can have a third reason. As the boundary layer rises, organics can be diluted more because of evaporative loss associated with gas-particle partitioning, while the non-volatile sulfate does not.

Answer:

We thank the referee for the insightful comment. We do agree that the evaporation of organics could have taken place during the PBL development. In Fig. 4 in the manuscript, we have shown that the calculated SVOOA concentrations (light pink) were generally higher than the measured ones. As pointed out by the referee, this might be also due to SVOOA evaporation. Thus, we have rewritten the text from L28 in Page 8 to L6 in Page 9 by adding discussion on the evaporation issue.

We changed “In addition, when taking into account the PBL dilution in calculated LVOOA concentrations (pink lines in Figure 4) the calculated concentrations are clearly lower than the measured concentrations while calculated SVOOA concentrations were generally higher than the measured ones. The discrepancy between the modeling and measurements could be interpreted by the mixing of LVOOA rich aerosol from the residual layer to the ground layer, and/or by the partitioning of organic vapors between aerosol and gas phase. To get more detailed and quantitative information on these processes, gas phase measurements of organic vapors would be needed. Unfortunately, quantitative data of organic vapor concentrations is not available for this measurement campaign. Overall, it is likely that the temporal profiles of organic concentrations in the beginning of new particle formation were subjected to the interplay of mixing of LVOOA rich OA from residual to boundary layer and partitioning of organic vapors during the boundary layer evolution and new particle formation.” to “**In addition, when taking into account the PBL dilution, in calculated LVOOA concentrations (pink lines in Figure 4) are clearly lower than the measured concentrations. The discrepancy between the modeling and measurements could be interpreted by the mixing of LVOOA rich aerosol from the residual layer to the ground layer, and/or by the partitioning of organic vapors between aerosol and gas phase. To get more detailed and quantitative information on these processes, gas phase measurements of organic vapors would be needed. Unfortunately, quantitative data of organic vapor concentrations is not available for this measurement campaign. For SVOOA component, the calculated concentrations were generally higher than the measured ones, which indicates that evaporation of SVOOA could have taken place due to the dilution mixing. Overall, it is likely that the temporal profiles of organic concentrations in this study were subjected to the interplay of mixing of LVOOA rich OA from residual to boundary layer and partitioning of organic vapors during the boundary layer evolution and new particle formation.**”

2. This points to another question of the PBL model. The PBL model only considers the vertical dilution. In fact, as shown in Figure 2, the wind speed also has a significant change before the new particle formation period, increasing from 0.3 m/s to 1.5 m/s. Although the wind speed is overall low, such an increase can have a big impact on horizontal dilution.

Answer:

The wind speed (WS) was increasing in Fig. 2, with an average value of 0.72 ± 0.44 m/s during the studied period in E0429. As pointed out by the reviewer, we didn't take the dilution due to the horizontal mixing in the account. As the Hyytiälä measurement station is surrounded by the large area of boreal forest, it can be assumed that the mixing is significantly less important than in the case of a point source. Anyhow, we would like to point out, if the horizontal mixing would have been taken into account in the calculations, the resulted dilution model concentrations would have been lower than those presented in Figure 4, further supporting the conclusion according to which the major part of sulfate is originated from vertical turbulent mixing of the sulfate-rich aerosols from the residual layer.

Accordingly, we deleted our argument in Line 29-32 in Page 7: ~~“Since meteorological conditions seem to be stagnant during those periods (relatively stable wind speed (WS) and wind direction (WD) in panel I, Fig. 2 and Fig S14), the perturbation of advected sulfate species from local sources likely had negligible effect on their concentrations.”~~

We also added a discussion on possible effects of horizontal dilution in Line 18, Page 8 in the manuscript: ~~“It should be taken into account, that the horizontal dilution due to the increasing wind speed during the investigated period (wind speed increases from 0.3 to 1.5 m/s) was not taken into account in the analysis. Horizontal dilution could affect the dilution although in Hyytiälä, where the station is surrounded by the homogeneous forested area, the effect is minor.”~~

3. The quantification of AMS is a bit strange. The author used a collection efficiency of 0.85 according to the comparisons with DMPS measurements. However, AMS reported 9% higher mass concentrations than those of DMPS. It seems that the AMS CE was underestimated. Typical values of 0.5 or 1 are used in field campaigns. In addition, which size ranges of DMPS the authors use for comparisons, 3 – 1000 nm?

Answer:

The estimation of CE was based on the comparison of AMS volume concentration to DMPS measurement. However, the comparison was prioritized to the new particle formation periods that this piece of work focuses on. Fig. C1 below shows a comparison of AMS-derived volume concentration (vol. conc.) vs DMPS-vol. conc. in E0429. AMS-vol. conc. was slightly higher than DMPS vol. conc. in the nucleation period (in orange bar), but was becoming lower in the aerosol growth period (in gray bar). The reasons for the slight inconsistency of two sets of data are (1) uncertainties of applied aerosol bulk densities when we convert AMS-mass concentration to volume concentration. This study applied a constant density of 1.75 g/cm^3 for the SO_4 , NO_3 and NH_4 fragments. When the aerosol molecular composition varies in the atmosphere (for example, different amount of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4NO_3 and H_2SO_4 in the orange bar from those in the gray shaded area), the approach could bring errors to the conversion from mass to volume concentrations, (2) possible differences in particle composition and hence phase related properties during these periods, and (3) possibly other minor issues with measurement fluctuation of two instruments. Hence, the employed of CE 0.85 is a compromised value after comparison between AMS- and DMPS-derived volume concentrations. For the entire campaign, AMS observed about 7% higher volume concentration than those of DMPS (not 9%, Fig. S4 in the supplementary materials). We still believe that CE 0.85 is within the range of uncertainties and is a reasonable estimation in this study.

The measurement size range of DMPS is 3-1000nm.

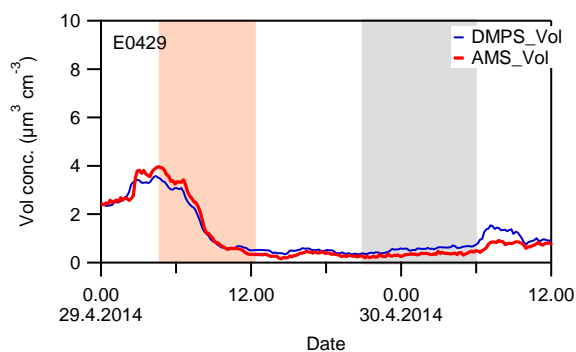


Figure C1. AMS- and DMPS- derived volume concentrations in E0429, assuming a CE of 0.85 for AMS. The orange and gray shaded bars were marked for analysis, the same periods indicated in Fig. 2 in the manuscript.

3. The authors identified three SV-OOA factors with different time series. I am wondering if HOMs correlates one of them or the combined one?

Answer:

The increase of SVOOA in the nighttime (gray bar in Fig. 2) is only due to the increase in SVOOA2 (see Fig.C2 below). Hence, HOMs correlates with SVOOA2. SVOOA2 shows good correlation with measured monoterpene VOCs and is identified as a biogenic SOA factor (Fig. S10 in supplementary information).

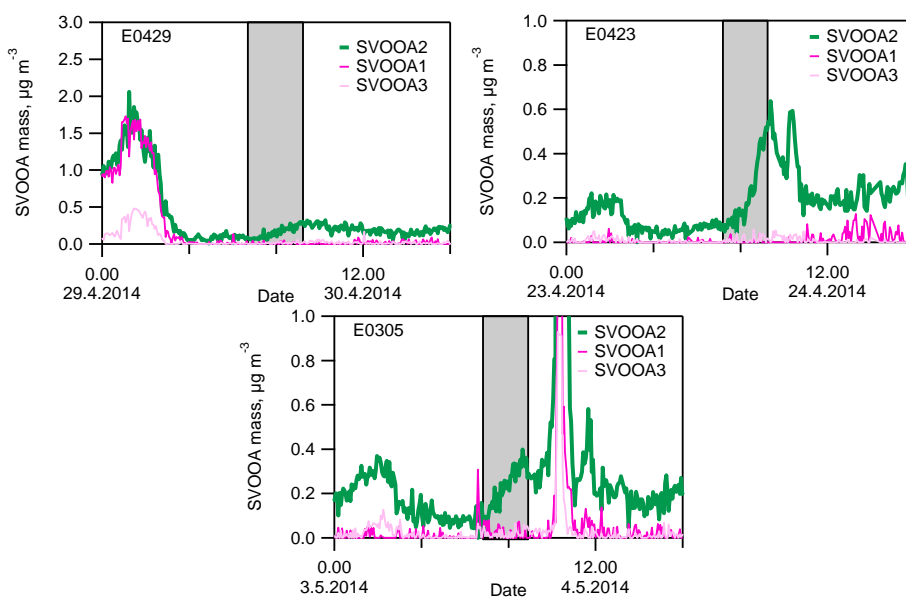


Figure C2. Time series of three SVOOA factors in the new particle formation periods.

4. This manuscript missed the very important size-resolved chemical information from SP-AMS.

Answer:

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. C3). 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.

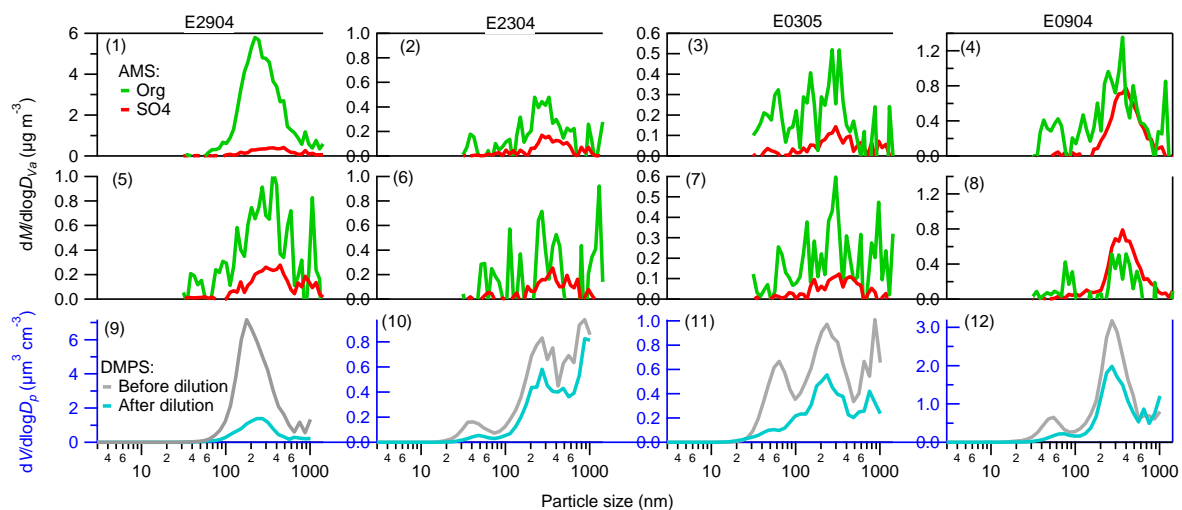


Fig. C3 Size distributions of aerosol particles before and after PBL dilution mixing in four events. The time periods defined as before dilution and after dilution were tabulated in table S1. Panels (1)-(4): aerosol mass size distributions of Org and SO₄ before dilution by AMS; (2)-(8): aerosol mass size distributions of Org and SO₄ 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