Comments on the revised version of the manuscript "Estimation of sulphuric acid concentrations…" by Lisa J. Beck et al.

The authors have taken up most of the comments by the reviewers and it has considerably improved. However, there is still one remaining issue that should be addressed in a minor revision, which basically concerns the general comments of the original manuscript, which are recalled in the following:

1. "The balance equations (1) to (4) are a simplification probably containing the main processes. However, also with respect to the Lovejoy et al. (2004), they do not consider several processes of impact on ambient ions, perhaps most prominent the recombination and the clustering of sulfuric acid ion clusters with water and base molecules. The effect of losses due to recombination with positive ions should be discussed. Further, the APi-TOF may not show real ambient ion clusters as in the process of pumping away neutral molecules and transfer of ions into the high vacuum TOF region, weakly bound molecules are expected to be dissociated from the clusters in collisions. And condensation sink is, as correctly stated, expected to be dependent on mass and size of the clusters. Yet, effects are expected to be minor but should be discussed.

2. The made simplifications give rise to the following issue: each budget equation, excluding eq.(1), can be solved for H2SO4 on itself. In pseudo-steady state, (2) then yields

$[H2SO4] = CS\ [SA_{dimer}] / (k1\ [SA_{monomer}] - k2\ [SA_{dimer}])$

And (3) yields:

$[H2SO4] = CS\ [SA_{trimer}] / k2\ [SA_{dimer}]$

The constant k2 can be estimated from Lovejoy et al. (2004) to be very close to k1.

Thus, together with eq. (8) of the manuscript, three equations to determine H2SO4 can be derived. Obviously, these yield different approximations of H2SO4. The differences are due to incomplete balances and the made assumptions. It is recommended and expected that the authors discuss the corresponding differences."

It is appreciated that the authors now discussed the ion-ion-recommendation, effects of clusters with water and base molecules and thus the formulations in equations (1) to (8) improved. Also it is well recognized that the authors followed the suggestion to discuss the balance equations solved for sulfuric acid based on (2) and (4) in Fig. 4b.

However, the statements on page 9 of the track-changes revised manuscript "The estimated $H_2SO_4$ concentration from Eq. 2 is highly overestimated, since the losses of the $SA_{dimer}$ to the $SA_{trimer}$ are neglected… Eq. 4 … vastly underestimating the real concentrations." Are not convincing. The loss of dimer to the trimer is considered in Eq. 2 in the term "$-k_2\ [SA_{dimer}]$ $[H_2SO_4]$". And the argument that the loss of $H_2SO_4$ due to monomer and dimer production is not considered is not correct because Eq. 4 is a budget for trimers and not for $H_2SO_4$. If Eq. 2 and 4 would describe the correct budget including all relevant processes, they should yield the same concentration of sulphuric acid each. However, they are approximations and miss some budget relevant terms, obvious from the different results for sulfuric acid in Fig. 4a and b. And, as the Eq. 2 based budget overestimates, and Eq. 4 based budget underestimates the measured sulfuric acid, Eq. 8 formed from Eq. 2 and 4 partially compensate these effects and better fit the observations.

It is recommended that the authors revise the respective statements on page 9 (ll. 278-283), and critically justify the use of Eq. 8 pointing out the best fit with observations and thus judging the use of Eq. 8. However, associated generalizations in the conclusion should contain some appropriate carefulness.

We thank the reviewer for pointing out this mistake, as this was wrongly stated in the revised manuscript. We therefore corrected the statement to the following:

*"For the sake of completeness, the estimation of the H2SO4 concentration determined from Eqs. 2 and 4, assuming pseudo-steady state, are depicted in Fig. 4b."* The estimated $H_2SO_4$ concentration from Eq. 2 is overestimating, while solving Eq. 4 for $H_2SO_4$ is underestimating the real concentration as those equations are only approximations. By combining the various approximations, Eq. 8 yields in the best fit to the observed SA concentration.

Smaller comments (referring to lines in track-changes manuscript):

l. 180-185: Effects on CS of factor 2 are discussed here which might explain some of the deviations between the simple budgets and observations. Please comment.

We added to the paragraph as follows (colored in green):
*The enhancement of CS due to the presence ions has been shown to reach a maximum value of 2 when the pre-existing particle population is centered at very small sizes (< 10 nm in diameter) and to decrease toward the value of 1 when it is located at sizes > 100 nm (Mahfouz and Donahue, 2021).* The impact of ions on CS and estimated SA concentrations depends thereby on the environmental conditions determining the size distribution and charges of the pre-existing particle population. Neglecting the size-dependency of CS between the SA monomers, dimers and trimers causes additional errors in estimated SA concentrations; however, it is difficult to determine this effect in ambient measurements having limited data and instrumentation.

l. 287: Assuming the CS at Neumayer Station to be constantly $1\ 10^{-3}\ s^{-1}$ appears to be a substantial simplification and might explain the offset between estimate and observation. Please comment.

We agree with that and therefore added to the paragraph as follows (colored in green):

*The presented method was also applied to measurements taken at the Neumayer Station III, Antarctica, in order to test it in a different environment. Here, we used the condensation sink reported by Weller et al. (2015) at Neumayer Station of $1 \times 10^{-3}\ s^{-1}$. Figure 6 shows a three-week period between 24 December 2018 and 14 January 2019. The calibration factor of the CI-APi-TOF used for measuring the sulfuric acid concentration is $4.9 \times 10^9$. Here, the estimated sulfuric acid concentration underestimates the measured concentration when the $SA_{tetramer}$ and $NH_3(H_2SO_4)_3HSO_4$-cluster show high concentrations (Fig. 6c). A possible explanation for the underestimation might be the neglect of the growth of sulfuric acid to oligomers larger than the tetramer, as well as its clustering with bases and water (Fig. 6b and c). In coastal Antarctica, the main nucleating mechanism was observed to be negative ion-induced sulfuric acid-ammonia nucleation, acting as a major sink for sulfuric acid molecules due to its clustering with bases (Jokinen et al., 2018). Including the $SA_{tetramer}$ and $SA_{tetramer}$ clustered with $NH_3$ in the estimation equation improved the correlation ($R^2$) from 0.48 to 0.54.* Furthermore, as mentioned above, the value of CS for Neumayer was

*assumed to be constant ($10^{-3}$ $s^{-1}$) due to the lack of data needed for its calculation. This simplification certainly causes additional errors in estimated SA concentrations, especially during periods of high sea salt concentrations causing potentially large variations in values of CS. Nevertheless, the diurnal variation of the SA concentration is represented well by this method. During times with lower sulfuric acid concentrations, our method gives higher values than the measured concentrations (Fig. 6).*