

Comments on the revised version of the manuscript “Estimation of sulphuric acid concentrations...” by Lisa Johanna 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

$$[\text{H}_2\text{SO}_4] = \text{CS} [\text{SA}_{\text{dimer}}] / (k_1 [\text{SA}_{\text{monomer}}] - k_2 [\text{SA}_{\text{dimer}}])$$

And (3) yields:

$$[\text{H}_2\text{SO}_4] = \text{CS} [\text{SA}_{\text{trimer}}] / k_2 [\text{SA}_{\text{dimer}}]$$

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-recombination, 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 H₂SO₄ 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 “-k₂ [SA_{dimer}] [H₂SO₄]”. And the argument that the loss of H₂SO₄ due to monomer and dimer production is not considered is not correct because Eq. 4 is a budget for trimers and not for H₂SO₄. 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 generalisations in the conclusion should contain some appropriate carefulness.

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

I. 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.

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