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Comment on amt-2021-259

Anonymous Referee #1

Referee comment on "Estimation of sulfuric acid concentration using ambient ion composition and concentration data obtained by Atmospheric Pressure interface Time-of-Flight ion mass spectrometer" by Lisa J. Beck et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-259-RC1>, 2021

The manuscript "Estimation of sulphuric acid concentrations..." by Lisa Johanna Beck et al. is generally well written and addresses an important subject in atmospheric research: an approximation method of sulfuric acid concentrations based on sulphuric cluster ion distributions measured by APi-TOF-MS. It is a short paper focussing on deriving one equation and validating it against observations. However, there are some issues with simplifications and the validations should be applied to a wider field of data covering different atmospheric conditions.

General comments:

- The balance equations (1) to (4) are a simplification probably containing the main processes. However, also with respect to 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.
- 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 k_2 can be estimated from Lovejoy et al. (2004) to be very close to k_1 .

Thus, together with eq. (8) of the manuscript, three equations to determine H_2SO_4 can be derived. Obviously, these yield different approximations of H_2SO_4 . The differences are due to incomplete balances and the made assumptions. It is recommended and expected that the authors discuss the corresponding differences.

- In section 3 "Validation" the estimated and measured concentrations of a period of 8 days are compared. Though I agree that above $2 \cdot 10^6$ molecules cm^{-3} agreement is good in this logarithmic presentation, there is also a period starting in the evening of May 26 with larger deviations. Together with some night-time overestimations of the approximation, there remains the question if the agreement in the five consecutive days 19-25 May was achieved accidentally. It is recommended to discuss this question. From Fig. 3, the trimer makes the difference in the last period, is there any explanation? Overall, recommending the applicability of eq. (8) for general use appears premature and will need further proof that eq. (8) can yield reasonable estimates under varying temperature, humidity and pressure conditions.

Specific comments:

- L. 20-23: It is recommended to be more careful in claiming the theoretical expression for H_2SO_4 may be used under various atmospheric conditions (see also general comment 3)
- L. 24: "developed estimate works very well..." is a rather qualitative description, better quantify by objective measures.
- L. 29-36: Some credit should be given to early ambient ion distribution and sulphuric acid measurements by the Eisele and Arnold groups.
- L. 44-48: It is unclear if this is just an estimate or based on experimentally determined detection limits of the described system. Please, be clearer.
- L. 60-62: Proxies for H_2SO_4 and the here presented estimation based on atmospheric ions are both using several assumptions and it is not clear which approach is better under which conditions. Thus, either demonstrate results by both approaches and judge the agreement, or be more cautious in presenting an advantage of the new approach, which is rather tentative.
- L. 74: "... we theoretically explain ...". Here, and later on, I'd recommend to be more careful in the wording, as the derived formula is an approximation of the H_2SO_4 concentrations based on the ion abundances.
- Conclusion: It is recommended to be more cautious and precise and avoid "...give accurate enough..." and "... a reliable estimate...".