In this file, the review comments are in black and our responses in green. The added sentences are in *italic*.

RC1

The manuscript "Estimation of sulphuric acid concentrations..." by Lisa J. 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.

We thank the reviewer for the very constructive comments, which we answer below.

General comments:
RC1: "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."
AC: This is correct, we do neglect the losses of sulfuric acid to clusters with water and base molecules. We also tested our method with a dataset from Neumayer Station III, Antarctica, where the method is underestimating the actual sulfuric acid concentration, especially on days when a new particle formation event was ongoing. One reason for the underestimation could be the neglect of the clusters of sulfuric acid with bases. We tested the method including also the formation of the tetramer, as it was abundant in a higher concentration than at SMEAR II station. The $R^2$ between 6 – 18 UTC of the estimated sulfuric acid concentration at Neumayer Station III is 0.29 (RMSE: $1.68x10^{-6}$ $cm^{-3)}$ using the presented equation 8 in the manuscript. Including also the tetramer in the estimation equation, the $R^2$ resulted in 0.33 (RMSE: $1.63x10^{-6}$ $cm^{-3}$) and only slightly improved the estimation (note for later discussion: the $R^2$ and RMSE values do **not** include the ion-ion recombination which is discussed below).

For the neglect of the clustering with bases, we added the following information in the manuscript:

*Furthermore, the derivation neglects the losses of $SA_{trimer}$ to the $SA_{tetramer}$ and larger clusters, as well as the clustering of sulfuric acid ion clusters with water and base molecules, such as $NH_3$. Those simplifications can cause an underestimation of the $H_2SO_4$ concentration with the presented method. If necessary, the method can easily be adapted, and bigger clusters can be included in the equation.*

As will be discussed below, we included the ion-ion recombination in the revised manuscript. We also included a brief statement regarding the correlation ($R^2$) at Neumayer Station when including the $SA_{tetramer}$ and $SA_{tetramer}$ + $NH_3$ in the method. Since ion-ion recombination is considered in those numbers, they differ from our statement above. We state in the manuscript as follows:

*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.*

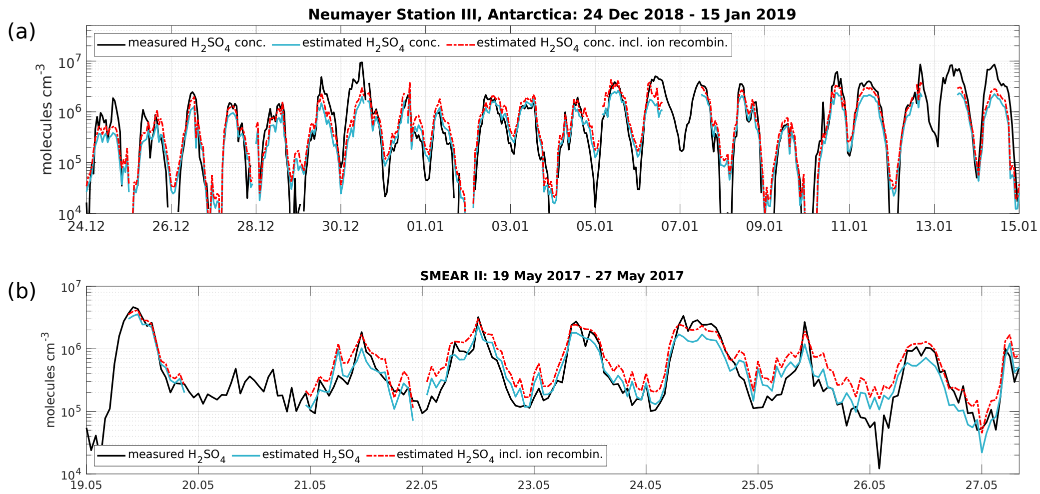
AC: Further, as the reviewer stated correctly, we did not consider the ion-ion recombination in our presented method which causes additional errors. Therefore, we implemented the losses of charged sulfuric acid clusters due to recombination with positive ions in our equations. We used the equation $\alpha \cdot [SA_i] \cdot N_{pos}]$ (Kontkanen et al., 2013) where alpha is the ion-ion recombination coefficient ($1.6x10^{-6}$ $cm^{-3}$ $s^{-1}$), $[SA_i]$ is the concentration of sulfuric acid clusters (monomer, dimer or trimer) and $N_{pos}$ is the concentration of positive small ions. The resulting equation is:

$$[H_2SO_4] = \frac{(CS + \alpha \cdot N_{pos}) \cdot ([SA_{dimer}]+[SA_{trimer}])}{k_1 \cdot [SA_{monomer}]}. \quad (8)$$

We included the ion-ion recombination in our method in the revised manuscript.
For the concentration of $N_{pos}$, we used the measurements with from a Neutral cluster and Air Ion Spectrometer (NAIS, Airel Ltd., Mirme and Mirme, 2013), however if those measurements are not available, $N_{pos}$ can be assumed to be in the range of 500 – 1000 $cm^{-3}$ (Hirsikko et al., 2011).
In the figure below we show the validation of our method on a dataset from Neumayer Station III, Antarctica, and at SMEAR II station with the method presented in our first manuscript (blue solid line) and the method including the ion-ion recombination for the charged sulfuric acid clusters (red dashed line). With consideration of the ion-ion recombination, the estimation of the sulfuric acid concentration has improved at both stations.
At Neumayer Station III, on days when negative ion-induced nucleation was ongoing, e.g. on 14 January 2019, however, the estimated concentration is still underestimating which might be the result of the neglected clustering with bases as discussed above.
The estimation of the sulfuric acid concentration at SMEAR II station also improved during daytime. During night-time, the method is overestimating. The table below shows the RMSE and $R^2$ of the originally presented method and the errors when including the ion-ion recombination for both locations. A table with RMSE and $R^2$ is also included in the revised manuscript.

Another possible reason for the underestimation at Neumayer could be that the CS might be higher than measured due to e.g. intermittent high concentrations of sea salt which cannot be determined reliably. Further, it should be mentioned that the real CS for ions is probably higher than the one used in the usual CS calculations as ions are more likely to condense on pre-existing particles than neutral compounds (Mahfouz and Donahue, 2021). This enhancement of CS has not been taken into account in our calculations, but we state in the manuscript as follows:

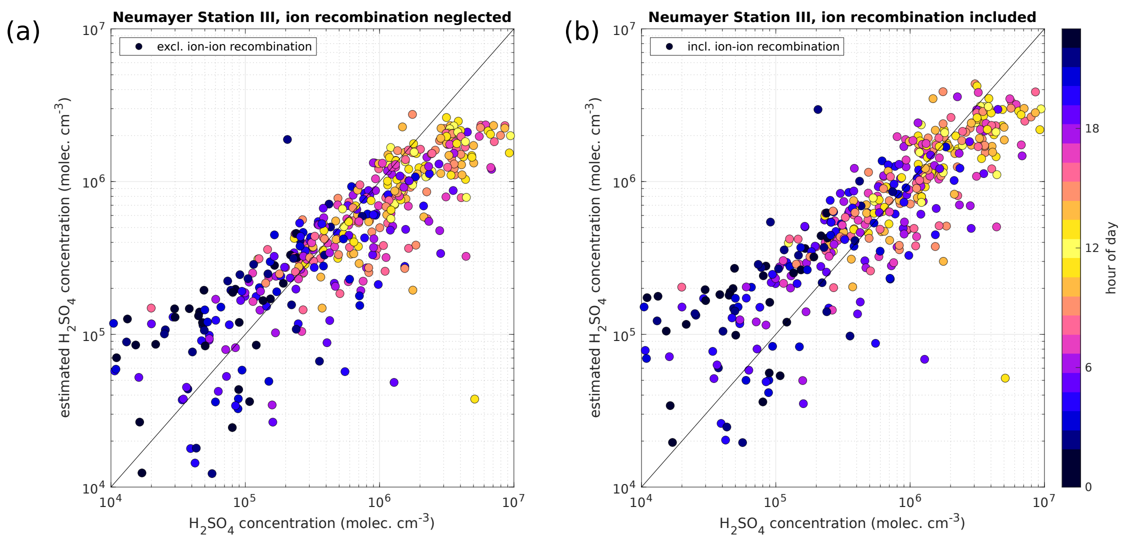
"Besides the steady-state assumption, it should be noted that in deriving eq. 8 monomers, dimers and trimers were assumed to have the same loss rate (CS) onto pre-existing aerosol particles. This causes an additional, yet minor, uncertainty in the estimated $H_2SO_4$ concentrations, as such loss rates are dependent on the size/mass of the clusters (e.g. Lehtinen et al., 2007; Tuovinen et al., *2021). […] Additionally, the CS for ions is higher than for neutral compounds. The enhancement of CS has shown to reach a maximum value of 2 when the pre-existing particles are < 10 nm and decreases to 1 when the pre-existing particles are > 100 nm, as shown by Mahfouz and Donahue (2021). "*



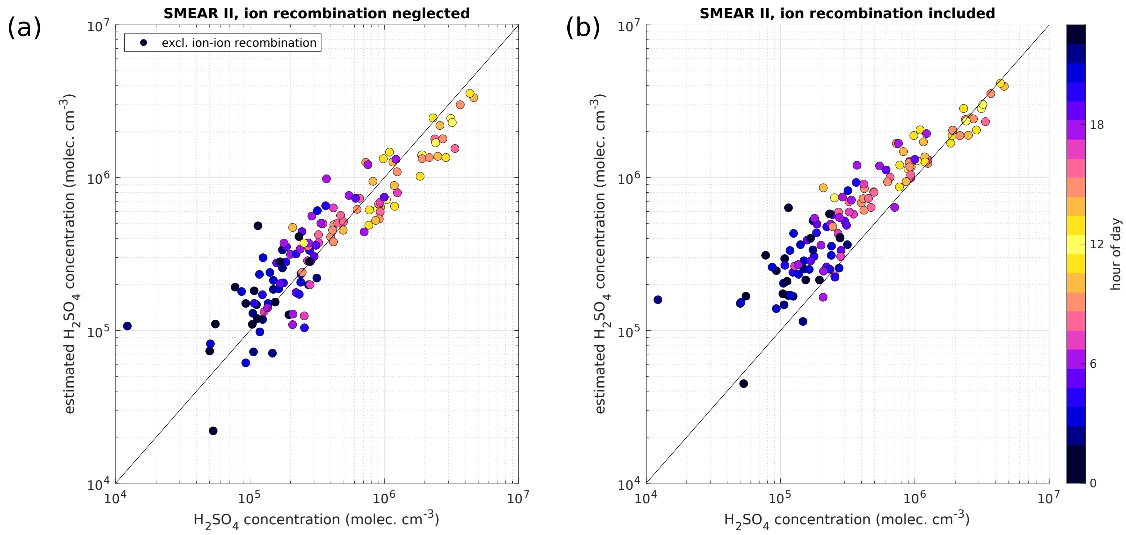

Time series of measured sulfuric acid concentration (black), the estimated sulfuric acid concentration based on our proposed method (blue) and the estimation including the ion-ion recombination (red) at (a) Neumayer Station III, Antarctica, from 24 December 2018 – 14 January 2019 and (b) SMEAR II, from 19 May – 27 May 2017.

Table 1: Root mean square error and $R^2$ for SMEAR II and Neumayer Station III. The day- and night-time are split in 6 – 18 local time (LT) and 18 – 6 LT, respectively. The root mean square error was calculated for the originally introduced method which neglected the ion recombination and including the recombination. For SMEAR II station, we also show the RMSE and $R^2$ of the $H_2SO_4$ proxy calculated with the introduced method by (Dada et al., 2020).

| | **Root mean square error (RMSE)** | | | | |
|---|---|---|---|---|---|
| | **SMEAR II** | | | **Neumayer Station III** | |
| | Neglecting ion recombination | Including ion recombination | $H_2SO_4$ proxy | Neglecting ion recombination | Including ion recombination |
| Daytime (06–18 LT) | $5.0 \times 10^5$ cm$^{-3}$ | $4.12 \times 10^5$ cm$^{-3}$ | $5.54 \times 10^5$ cm$^{-3}$ | $1.68 \times 10^6$ cm$^{-3}$ | $1.43 \times 10^6$ cm$^{-3}$ |
| Night-time (18–06 LT) | $3.54 \times 10^5$ cm$^{-3}$ | $3.23 \times 10^5$ cm$^{-3}$ | $4.25 \times 10^5$ cm$^{-3}$ | $2.54 \times 10^7$ cm$^{-3}$ | $1.63 \times 10^6$ cm$^{-3}$ |
| | **$R^2$** | | | | |
| Daytime (06–18 LT) | 0.78 | 0.85 | 0.78 | 0.29 | 0.48 |
| Night-time (18–06 LT) | 0.83 | 0.85 | 0.84 | -154 | 0.37 |




Measured (horizontal axis) and estimated (vertical axis) sulfuric acid concentration from Neumayer Station III, Antarctica. The left figure (a) shows the method without ion-ion recombination, the figure on the right (b) shows the method including the ion-ion recombination. The colouring indicates the hour of the day (local time).




Measured (horizontal axis) and estimated (vertical axis) sulfuric acid concentration from SMEARII, Finland. The figure on the left (a) shows the method without ion-ion recombination, the figure on the right (b) shows the method including the ion-ion recombination. The colouring indicates the hour of the day (local time).

RC1: "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."

AC: The APi-TOF only detects roughly 1% or less of the actual ambient ion cluster concentration (Junninen et al., 2010). In order to quantify how many ions are reaching the detector of the APi-TOF, we included the transmission efficiency calibration curve in the manuscript. Here, the concentration of ions measured by APi-TOF is compared to the concentration measured with an electrometer for different size ranges. We included the correction of the different ions ($SA_{monomer}$, $SA_{dimer}$, and $SA_{trimer}$) accordingly for the validation of the method, which improved the outcome of the estimated SA concentration.

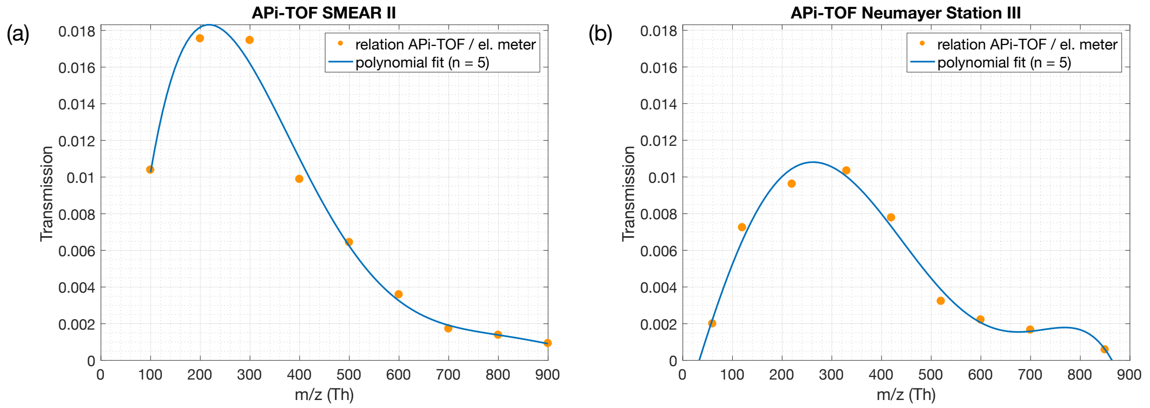



**Figure 1** Ion transmission of the APi-TOFs used in this study. The transmission efficiency was determined via production of charged particles with a NiCr wire. The concentration of the size selected ions with a Hermann nano differential mobility analyser (HDMA, Hermann, 2000) were measured with an electrometer and an APi-TOF in parallel. A more detailed description can be found in Junninen et al. (2010). Panel (a) shows the transmission efficiency of the APi-TOF used for measurements at SMEAR II Station, Hyytiälä, Finland. Panel (b) shows the transmission efficiency used for measurements at Neumayer Station III.

In our study, we did not quantify the fragmentation of weakly bound molecules within the APi-TOF. The fragmentation due to the voltage of the electrodes within the APi-TOF have been studied by Passananti et al. (2019). The charged sulfuric acid dimer is a very stable cluster with an evaporation rate of $2.7 \times 10^{-15}$ $s^{-1}$, while the charged sulfuric acid trimer is a little less stable with an evaporation rate of $5.6 \times 10^{-3}$ $s^{-1}$ (Ortega et al., 2014). If a charged sulfuric acid trimer is fragmented, it loses a sulfuric acid molecule and will be detected as a sulfuric acid dimer. In our method, this would not affect the estimated concentration, as the numerator contains the sum of sulfuric acid dimer and trimer. However, the fragmentation of bigger clusters and clusters with bases might affect the estimated sulfuric acid concentration.

The CS is dependent on the composition, mass and size of the cluster. We included a short paragraph in the manuscript as follows:

*According to Tuovinen et al. (2021), the CS of $H_2SO_4$ clusters decreases with increasing number of $H_2SO_4$ molecules. The study shows that the CS of the $SA_{dimer}$ clustered with ammonia decreases to 68% (compared to one $H_2SO_4$ molecule) and for $SA_{pentamer}$ with four ammonia molecules to 42%. However, the order of magnitude of the CS remains the same, and the effect on the estimation of the $H_2SO_4$ concentration is assumed to be negligible.*

RC1:

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 [SAdimer] / (k1 [SAmonomer] - k2 [SAdimer]) And (3) yields:

[H2SO4] = CS [SAtrimer] / k2 [SAdimer]

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.

AC: The calculated sulfuric acid concentration from equation 2 and equation 4 were added to the manuscript and briefly discussed. As expected, the values resulting from equation 2 are highly overestimating, while the results from equation 4 underestimating the sulfuric acid concentration in both locations where we validated the method. We state in the manuscript:

*For the sake of completeness, the estimation of the $H_2SO_4$ 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 highly overestimating, since the losses of the $SA_{dimer}$ to the $SA_{trimer}$ are neglected. When solving Eq. 4 for $H_2SO_4$, only the needed $H_2SO_4$ for the formation of the trimer is considered and the monomer and dimer production are neglected. Consequently, the resulting estimated $H_2SO_4$ concentration is vastly underestimating the real concentration.*

We added the results of the estimated sulfuric acid concentration in the former Fig. 2 (now Fig. 4):

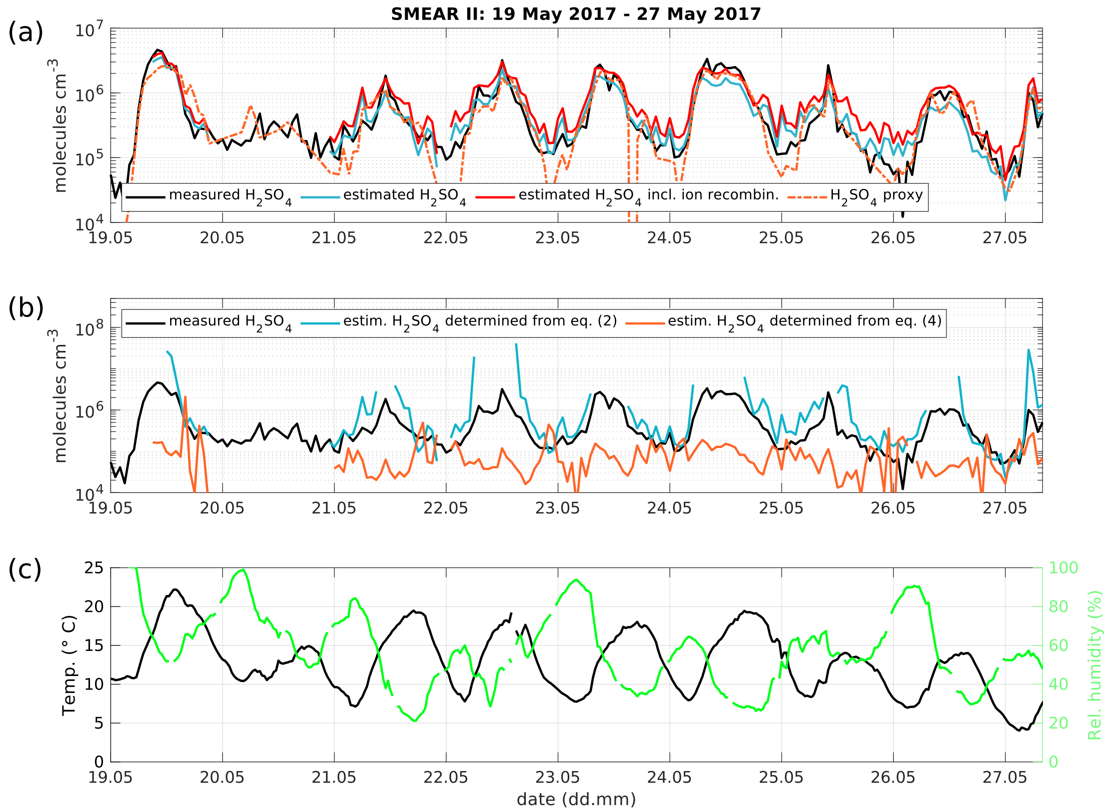



**Figure 4** (a) Time series of measured $H_2SO_4$ concentration from the CI-APi-TOF (black) and estimated $H_2SO_4$ concentration from the APi-TOF (blue), estimated $H_2SO_4$ concentration including ion-ion recombination (red) and $H_2SO_4$ proxy from Dada et al. (2020) (orange dashed) between 19 and 28 May 2017. The concentration is given in molecules cm$^{-3}$. (b) Measured $H_2SO_4$ concentration as in panel (a) in black and determined concentration from eq. 2 (blue) and eq. 4 (orange). (c) Temperature and relative humidity.

RC1: In section 3 "Validation" the estimated and measured concentrations of a period of 8 days are compared. Though I agree that above $2\times10^6$ 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.

AC: In order to test the method in a different environment, we applied it on a three-week dataset from Neumayer Station III in Antarctica and added the results in the manuscript. The estimated sulfuric acid concentration is representing the measured sulfuric acid concentration quite well and captures the diurnal variation. However, the method is underestimating the concentration on some days. One reason therefore is most likely due to the neglect of the formation of bigger oligomers than the trimer as well as the clustering with other bases. Therefore, we show the time series of the sulfuric acid monomer, dimer, trimer, tetramer and sulfuric acid tetramer clustered with $NH_3$. From the time series we can determine that the method is specifically underestimating on days when the $SA_{tetramer}$ and $NH_3(H_2SO_4)_3HSO_4$- concentrations are high. We tested if the method can be improved by including more oligomers (tetramer and pentamer of sulfuric acid), however it did not improve the estimation of sulfuric acid significantly: the correlation ($R^2$) changed from 0.48 (without $SA_{tetramer}$ and $SA_{tetramer}$-$NH_3$ cluster) to 0.54 (including $SA_{tetramer}$ and $SA_{tetramer}$-$NH_3$ cluster). Still, our proposed method can easily be adapted, and bigger clusters can be included in the estimation method if needed.

As discussed previously, the neglect of ion-ion recombination in our originally proposed method causes additional errors in the estimation of the concentration. As stated above, including the recombination of the negatively charged SA cluster considerably improved the method. We therefore include the ion-ion recombination in the revised manuscript and in the presented figure below.

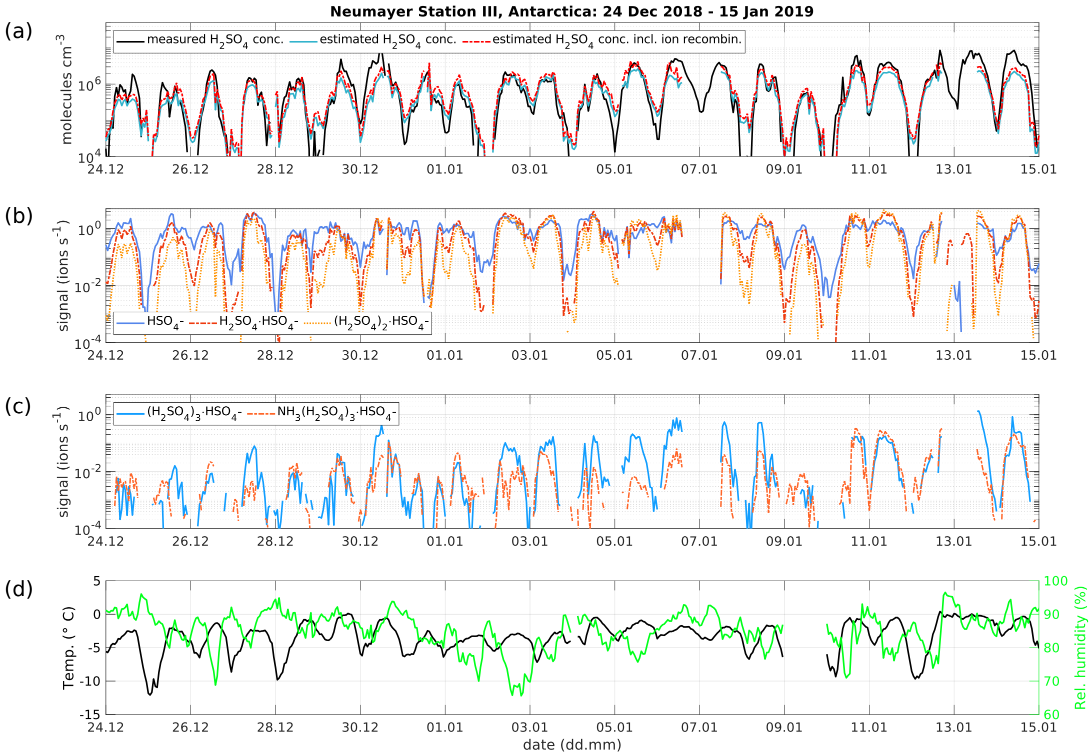



**Figure 6** (a) Time series of measured $H_2SO_4$ concentration from the CI-APi-TOF (black), estimated $H_2SO_4$ concentration from the APi-TOF (blue), and estimated $H_2SO_4$ concentration including ion-ion recombination (red) between 24 December 2018 and 15 January 2019 at Neumayer Station III, Antarctica. The concentration is given in molecules cm$^{-3}$. (b) Time series of the bisulphate ion ($HSO_4^-$, $SA_{monomer}$), $H_2SO_4$ clustered with bisulphate ($H_2SO_4 \cdot HSO_4$-, $SA_{dimer}$), two $H_2SO_4$ molecules clustered with the bisulphate ion ($(H_2SO_4)_2 \cdot HSO_4$-, $SA_{trimer}$) and (c) three $H_2SO_4$ molecules clustered with the bisulphate ion ($(H_2SO_4)_3 \cdot HSO_4$-, $SA_{tetramer}$) as well as the $SA_{tetramer}$ clustered with $NH_3$. (d) Temperature and relative humidity measured at Neumayer Station III.

Specific comments:

RC1: L. 20-23: It is recommended to be more careful in claiming the theoretical expression for H2SO4 may be used under various atmospheric conditions (see also general comment 3)

AC: we rephrased in the Abstract to:

*Here, we propose a theoretical method to estimate the SA concentration based on ambient ion composition and concentration measurements that are achieved by APi-TOF alone.*

RC1: L. 24: "developed estimate works very well..." is a rather qualitative description, better quantify by objective measures.

AC: We included the root mean square error and correlation ($R^2$) in the manuscript, to be more precise. The values are shown as table and also included in the revised text. The finalised table of the revised manuscript is shown below:

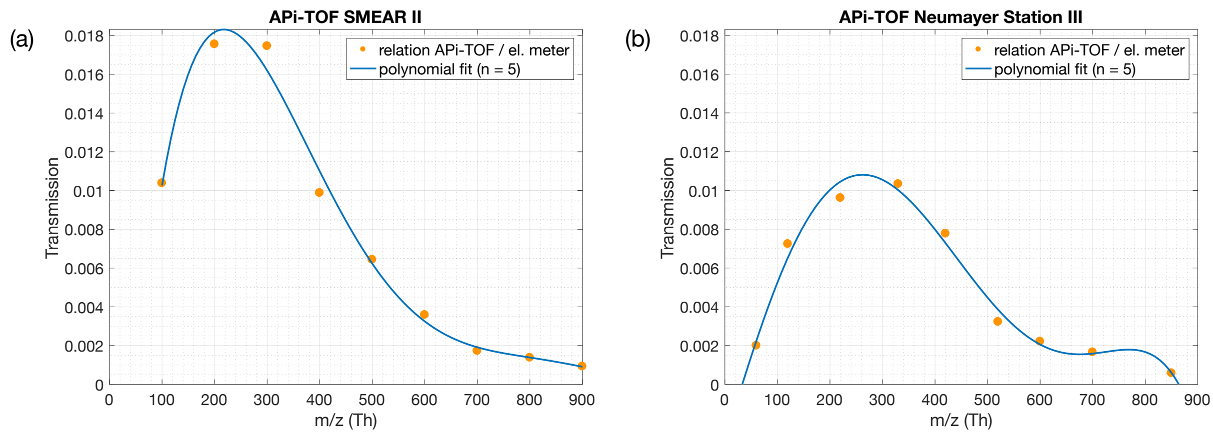
**Table 1:** Root mean square error (RMSE) and $R^2$ of the estimated $H_2SO_4$ concentration at the SMEAR II station and Neumayer Station III. The day- and night-time are split in 06:00 – 18:00 local time (LT) and 18:00 – 06:00 LT, respectively. For the SMEAR II station, we also show the RMSE and $R^2$ of the $H_2SO_4$ proxy calculated with the introduced method by (Dada et al., 2020).

| | **Root mean square error (RMSE)** | | |
|---|---|---|---|
| | **SMEAR II** | | **Neumayer Station III** |
| | Estimated $H_2SO_4$ eq. (8) | $H_2SO_4$ proxy | Estimated $H_2SO_4$ eq. (8) |
| Daytime | $4.12 \times 10^5$ cm$^{-3}$ | $5.54 \times 10^5$ cm$^{-3}$ | $1.43 \times 10^6$ cm$^{-3}$ |
| Night-time | $3.23 \times 10^5$ cm$^{-3}$ | $4.25 \times 10^5$ cm$^{-3}$ | $1.63 \times 10^6$ cm$^{-3}$ |
| | **$R^2$** | | |
| Daytime | 0.85 | 0.78 | 0.48 |
| Night-time | 0.85 | 0.84 | 0.37 |

RC1: L 29-36: Some credit should be given to early ambient ion distribution and sulphuric acid measurements by the Eisele and Arnold groups.
AC: We included Arnold and Fabian (1980) and Eisele (1989) in the introduction as follows:

*A first attempt of estimating the sulfuric acid concentration via the concentration of atmospheric ions was introduced by Arnold and Fabian (1980), followed by Eisele (1989) under the assumption that most* $H_2SO_4$ *molecules are charged by reacting with* $NO_3^-$*.*

RC1: 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.
AC: We included the transmission efficiency calibration results of the two APi-TOFs used in the study (one at SMEAR II station, one at Neumayer Station, which was now added in the revision process). The transmission curves show, that 1-1.8% of the ions with a mass smaller than 400 Th are transmitted through the APi-TOF used at SMEAR II station and 0.5 – 1% of the ions with a mass of 100 – 500 Th are transmitted through the APi-TOF used at Neumayer Station III.




RC1: L. 60-62: Proxies for H2SO4 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.
AC: We rephrase the statement to be more cautious to:

*In circumstances, where the required data for* $H_2SO_4$ *proxies is not available, but measurements with an APi-TOF were conducted, the* $H_2SO_4$ *concentration can be obtained by the ion mass spectra.*

RC1: 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 H2SO4 concentrations based on the ion abundances.

AC: The sentence was corrected to:

*In order to estimate the sulfuric acid concentration ($H_2SO_4$) using measured naturally charged ions (see Fig. 2), we approximate this concentration by following the bisulphate ion $HSO_4$-, herein denoted $SA_{monomer}$, the dimer cluster $H_2SO_4 \cdot HSO_4$- ($SA_{dimer}$) and trimer cluster $(H_2SO_4)_2 \cdot HSO_4$- ($SA_{trimer}$).*

RC1: Conclusion: It is recommended to be more cautious and precise and avoid "...give accurate enough..." and "... a reliable estimate...".

AC: We rephrased the text in order to be more precise and considering the added dataset from Antarctic atmosphere. We also included the values of correlation in the conclusions:

*The estimation agrees well with the measured concentration during daytime in the boreal forest ($R^2$ = 0.85), indicating that the estimation is able to represent the diurnal variation and trend of $H_2SO_4$ concentrations during most of the time when active clustering of sulfuric acid is inducing the initial step(s) of atmospheric new particle formation. However, in an atmosphere, where sulfuric acid is the dominating pathway for initiating new particle formation, the method might underestimate the $H_2SO_4$ concentrations, as this method does not include the rapid clustering to bigger of sulfuric acid clusters and clustering with bases directly, e.g. in the Antarctic atmosphere ($R^2$ = 0.48; during daytime).*

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