

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

General comments:

RC2: The manuscript by Beck et al. presents the derivation of an equation to approximate sulfuric acid concentrations in the atmosphere using API-TOF data when CI is not available. The manuscript is fairly short and as such focuses on a narrow topic, albeit an important parameter that can be observed in the atmosphere by (CI-)API-TOF. I understand that this can be of use to the community of API-TOF users and for measurements of sulfuric acid in new particle formation studies, and would therefore support publication after reviewer comments have been addressed. I would however have hoped for a somewhat more comprehensive study and especially evaluation of the proposed approximation, and would encourage the authors to expand especially the validation section with more datasets, which must be available to them. How well does their approximation compare to the other proxies mentioned in the introduction? Are there other data than CI-API-TOF data available to validate the approximation?

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

AC: We included the sulfuric acid proxy from Dada et al. (2020) for the SMEAR II dataset.

Further, we included a three-week period from Neumayer Station III to validate the method. Unfortunately, we did not have enough variables to calculate the sulfuric proxy for Neumayer Station III.

The validation shows, that at Neumayer Station, the estimation with our method is underestimating the concentration during daytime. But, as reviewer 1 stated correctly, we neglected the ion-ion recombination in our method. By including the recombination term, the correlation (R^2) of the estimated sulfuric acid concentration during daytime improved from 0.29 to 0.48. The term in the equation for ion-ion recombination is especially relevant in atmospheres, where the CS is low, like for example at Neumayer Station III.

On days, when the concentration of larger sulfuric acid clusters and clusters of sulfuric acid and a base is high and nucleation was ongoing, the estimated concentration was however still too low (e.g. 14 January 2019 at Neumayer Station). Therefore, we conclude, that the neglect of those clusters causes errors, especially in atmospheres, where the main mechanism for new particle formation is involving negative ion induced sulfuric acid nucleation (Jokinen et al., 2018).

In the table below, we show the correlation and root mean square errors of our previously presented method (neglecting ion recombination) as well as the renewed method including ion-ion recombination and the SA proxy (only for SMEAR II station).

Table 1: Root mean square error (RMSE) 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)	$5.0 \times 10^5 \text{ cm}^{-3}$	$4.12 \times 10^5 \text{ cm}^{-3}$	$5.54 \times 10^5 \text{ cm}^{-3}$	$1.68 \times 10^6 \text{ cm}^{-3}$	$1.43 \times 10^6 \text{ cm}^{-3}$
Night-time (18–06 LT)	$3.54 \times 10^5 \text{ cm}^{-3}$	$3.23 \times 10^5 \text{ cm}^{-3}$	$4.25 \times 10^5 \text{ cm}^{-3}$	$2.54 \times 10^7 \text{ cm}^{-3}$	$1.63 \times 10^6 \text{ cm}^{-3}$
	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

The figure below shows the validation of the estimated SA concentration for Neumayer Station III. The time series in panel (a) shows the resulting SA concentration with our previously suggested method (blue solid line) and including ion-ion recombination (red dashed line). For the revised manuscript, we included the ion-ion recombination, as suggested by reviewer 1.

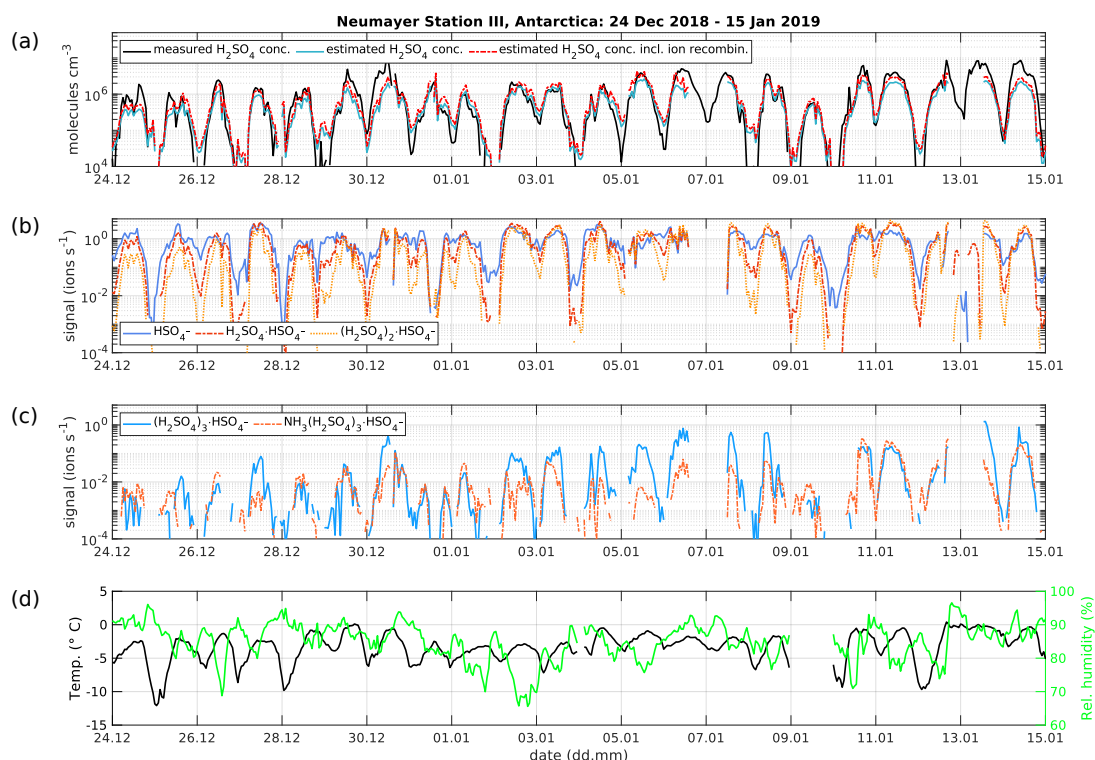


Figure 6 (a) Time series of measured H_2SO_4 concentration from the CI-API-TOF (black), estimated H_2SO_4 concentration from the API-TOF (blue), and estimated H_2SO_4 concentration including ion-ion recombination (red) between 24 December 2018 and 15 January 2019 at Neumayer Station III, Antarctica. The concentration is given in molecules cm^{-3} . (b) Time series of the bisulphate ion (HSO_4^- , $\text{SA}_{\text{monomer}}$), H_2SO_4 clustered with bisulphate ($\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$, SA_{dimer}), two H_2SO_4 molecules clustered with the bisulphate ion ($(\text{H}_2\text{SO}_4)_2 \cdot \text{HSO}_4^-$, $\text{SA}_{\text{trimer}}$) and (c) three H_2SO_4 molecules clustered with the bisulphate ion ($(\text{H}_2\text{SO}_4)_3 \cdot \text{HSO}_4^-$

Unfortunately, we do not have other data available than from CI-API-TOF to compare our method to.

RC2: Figure 1 presents a spectrum in ions per second (the captions mentions time and day but not location, this should be added),

AC: we added the location, and also a spectrum from Antarctica, as data from there was included for further validation.

RC2: Figures 2 and 4 molecules per cm^3 . No information is given on conversion factors or sensitivity assumptions. This is especially important when comparing CI-API-TOF and API-TOF. Related to that, how reproducible are ratios of SA monomers, dimers, trimers between API-TOF instruments? Can it be assumed that all clusters are detected with equal sensitivity? Can the authors elaborate on that?

AC: We added the transmission calibration of the used API-TOFs as a figure and implemented the transmission efficiency of each ion in the calculations. We state in the manuscript:

As the transmission of clusters within an APi-TOF depends on the tuning of the instrument and on the pressures within its chambers, the transmission efficiency needs to be considered, in order to get reliable concentrations of the $SA_{monomer}$, SA_{dimer} , and SA_{trimer} . Fig. 1 shows the transmission efficiency curve of the APi-TOF used at the SMEAR II station and Neumayer Station III. The effect of applying the transmission correction to the different SA clusters is depicted in Fig. 3 for the time series at the SMEAR II station. All ion signals were normalised to a transmission of 1%. As can be determined from Fig. 1a, the $SA_{monomer}$'s transmission at SMEAR II was $\sim 1\%$, while the dimer and trimer were corrected by a factor of $1/1.8$ and $1/1.65$, respectively. The correction was also applied on the ions measured at the Neumayer Station III according to the APi-TOF's transmission (Fig. 1b).

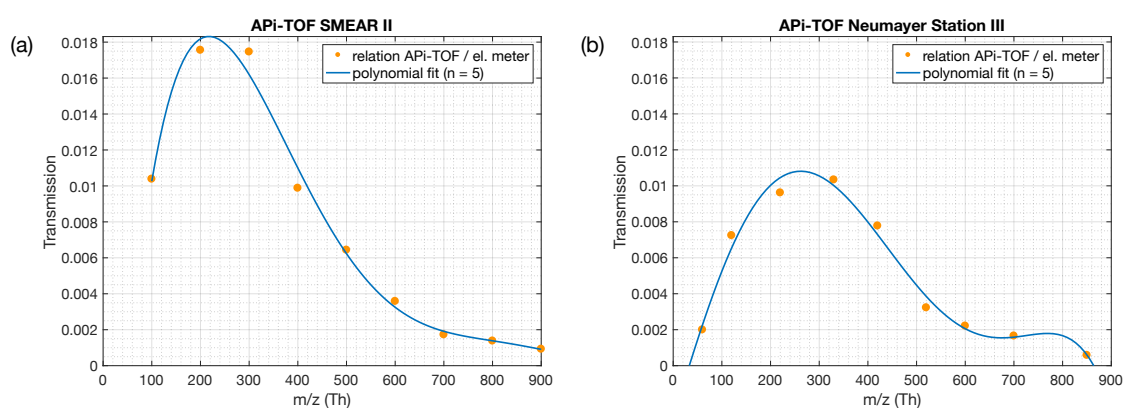


Figure 1 Ion transmission of the APi-TOFs used in this study. The transmission efficiency was determined via production of charged particles with a NiCr wire. The concentration of the size selected ions with a Hermann nano differential mobility analyser (HDMA, Hermann, 2000) were measured with an electrometer 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 the SMEAR II Station, Hyytiälä, Finland. Panel (b) shows the transmission efficiency used for measurements at the Neumayer Station III.

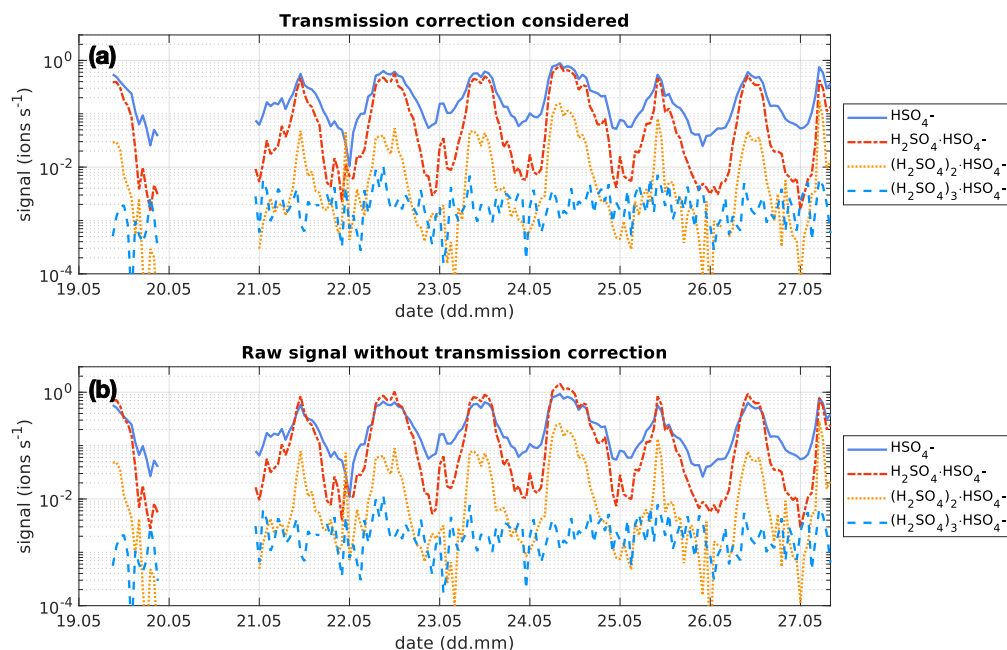


Figure 3 Time series of the bisulphate ion (HSO_4^- , $\text{SA}_{\text{monomer}}$), H_2SO_4 clustered with bisulphate ($\text{H}_2\text{SO}_4\cdot\text{HSO}_4^-$, SA_{dimer}), two H_2SO_4 molecules clustered with the bisulphate ion ($(\text{H}_2\text{SO}_4)_2\cdot\text{HSO}_4^-$, $\text{SA}_{\text{trimer}}$) and three H_2SO_4 molecules clustered with the bisulphate ion ($(\text{H}_2\text{SO}_4)_3\cdot\text{HSO}_4^-$, $\text{SA}_{\text{tetramer}}$) between 19 and 27 May 2017 at SMEAR II station, Hyytiälä, Finland. The concentration is given in ions s^{-1} as measured by the API-TOF. The upper panel shows the concentration of the clusters considering the transmission efficiency of the instrument (see Fig. 1). The lower panel shows the concentration of the clusters without that correction and assuming a constant transmission efficiency of 1% for all ions.

Further, we added the calibration factor for both CI-API-TOFs in the text. The CI-API-TOFs were calibrated with sulfuric acid, based on the proposed method by Kürten et al. (2012). The calibration factor of the CI-API-TOF at SMEAR II station is 2.5×10^9 and 4.9×10^9 for the CI-API-TOF at Neumayer Station III.

Technical comments:

Title: Since the technique is mentioned as abbreviation in the title, I suggest using its full name in the title as well.

We rephrased the title as suggested to: *“Estimation of sulfuric acid concentrations using ambient ion composition and concentration data obtained by Atmospheric Pressure interface Time-of-Flight ion mass spectrometer”*

RC2: Line 18 – 19: Move “CI” behind “chemical ionization” and remove it from “(CI-API-TOF)”

AC: We added the CI abbreviation behind “chemical ionization”, as requested.

RC2: Line 33: “detect this concentration” – at all? Quantitatively? Can the authors be more specific?

We added the following text (written italic) to be more specific about the challenges regarding the measurement of sulfuric acid:

However, ambient concentrations of H₂SO₄ are low, commonly less than a part per trillion by volume ($\sim 2 \cdot 10^7$ molecules cm⁻³), making it challenging to *measure it*. During the recent years there have been instrumental developments towards a reliable detection of H₂SO₄ in the atmosphere, particularly via the development of a Chemical Ionisation Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-API-TOF, Jokinen et al., 2012), using nitric acid as a reagent ion. *Still, the measurement technique with CI-API-TOF is relatively challenging, as a thorough calibration i.e. with sulfuric acid as proposed by Kürten et al. (2012), is needed in order to get reliable numbers. Furthermore, the loss of sulfuric acid to surfaces, such as an inlet, and the correct flow rates must be known and characterised.*

RC2: Line 34: Not clear to me what is meant by “clear steps”

AC: we rephrased the sentence to:

During the recent years there have been *instrumental developments* towards a reliable detection of H₂SO₄ in the atmosphere, particularly via the development of a Chemical Ionisation Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-API-TOF, Jokinen et al., 2012), using nitric acid as a reagent ion.

RC2: Line 38: “During the past decade or so” sounds rather colloquial, suggest rewording

AC: We removed the phrase “or so” and introduce the sentence with:

During the past decade, ...

RC2: Line 46: should read “ions”

AC: Thank you for noticing the correction is implemented in the reviewed manuscript.

RC2: Figure 1: Red peaks could be labelled individually

AC: We added labels to the ions in the figure with the spectra (see figure below).

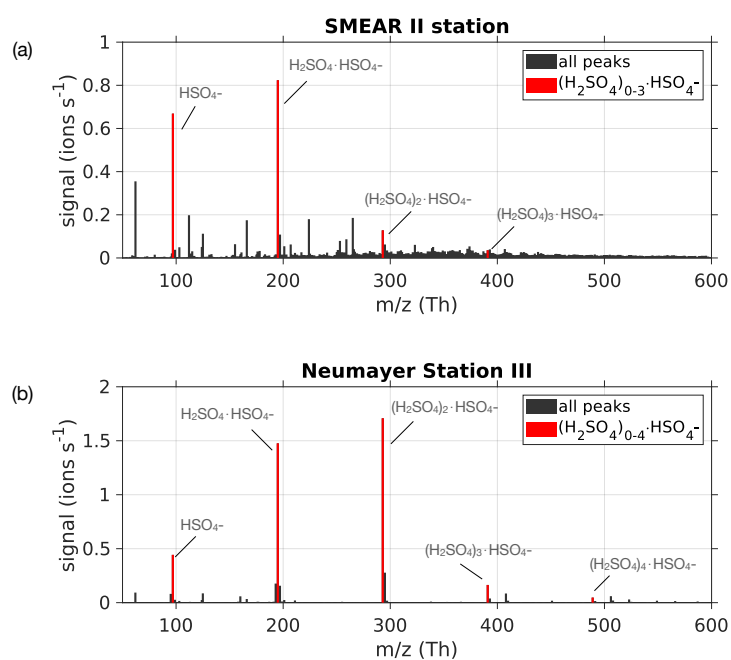


Figure 2 (a) Mass spectrum from 50 to 600 Th measured with the APi-TOF on 24 May 2017 during the time period 08:00 – 18:00 (local time) at SMEAR II station, Hyytiälä, Finland. (b) Mass spectrum from 14 January 2019 between 08:00 and 18:00 (local time) at Neumayer Station III, Antarctica during a new particle formation event. The bisulphate ion HSO_4^- and H_2SO_4 clusters containing it were used for the estimation of H_2SO_4 concentration, and are coloured in red.

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