Estimation of sulfuric acid concentration using ambient ion composition and concentration data obtained by Atmospheric Pressure interface Time-of-Flight ion mass spectrometer

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Abstract

Sulfuric acid (H_2SO_4, SA) is the key compound in atmospheric new particle formation. Therefore, it is crucial to observe its concentration with sensitive instrumentation, such as chemical ionisation (CI) inlets coupled to Atmospheric Pressure interface Time-of-Flight mass spectrometers (APi-TOF). However, there are environmental conditions and physical reasons when chemical ionisation cannot be used, for example in certain remote places or flight measurements with limitations regarding chemicals. 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. We derive a theoretical expression to estimate SA concentration and validate it with accurate CI-APi-TOF observations. Our validation shows that the developed estimate works well during daytime in the boreal forest (R^2 = 0.85), however it underestimates the SA concentration in e.g. Antarctic atmosphere during new particle formation events where the dominating pathway for nucleation involves sulfuric acid and a base (R^2 = 0.48).

1 Introduction

Sulfuric acid (H_2SO_4, SA) is the key compound in atmospheric new particle formation (e.g. Weber et al., 1995, 1996; Birmili et al., 2003; Kulmala et al., 2004; Kuang et al., 2008; Kerminen et al., 2010; Wang et al., 2011; Kulmala et al., 2014; Yao et al., 2018; Cai et al., 2021), therefore it is crucial to have accurate observations of its concentration. However, ambient concentrations of H_2SO_4 are low, commonly less than a part per trillion by volume (~$2 \cdot 10^7$ molecules cm^{-3}), making it challenging to measure it. During the recent years there have been instrumental developments towards a reliable detection of H_2SO_4 in the atmosphere, particularly via the development of a Chemical Ionisation Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-

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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.

During the past decade, Atmospheric Pressure interface Time-of-Flight mass spectrometers (APi-TOF, Junninen et al., 2010) have been deployed in several measurement campaigns where the use of a CI inlet was either not possible or desired. In these instances, the APi-TOF only observed the composition and concentration of ambient ions. The APi-TOF is capable of directly sampling and detecting naturally charged gas-phase ions, including molecular clusters, and is often being used to detect clustering processes as a first step of new particle formation on a molecular basis (e.g. Schobesberger et al., 2013; Jokinen et al., 2018; Beck et al., 2021). While a CI-APi-TOF at best has a limit of detection around ~10^4 molecules cm^{-3} (~ ppq level), the APi-TOF can detect approximately 1% of the ambient ion concentration (Fig. 1, Junninen et al., 2010). With an average ion concentration of ~1000 cm^{-3} per polarity (Hirsikko et al., 2011), the APi-TOF is measuring 10 ions $cm^{-3}s^{-1}$ with a limit of detection of ~0.01 counts per second, hence 0.1 ions cm^{-3}. This corresponds to approximately pps level ($100 \cdot 10^{-21}$), showing that the limit of detection of APi-TOF in comparison to CI-APi-TOF is lower by five orders of magnitudes.

A detailed description of the APi-TOF can be found in Junninen et al., (2010). Since concentrations of neutral clusters are below the detection limit of CI-APi-TOF in many atmospheric conditions and environments, using the APi-TOF is currently the only way to directly detect atmospheric clustering. Therefore, if we can estimate H_2SO_4 concentration particularly during initial steps of new particle formation, based on the same dataset, we can readily get better insight into the process itself.

Since there are only limited long term observations of H_2SO_4 concentrations, several proxies on this concentration have also been developed (e.g. Petäjä et al., 2009; Mikkonen et al., 2011; Lu et al., 2019; Dada et al., 2020). These proxies attempt to approximate the ambient H_2SO_4 concentrations using more readily measured quantities, in particular the sulfur dioxide concentration, (UV) radiation intensity and pre-existing particle number size distribution that can be used to calculate the condensation sink for gas-phase H_2SO_4. In circumstances where the required data for H_2SO_4 proxies are not available, but measurements with an APi-TOF were conducted, the H_2SO_4 concentration can be obtained from the ion mass spectra. 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^-.

Motivated by the reasonings outlined above, we derive here an expression to estimate H_2SO_4 concentration based primarily on APi-TOF observations and validate it.

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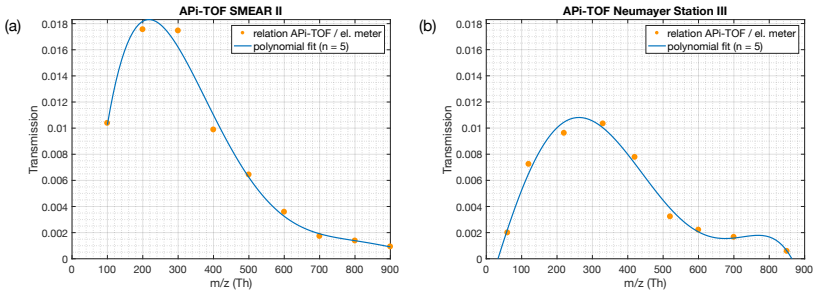

Figure 1 Ion transmission of the APi-TOFs used in this study. The transmission efficiency was determined via production of charged particles with a NiCr wire. The concentration of the size selected ions with a Hermann nano differential mobility analyser (HDMA, Hermann, 2000) were measured with an electrometer 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.

2 Theoretical estimation of sulfuric acid concentration with bisulphate ion and H_2SO_4 clusters

Ambient ion mass spectra have usually clear evidence of gas-phase H_2SO_4, predominantly in the form of bisulphate ion (HSO_4-) and its adducts involving H_2SO_4, forming so-called dimers ($H_2SO_4 \cdot HSO_4$-) as well as larger clusters (Ehn et al., 2010). These are due to the efficient scavenging of negative charge by ambient H_2SO_4 via proton donation, and due to the high stability of the sulfuric acid-bisulphate ion clusters, in particular for the dimer (Ortega et al., 2014). In order to estimate the sulfuric acid concentration (H_2SO_4) using the 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}). Any other H_2SO_4-containing ion clusters, in particular those larger than the SA_{trimer}, typically occur at much smaller concentrations and will be neglected here.

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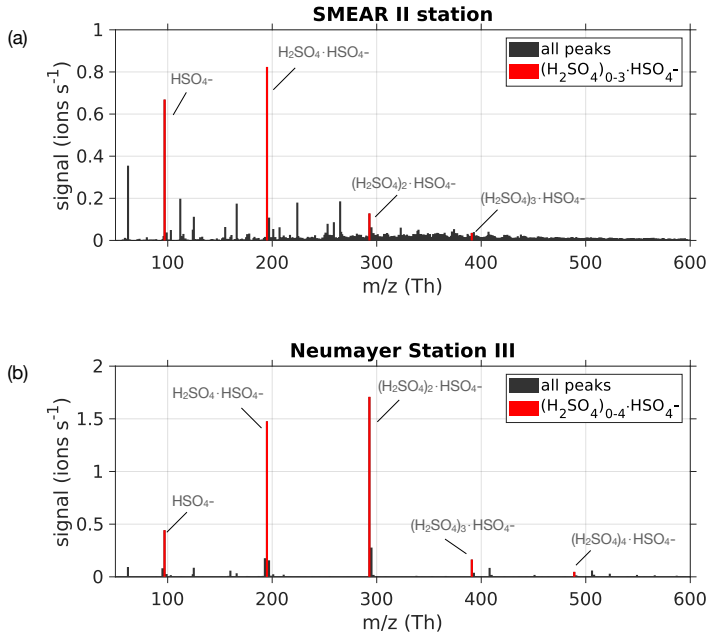

Figure 2 (a) Mass spectrum from 50 to 600 Th measured with the APi-TOF on 24 May 2017 during the time period 08:00 – 18:00 (local time) at SMEAR II station, Hyytiälä, Finland. (b) Mass spectrum from 14 January 2019 between 08:00 and 18:00 (local time) at Neumayer Station III, Antarctica during a new 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.

If we assume that the concentration of $SA_{monomer}$ depends generally on its production rate (P_1) and that its loss is by condensation onto aerosol particles (condensation sink, CS), to the SA_{dimer}, when clustering with another H_2SO_4 molecule, and to ion-ion recombination with positive ions (N_{pos}), we get the following equation for the $SA_{monomer}$ concentration:

$$\frac{d[SA_{monomer}]}{dt} = P_1 - CS \cdot [SA_{monomer}] - P_2 - \alpha \cdot [SA_{monomer}] \cdot N_{pos}, \quad (1)$$

where $P_2 = k_1 \times [SA_{monomer}] \times [H_2SO_4]$ is the dimer production rate due to $SA_{monomer}$-H_2SO_4 collisions, α ($\approx 1.6 \times 10^{-6}$ cm^3 s^{-1}) is the ion-ion recombination coefficient (Kontkanen et al., 2013), and the collision rate k_1 is assumed to be constant.

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For the dimer concentration we consider the production P_2, the loss due to CS, the clustering of the SA_{dimer} with H_2SO_4 with a rate constant k_2, and the ion-ion recombination:

$$\frac{d[SA_{dimer}]}{dt} = P_2 - CS \cdot [SA_{dimer}] - k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] - \alpha \cdot [SA_{dimer}] \cdot N_{pos} \quad (2)$$

And with substituting P_2, eq. 2 for SA_{dimer} changes to:

$$\frac{d[SA_{dimer}]}{dt} = k_1 \cdot [SA_{monomer}] \cdot [H_2SO_4] - CS \cdot [SA_{dimer}] - k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] - \alpha \cdot [SA_{dimer}] \cdot N_{pos} \quad (3)$$

Finally, to produce SA_{trimer} we consider the collision of the SA_{dimer} with H_2SO_4 and the loss to the CS and ion-ion recombination. For the sake of completeness, we would additionally have to consider the loss of $SA_{trimers}$ to form the tetramer $(H_2SO_4)_3 \cdot HSO_4$, however this additional term is rather small and will therefore be neglected in this derivation. Therefore, we get the simplified equation for SA_{trimer}:

$$\frac{d[SA_{trimer}]}{dt} = k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] - CS \cdot [SA_{trimer}] - \alpha \cdot [SA_{trimer}] \cdot N_{pos} \quad (4)$$

For simplification, we consider a pseudo-steady state condition for both dimers and trimers by setting the left-hand side of eqs. (3) and (4) to be zero, which is justified when the dimer and trimer concentrations change at rates smaller than their overall production and loss rates. Thereby, from eq. (3) we obtain:

$$k_1 \cdot [SA_{monomer}] \cdot [H_2SO_4] = CS \cdot [SA_{dimer}] + k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] + \alpha \cdot [SA_{dimer}] \cdot N_{pos} \quad (5)$$

and from eq. (4) we obtain:

$$k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] = CS \cdot [SA_{trimer}] + \alpha \cdot [SA_{trimer}] \cdot N_{pos} \quad (6)$$

If we now deploy equation (6) in equation (5) and solve for H_2SO_4, the result is:

$$k_1 \cdot [SA_{monomer}] \cdot [H_2SO_4] = CS \cdot [SA_{dimer}] + CS \cdot [SA_{trimer}] + \alpha \cdot [SA_{dimer}] \cdot N_{pos} + \alpha \cdot [SA_{trimer}] \cdot N_{pos} \quad (7)$$

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

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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 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). 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. 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).

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.

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From equation 8 we also see that the concentration of H_2SO_4 is proportional to relative concentrations of sulfuric acid monomers, dimers and trimers clustered with the bisulphate ion:

$$[H_2SO_4] \sim \frac{[SA_{dimer}] + [SA_{trimer}]}{[SA_{monomer}]} \quad (9)$$

To estimate the H_2SO_4 concentration with the ion mode APi-TOF, we can therefore use this theoretical approach, in particular Eq. 8. For the collision rate of H_2SO_4 with HSO_4- we use $k_1 = 2 \cdot 10^{-9}$ cm^3 molecule^{-1} s^{-1} as in Lovejoy et al., (2004). The value of CS is calculated based on Kulmala et al., (2012). Even if the CS was unknown due, for example, to the lack of particle measurements, the daytime variability of the H_2SO_4 concentration could still be estimated only by using the relation of the H_2SO_4-containing cluster with HSO_4-, as it is proportional to the H_2SO_4 concentration (see eq. 9). If the concentration of positive small ions is not available, it can be assumed to be in the range of 500 – 1000 cm^{-3} which is a reasonable approximation for the average concentration (Hirsikko et al., 2011).

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 ~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).

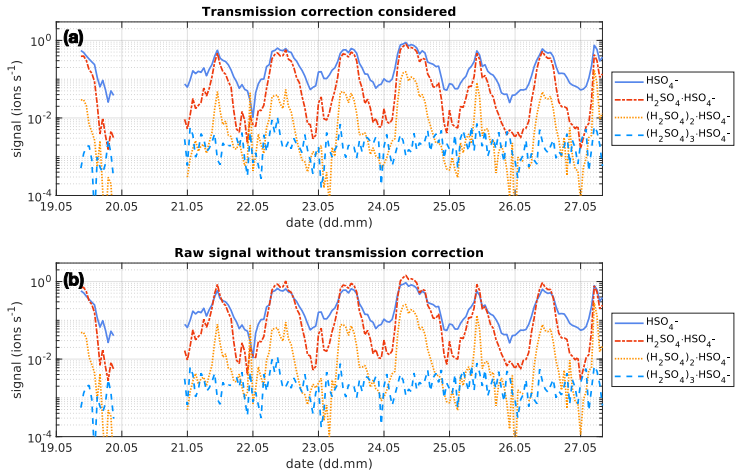

Figure 3 Time series of the bisulphate ion (HSO_4^-, $SA_{monomer}$), H_2SO_4 clustered with bisulphate ($H_2SO_4 \cdot HSO_4^-$, SA_{dimer}), two H_2SO_4 molecules clustered with the bisulphate ion ($(H_2SO_4)_2 \cdot HSO_4^-$, SA_{trimer}) and three H_2SO_4 molecules clustered with the bisulphate ion ($(H_2SO_4)_3 \cdot HSO_4^-$, $SA_{tetramer}$) 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.

3 Validation

We tested the expression derived above using a dataset collected during inter-comparison measurements at the SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005). In Fig. 4 we show the time series of the observed H_2SO_4 concentrations, measured with a CI-APi-TOF. The CI-APi-TOF was calibrated for sulfuric acid, based on the method by Kürten et al., (2012) and resulted in a calibration factor of 2.5×10^9. Additionally, we show the estimated sulfuric acid concentration based on APi-TOF measurements together with Eq. 8 and the sulfuric acid proxy concentration (Dada et al., 2020). The concentration of positive ions for the estimated sulfuric acid concentration was obtained from a Neutral cluster and Air Ion Spectrometer (NAIS, Airel Ltd., Mirme and Mirme, 2013).

The estimated H_2SO_4 concentration agrees with the measured one during most of the daytime. Between 06:00 and 18:00 local time, the correlation (R^2) between the estimated and measured H_2SO_4 concentration is equal to 0.85 with a root mean square error (RMSE) of 4.12×10^5 cm^{-3}. During night-time, the corresponding values are 0.85 and 3.23×10^5 cm^{-3} (Table 1).

The scatter plot in Fig. 5 shows that the estimated H_2SO_4 concentrations agree well with the observed one when H_2SO_4 concentrations are larger than 2×10^6 cm^{-3}, demonstrating that our method works particularly well at the SMEAR II station during conditions that favour the formation of H_2SO_4-containing clusters.

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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	4.12×10^5 cm^{-3}	5.54×10^5 cm^{-3}	1.43×10^6 cm^{-3}
Night-time	3.23×10^5 cm^{-3}	4.25×10^5 cm^{-3}	1.63×10^6 cm^{-3}
	R^2		
Daytime	0.85	0.78	0.48
Night-time	0.85	0.84	0.37

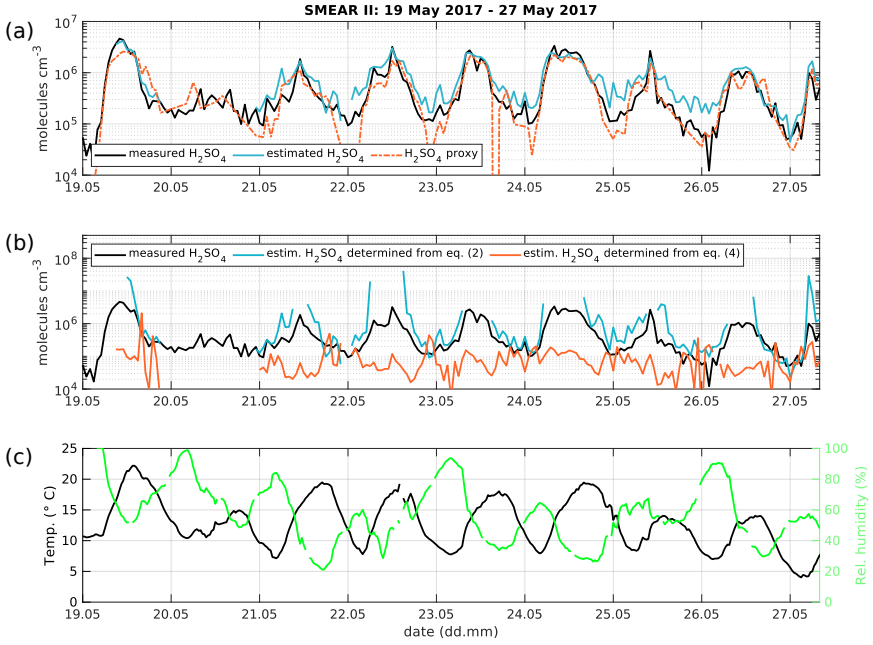

Figure 4 (a) Time series of measured H_2SO_4 concentration from the CI-APi-TOF (black) and estimated H_2SO_4 concentration from the APi-TOF (blue) and H_2SO_4 proxy from Dada et al. (2020) (orange) between 19 and 27 May 2017. The concentration

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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.

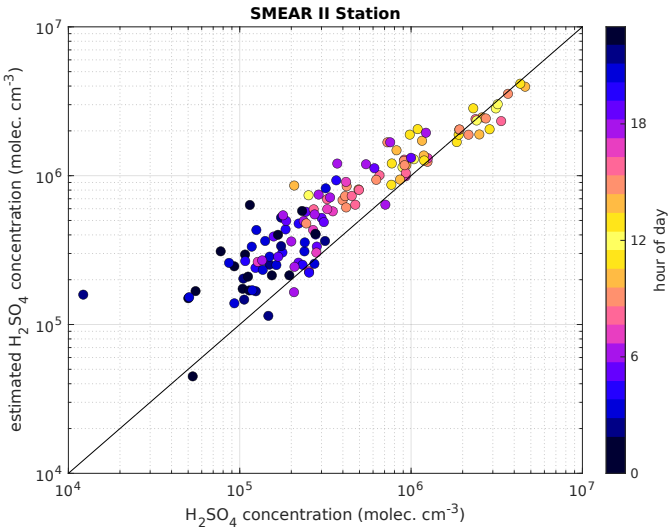

Figure 5 Measured H_2SO_4 concentration using a CI-APi-TOF (horizontal-axis) versus estimated H_2SO_4 concentration based on APi-TOF results (vertical-axis) at SMEAR II station. For the estimation of H_2SO_4, the transmission efficiency was taken into account. The colour is indicating the hour of the day and the black line is the 1:1 ratio. Between 08:00 and 16:00 local time, the concentrations are agreeing well. The shown data contains the time period from 19 to 27 May 2017. The overall correlation coefficient (Pearson) is 0.94.

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.

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 1×10^{-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 4.9×10^9. 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 neglection 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

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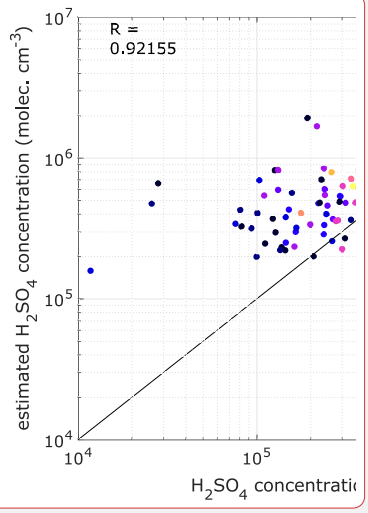

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negative ion-induced sulfuric acid-ammonia nucleation, acting as a major sink for sulfuric acid molecules due to its clustering with bases (Jokinen et al., 2018). Including the $SA_{tetramer}$ and $SA_{tetramer}$ clustered with NH_3 in the estimation equation improved the correlation (R^2) from 0.48 to 0.54. 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).

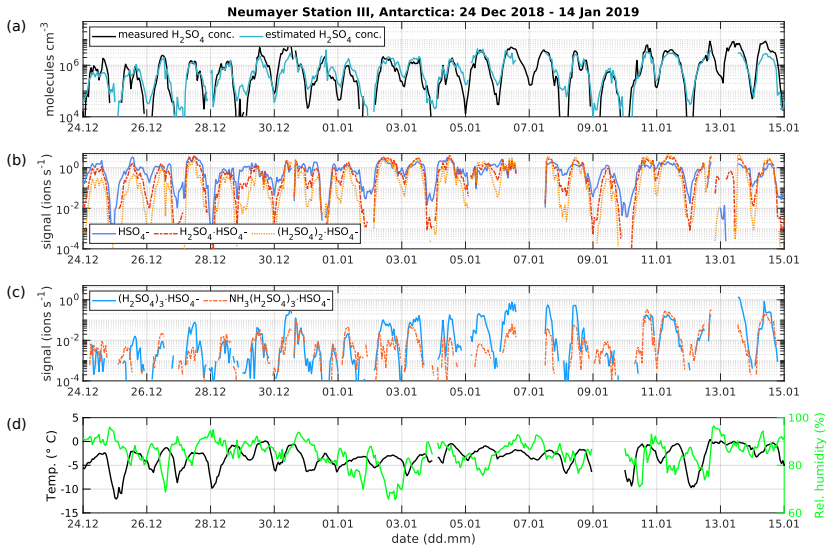

Figure 6 (a) Time series of measured H_2SO_4 concentration from the CI-APi-TOF (black) and estimated H_2SO_4 concentration from the APi-TOF (blue) between 24 December 2018 and 14 January 2019 at Neumayer Station III, Antarctica. The concentration is given in molecules cm^{-3}. (b) Time series of the 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.

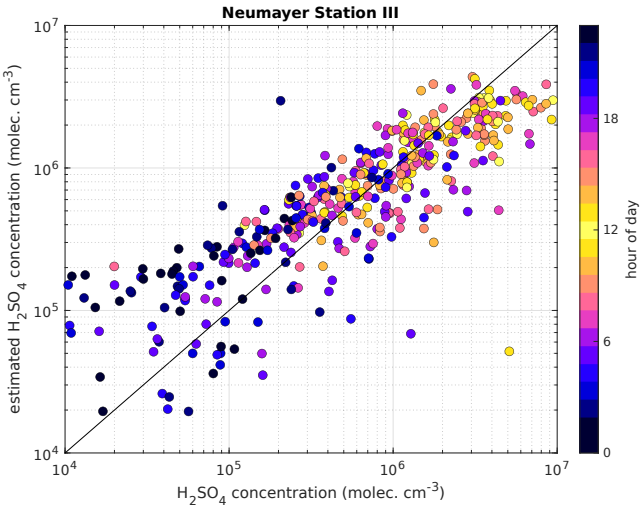

Figure 7 Measured H_2SO_4 concentration using a CI-APi-TOF (horizontal axis) versus estimated H_2SO_4 concentration based on APi-TOF results (vertical axis) at the Neumayer Station III. For the estimation of H_2SO_4, the transmission efficiency was taken into account. The colour is indicating the hour of the day and the black line is the 1:1 ratio. The shown data contains the time period from 24 December 2016 to 14 January 2019. The overall correlation coefficient (Pearson) is 0.77.

4 Conclusions

Here we derived a theoretical expression to estimate H_2SO_4 concentrations based on APi-TOF measurements of ambient ions. 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).

The APi-TOF's "ion mode", i.e. direct ion sampling without chemical ionisation, remains a crucial tool in many field deployments and laboratory studies, since it is extremely sensitive and allows for observing atmospheric clustering molecule by molecule, which in most cases is impossible when relying on chemical ionization. Therefore, having available a reliable estimate of H_2SO_4 concentration allows us to utilise the APi-TOF ion mode even more effectively.

Data availability

The data can be accessed via Zenodo (10.5281/zenodo.5266313).

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Author contribution

LJB, SS, VMK and MK designed the study. LJB and MS performed the measurements. SS and LJB derived the equations. LJB processed and analysed the data and performed the data visualisation. MK and VMK supervised the process. All authors commented and edited the paper.

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