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Reply on RC1

Marcel Zauner-Wieczorek et al.

Author comment on "Mass spectrometric measurements of ambient ions and estimation of gaseous sulfuric acid in the free troposphere and lowermost stratosphere during the CAFE-EU/BLUESKY campaign" by Marcel Zauner-Wieczorek et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-238-AC1>, 2022

(**Comments by the referee are in bold font**, answers by the authors are in regular font)

In the manuscript "Mass spectrometric measurements of ambient ions and estimation of gaseous sulfuric acid in the free troposphere and lowermost stratosphere during the CAFE-EU/BLUESKY campaign", M. Zauner-Wieczorek and co-authors present high-altitude measurements of ambient ion compositions over Europe using a state-of-the-art ion mass spectrometer (HR-API-TOF-MS).

Airborne deployments of such equipment for detailed ion measurements are rare, even more so for high altitudes (ULTS). Given that rarity of the methodology and resulting data and their analysis, I believe the paper overall is novel enough to justify publication in ACP. But due to the limited scope of the results and their discussion, I would recommend publication rather as a "measurement report" than a research article.

The manuscript is well written overall. Worth pointing out in particular is the good summary of relevant past studies in the Introduction section, which puts the study into proper perspective.

I have a two major comments relating to instrument performance, data analysis and the estimation of sulfuric acid concentrations, which I believe should be addressed prior to acceptance.

A couple of minor and technical comments are mostly suggestions that I hope would improve the paper further.

We would like to thank the Referee for their valuable feedback. Thanks to their suggestions, we believe that the manuscript could be significantly improved.

As the Referee notes, ion measurements are rare for the UTLS, especially in the last few decades. Moreover, measurements of gaseous sulfuric acid in the UTLS have been very few as discussed in the introductory part of our manuscript. Thus, the data set of ion measurements and the inferred gaseous sulfuric acid concentrations presented in our

manuscript are an important contribution in a scarce field of research. Therefore, we are convinced that the publication as a research article is justified.

Major comment 1:

Two issues came to mind that could affect the validity of this method for estimating gaseous sulfuric acid concentrations, but aren't mentioned (Equations 1).

One being the ion transmission as a function of mass (or m/z), which appears here is implicitly assumed to be the same for NO_3^- and HSO_4^- . Do the authors have any estimate on that transmission function, or how it could affect the outcome of Eqs. 1?

Heinritzi et al. (2016) studied the mass-dependent transmission of the very same HR-TOF-MS that we also used in this study. They used an Eisele-Tanner type corona discharge chemical ionisation source (Kürten et al., 2011) that was operated at the ambient pressure of around 1000 hPa. In that study, Heinritzi et al. (2016) found that at around $m/z = 100$, the transmission varies between 0.8 and 1.5 %. The most prominent differences to the former setup and the setup used in this study are the different inlet lines, the two critical orifices between the inlet line, the mid-pressure stage, and the ion source in the SCORPION setup, the lower pressure in the ion source of the SCORPION, and the different internal voltage settings of the TOF-MS. Beck et al. (2022a), who used a similar* *Tofwerk* HR-TOF-MS, found very similar values for the transmission. [* See the question in the minor comments about the mass spectrometer used by Junninen et al. (2010), which was also used by Beck et al. (2022a).]

Thus, a conservative estimate for the transmission difference between NO_3^- and HSO_4^- leads us to a scaling factor of maximum 2. This factor is within our overall experimental uncertainty.

For the future, we plan to perform a more detailed characterisation of the mass-dependent transmission via the HR-DMA method described by Heinritzi et al. (2016). Due to time restrictions and campaign planning, we could not conduct this so far. This will be subject of a technical paper on the SCORPION by Heinritzi et al. (in preparation).

Also, I believe that some possibly important sinks of NO_3^- and HSO_4^- ions are being neglected by only considering R1. I am thinking specifically of adduct formation (with neutral molecules) that these ions are known to contribute to - potentially "consuming" a considerable portion of NO_3^- and/or HSO_4^- . Major candidates, also in the free troposphere, could be HNO_3 and H_2SO_4 , as well as organic acids. See several papers cited (e.g., Frege et al., 2017, 10.5194/acp-17-2613-2017; Ehn et al., 2010, 10.5194/acp-10-8513-2010) and also the data presented in the manuscript itself (e.g., Fig. 2). Could the authors elaborate on the role of such clusters for the accuracy of Eqs. 1?

If I missed here something explained in the 1980s papers, it could be helpful to summarize the key points of those studies regarding Eqs. 1, as many (myself included) do not have free access to many of those older studies.

We are sorry for the misunderstanding. Eq. (1a) and (1b) already include the clusters of NO_3^- and HSO_4^- with HNO_3 and H_2SO_4 . The ions/ion clusters NO_3^- , $(\text{HNO}_3)\text{NO}_3^-$, and $(\text{HNO}_3)_2\text{NO}_3^-$ are called nitrate core ions or NO_3^- core ions. The ions/ion clusters HSO_4^- , $(\text{HNO}_3)\text{HSO}_4^-$, and $(\text{H}_2\text{SO}_4)\text{HSO}_4^-$ are called hydrogen sulfate core ions or HSO_4^- core ions.

We calculated $[H_2SO_4]$ for both the ratio of HSO_4^-/NO_3^- only and for the ratio of the respective sum of the core ions and found that the difference is not significant. This can well be explained by the fact that, in our data set, the count rates of NO_3^- and HSO_4^- are higher than the count rates of the clusters and, thus, the unclustered ions dominate the calculation using all core ions.

We changed the introduction of Sect. 2.4 and the explanation of Eq. (1a) slightly, in order to avoid misunderstandings and to include the key points of the derivation of Eq. (1a) by Arnold and Qiu (1984):

p. 8, l. 201ff.: "To quantify the number concentration of gaseous sulfuric acid, we used the steady-state method developed by Arnold and Fabian (1980), which is described in more detail by Arnold and Qiu (1984). This is based on the assumption that hydrogen sulfate ions are virtually only produced by charge transfer from nitrate to sulfuric acid, as given in Reaction (R1):

[Reaction (R1)]

Nitrate and hydrogen sulfate ions cluster with HNO_3 and H_2SO_4 ligands, yielding $(HNO_3)_mNO_3^-$, called nitrate core ions, and $(H_2SO_4)_k(HNO_3)_mHSO_4^-$, called hydrogen sulfate core ions, respectively (see also Sect. 1). Assuming negligible other source reactions for HSO_4^- core ions, a negligible aerosol sink, and subsequent ion-ion recombination after the reaction, Arnold and Qiu (1984) presented Eq. (1a) to calculate the number concentration of sulfuric acid from the ratio of the product ions (i.e. the HSO_4^- core ions) and the precursor ions (i.e. the NO_3^- core ions) for steady-state conditions:

[Eq. (1a)]"

And sub-comment 4: Have the authors attempted the method suggested by Beck et al. (2021a; brought up in this study's introduction)? Theirs was somewhat simplified too, but differently.

In the method presented by Beck et al. (2022a), the number concentration of gaseous sulfuric acid is calculated using the concentrations of the sulfuric acid monomer, dimer, and trimer. Because we barely observe the dimer (see Fig. 2 of the manuscript) and we are unable to detect the trimer in our data, it is, unfortunately, not possible to derive the sulfuric acid concentration with the method proposed by Beck et al. for our data set.

Major comment 2

Overall, are the authors able to comment on the ion transmission of their instrument (either as deployed, or as expected from pre- or succeeding experiments)? This comment relates to my comment above, but I am also thinking about the instrument's sensitivity overall. The signal intensity appears to be quite low here, whereas other studies, using a similar base mass spectrometers, appear to have obtained richer, less noisy spectra (e.g., Ehn et al., 2010, 10.5194/acp-10-8513-2010; Frege et al., 2017, 10.5194/acp-17-2613-2017).

Is that so, or just appearing that way to this reviewer? For example, do ground-based deployments mainly benefit from being able to average over longer measurement times? But Table 1 suggests that substantial averaging times were in fact available here. Also the airborne APi-TOF-based data in Beck et al. (2021, under review, 10.5194/acp-2021-994) appears to have "richer" spectra, at around 10 min averaging it seems. Though they do

seem less rich in the instances where they measured in the (lower) free troposphere.

If this is all just how things are in the UTLS: Have the authors gathered any experience of how the SCORPION/APi-TOF performs near the surface (or even on the ground)?

The signal intensity of our data set is lower and the mass spectrum less rich compared to other APi-TOF-MS studies at ground or in the lower free troposphere for several reasons:

- The abundance of ions is generally higher in the UTLS compared to the boundary layer because of the stronger exposition to galactic cosmic rays (GCRs). However, as described in the introductory section of the manuscript, in the UTLS there are virtually only NO_3^- and HSO_4^- anions and their clusters with HNO_3 and H_2SO_4 , which explains the less rich mass spectrum.
- The limited measurement times in the APi mode at different altitudes constitute a disadvantage compared to ground-based, locally fixed measurements where averaging times can be chosen more generously. Nevertheless, the boxplots in Fig. 3 and 5 are based on the 30 s averaged data points.
- Due to the specific setup in the aircraft, there are unavoidable losses along the way towards the APi-TOF-MS. The inlet line is 1.7 m long and there are two critical orifices that are necessary to ensure a constant pressure of 200 hPa inside the "ion source" (in the APi mode, the ion source region merely functions as a pressure controlled pre-chamber before entering the first vacuum chamber of the APi-TOF-MS). These lead to inevitable losses and, thus, a decreased sensitivity.
- Furthermore, the internal voltage settings of the APi-TOF-MS, including the multi-channel plate (MCP) detector, were not optimal during the CAFE-EU/BLUESKY campaign, which was our first aircraft-based campaign with this setup. Measurements of ambient ions near the surface showed that with optimised internal voltage settings, the signal-to-noise ratio could be improved and the de-clustering of cluster ions could be reduced. We were able to clearly distinguish the dimers $(\text{HNO}_3)_2\text{NO}_3^-$ and $(\text{H}_2\text{SO}_4)_2\text{HSO}_4^-$ from the background noise even for shorter averaging times (e.g. half an hour). We are looking forward to future measurement campaigns with optimised voltage settings.

In that respect, Fig. 2 could benefit from stating also in the caption, how long of a total average is shown. Line 253 suggests it is even a campaign-average, which would mean a total averaging time of 6 hours (if I understand correctly, and using Table 1)!? And not, for instance, an example of a 30-s spectrum, in which case the signal-to-noise would actually be quite good, on first glance ... but then, on the other hand, I would be rather surprised at the bleakness of the spectra, i.e. absence of additional peaks appearing with longer averaging (unless that was a feather of the UTLS)...

There is also a "minor comment" on Section 2.1 below that relates to this issue.

Figure 2 indeed shows a campaign-wide averaged mass spectrum. For more clarity, we added the averaging duration to the caption:

p. 11, l. 273f.: "Figure 2: Mass spectrum of ambient negative ions averaged for all measurements in the negative APi mode (i.e. averaged over 6 h). ..."

Minor comments:

Line 27:

Does the presence of ions in ambient air really qualify the atmosphere as a "plasma" (even a "diluted" one)? For example, I wouldn't consider a dust storm a "diluted solid"...

We found the perspective of a high energy physicist thought-provoking to view Earth's atmosphere as a "diluted plasma". However, this concept does not contribute to the actual topics discussed in the manuscript so that we deleted this term to avoid confusion:

p. 2, l. 27f.: "Earth's atmosphere not only contains neutral gases, but also ions in the gas phase that play a crucial role in several atmospheric processes..."

Line 53: Could add recent paper by Beck et al. (2021; still in ACPD it appears; doi 10.5194/acp-2021-994).

We added the paper by Beck et al. (2022b).

Lines 62-74: The paragraph may give the impression that vertically resolved nitric acid measurements are rarer than they are. Airborne nitric acid mixing ratio measurements go back at least to the PEM campaigns in the 1990s (Hoell et al., 1997, 1999; doi: 10.1029/97JD02581, 10.1029/1998JD100074). The most sensitive recent methods may be CIMS, e.g. using I- or CF3O-, deployed on aircraft on multiple occasions (e.g., Lee et al., 2018, doi 10.1029/2017JD028082; Dörich et al., 2021, doi 10.5194/amt-14-5319-2021). I suggest slightly extending that part of the introduction accordingly.

We extended the part about HNO₃ measurements accordingly:

p. 3, l. 74ff.: "Early airborne measurements of nitric acid were performed in the 1990s (Hoell et al., 1997; Hoell et al., 1999). Iodide-adduct Chemical Ionisation Mass Spectrometry (CIMS) is one of the most sensitive methods used nowadays for airborne HNO₃ detection (Lee et al., 2018; Dörich et al., 2021). Measurements in the upper troposphere and lower stratosphere (UTLS) showed that..."

Section 2.1:

It is not unambiguously clear that the base mass spectrometer is (presumably!) identical to that first described in Junninen et al. (2010), as introduced in the Introduction.

The hardware of the MS is identical to the one used by Junninen et al. (2010), however, the pumping architecture is different so that we are hesitant to call both base mass spectrometers identical.

In addition, it could be instructive to provide more detail regarding how operation with the SCORPION inlet, even when rendered inert with all voltages disabled, differed from the "default" operation of the TOF-MS to measure atmospheric ions. And in that respect, have the authors tried to quantify ion transmission losses due to the presence of the SCORPION inlet?

All these could be of interest for readers engaged (or thinking about) ambient ion measurements using (the Tofwerk) TOF-MS.

To switch from Chemical Ionisation (CI) mode ("default" mode) to Atmospheric Pressure inlet (API) mode, only the internal voltages of the ion source, including the corona voltage, needed to be switched off. The gas flows inside the ionisation region were kept on because the contamination of HNO_3 was excluded by implementing a counter flow regime with a separate exhaust flow close to the corona needle.

In CI mode, we have performed experiments to quantify transmission losses due to the inlet line, however, we have not yet fully analysed those data sets. Using the Gormley-Kennedy equation (Gormley and Kennedy, 1949), we estimate a loss of around 50 % for gaseous sulfuric acid. Losses inside the pressure stage are covered by the experimentally determined calibration factor when using the CI mode.

With regards to the ambient ion measurements presented in this manuscript, we assume that the difference in the wall losses to the inlet line and the critical orifices between NO_3^- and HSO_4^- are negligible. Because we only report relative values for the atmospheric ions and use the ratio of nitrate and hydrogen sulfate core ions, this does not affect the inferred concentration of sulfuric acid.

Line 138: Any particular reason, why the mass resolution was "only" up to 3000? I recall somewhat higher numbers at least for Tofwerk's "H-TOF" (which I imagine was used).

The mass resolution depends on the mass range and is typically in the range of 3000 for m/z values around 100 and increases with increasing m/z , experiencing a plateau of around 4000 for $m/z > 300$. The mass resolution also depends on the internal voltage settings of the TOF-MS. The official value given by the producer may be higher, however, the real values in the lab or in the field often differ from the ones given by the producer.

Also, how good of a mass accuracy (ppm) was achieved?

The mass accuracy was around 5 ppm for NO_3^- .

Section 2.3, 1st paragraph: Was some sort of noise reduction necessary as well, or was the noise negligible compared to total ion counts (given there was no ionization source)?

First of all, we average the 1 s raw data files to 30 s to diminish the noise. Afterwards, we performed a baseline subtraction as a standard procedure to process the averaged data, i.e. subtracting the average electronic noise from the mass spectra.

We added the information on the baseline subtraction to the manuscript:

p. 8, l. 186f.: "The subsequent post-processing included a detailed mass calibration, baseline subtraction, peak identification, and peak integration."

Line 187: Do the authors mean "INdependent"? Then I would understand that part better, I think. Else, please clarify.

These background peaks appeared at different m/z ratios, depending on what sample gases we used. For synthetic air, peaks were observed that can be assigned to O^- , O_2^- , N^- , and N_2^- , amongst others. When using pure nitrogen, the O-related signals were not detectable. With argon, none of the aforementioned ions were detectable, but we observed Ar^+ in the positive mode, instead.

We specified the sentence in the manuscript for more clarity:

p. 8, l. 190ff.: "These background peaks were likely caused by internal chemical processes in the mass spectrometer as their respective appearances were dependent on the sample gas such as synthetic air, nitrogen, or argon."

Line 277 & Fig. 3: How high was the tropopause? Could be nice to indicate the range of its heights in Fig. 3.

The tropopause was typically between 10 and 11 km. We added the tropopause range to Fig. 3 and adapted the caption accordingly:

p. 12, l. 304f.: "The grey shadow indicates the range of the tropopause."

We also added this information in the opening of Sect. 3.1.2:

p. 12, l. 286ff.: "Figure 3 shows the altitude dependence of the most abundant ions and of gaseous sulfuric acid. Furthermore, the range of the tropopause (10 to 11 km) is indicated by a grey shadow."

Fig. 3: Not sure of "ncps" is the most intuitive unit for the "normalized count rate" in this case. As count rates are simply divided by the total count rate, the result is just a (unitless) fraction, as indicated also in the main text actually. (Of course, one could in principle multiply with "1 cps" ... but I don't see a conceptual reason for that.)

For more clarification, we added the mention of the normalised count rates in Sect. 2.3:

p. 8, l. 187f.: "The integrated peak values were normalised by the total ion count, yielding the normalised count rates, nCR ."

Furthermore, we changed the labels of the x-axes in Fig. 3 (a) to (c) to nCR (respective ion) and adapted the caption accordingly:

p. 12, l. 301ff.: "Figure 3: Altitude-resolved box plots of the normalised count rates nCR of (a) NO_3^- , (b) $(HNO_3)NO_3^-$, and (c) HSO_4^- (all dimensionless), and (d) the number concentration of gaseous H_2SO_4 (in cm^{-3})."

Technical comments:

Line 235: "However" appears not to fit.

We changed it to "Moreover".

Line 269: "comparably" probably the wrong word.

We changed it to "comparatively".

Line 302: "points between the 25 % and the 75 % percentiles, i.e. the boxes contain the medium half of the data points" ... That's all fine. But FYI, I believe that thing can also be called the "interquartile range" (or IQR). Not sure how prevalent the term is in our field.

We changed it to "interquartile range" (also for Fig. 5).

Line 285: See above (L269) ... "relatively" or "comparatively"?

We changed it to "comparatively".

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