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Comment on acp-2022-238

Anonymous Referee #1

Referee 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-RC1>, 2022

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.

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?

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.

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.

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)?

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.

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"...

Line 53:

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

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.

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. 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.

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).

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

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)?

Line 187:

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

Line 277 & Fig. 3:

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

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.)

Technical comments:

Line 235:

"However" appears not to fit.

Line 269:

"comparably" probably the wrong word.

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.

Line 285:

See above (L269) ... "relatively" or "comparatively"?