Review comments: Chemical precursors of new particle formation in coastal New Zealand, M. Peltola et al., 2022

This manuscript presents ion measurements from a remote site in the southern hemisphere using an atmospheric pressure interface time of flight spectrometer (APi-ToF) with no chemical ionisation inlet to capture ambient anions. This is an extensive dataset spanning seven months, and the accompaniment to a previous high quality paper published by the same authors (Peltola et al., 2022). The subject is of great scientific interest as it presents a comprehensive dataset in a highly unstudied area. The manuscript is well written, and figures are beautifully presented but would be greatly strengthened by some further analysis. Some key calculations can be done from the size distribution data (formation rates and ion-ion recombination rates at low diameters), some ion signals can possibly be assigned formulae with some careful thought, and if the averaging time is increased, some more mechanistic insight may be possible from the mass spectra. I highly recommend publication in ACP once a few comments are addressed.

Specific comments

Line 10: Should this say bisulphate, rather than sulphate? Or maybe sulphur-containing ions?

Line 69: If mentioning the sea surface microlayer, maybe reference (Mungall et al., 2017)

Line 98: It would be nice to have some more details here about the running conditions for the PSM, I presume it was used in scanning mode, how long did each scan take, and how was the data inversion performed? Chan et al., 2020 presents four different techniques for inverting this data that give slightly different results. Was there any data pre-processing?

Line 116: How many NPF events fall into this 4.3% of data coverage?

Line 117: How does this compare to the Potential Source Contribution Function? I.e., as discussed by (Fleming et al., 2012).

Line 130, Figure 2 & 3: These figures are very visually striking, but to me it is quite difficult to see the correlation between most of these species unless the correlations are particularly positive or negative. Would it make sense to reduce the alpha for lines corresponding to R values close to zero perhaps, as we are mostly concerned with stronger correlations?

Line 139: “Pure sulfuric acid clusters were detected up to the trimer”. Do you mean sulphuric acid-bisulphate clusters? Also, is this referring to your dataset here, or Junninen et al.?

Line 153: It would be nice to say how you went about deciding what peaks to assign formulae to, and what could not be fit. What possible combination of atoms did you look at? What error (i.e. in ppm) did you deem acceptable?

Line 171: Why is this a good reason to put them in another group? Do you infer that $HI_2O_6^-$ has a different source than the other two iodine compounds from this?

Line 181: I’m not sure I understand the rationale here. Peaks in group “Other1” and “Other3” correlate with each other, but why is that important for the main thrust of the paper (aerosol formation?), especially when these contain 2 and 3 peaks, respectively. What counts as a “strong correlation” here?

I understand the grouping of “Other2” and “Other4” as they correlate with aerosol concentrations (I presume this means total number concentrations from your CPC? Or is this N100 from integrating across the size distribution measurements). I will also echo the other reviewer here and suggest digging deeper to try and assign more of these mass spectral peaks. For example, your “Other4” group contains peaks which very well could be of the formulae $C_xH_yO_zN_1NO_3^-$. Some quick calculations show me that the peak at 339.024 m/Q would be about 150 *ppm* away from $C_{10}H_{15}O_8NNO_3^-$, and the peak at 373 about 150 *ppm* away from $C_{10}H_{17}O_{10}NNO_3^-$, the same with the two other ions. This discrepancy in mass could easily be mass calibration related perhaps

Line 194: It would be nice to substantiate the claim about halogen anions from the ocean with a reference

Line 213: Are you confusing the NO_3 radical with the nitrate anion here?

Line 225: I'm not sure you can substantiate this claim with your data here, how do you know this is explained by a higher condensation sink, rather than a lower source strength? The CS has been calculated for this dataset (Peltola et al., 2022). It might be helpful to use this here.

Line 235: Again, a reference r.e. these sources would be nice

Line 256: As this discussion doesn't add much to the overall discussion of iodine oxides, why not include it with the sum of iodine anions?

Line 266: I am not sure organosulphate is the correct term for a HOM-bisulphate cluster as this usually refers to molecules with a $R\text{-}SO_4^-$ functional group

Line 282: This nighttime peak in Other4 is somewhat consistent again with what was observed for Organonitrate-nitrate anion clusters in previous work (Bianchi et al., 2017)

Figure 6: Why are groups Other1-4 not included here?

Line 331: Just a note on this section: it may be useful also to try something like the potential source contribution function (PSCF) to simply identify the regions leading to the highest ion signals. This will exclude some of your data and perhaps highlight just the strongest source regions.

Line 340: The $H_2SO_4HSO_4^-$ cluster is a good indicator of NPF in Beijing, but what about this dataset?

Line 379: I think it should be possible to see some larger clusters during NPF events in the mass spectra, even with a suboptimal instrument tuning. Is it possible to average across the entire NPF event? Possibly when the ion concentrations from the NAIS are elevated. This may help the data interpretation somewhat

Figures 9, 10, 12, 13: It might be nice to see these in a non-stacked fashion to simply see how, for example, $H_2SO_4HSO_4^-$ behaves more clearly. These could simply go in the appendix.

Line 427: Why not investigate the correlation with the formation rates? The J_{10} is available from the previous publication from this dataset, and the formation rate at lower sizes can be calculated from the available NAIS and PSM data, better yet, the ion-ion recombination rates can be calculated, which fit very nicely with the APi-ToF measurements. You may then find much better correlations with your ion signals.

References

Bianchi, F., Garmash, O., He, X., Yan, C., Iyer, S., Rosendahl, I., Xu, Z., Rissanen, M. P., Riva, M., Taipale, R., Sarnela, N., Petäjä, T., Worsnop, D. R., Kulmala, M., Ehn, M., and Junninen, H.: The role of highly oxygenated molecules (HOMs) in determining the composition of ambient ions in the boreal forest, Atmos. Chem. Phys., 17, 13819–13831, https://doi.org/10.5194/acp-17-13819-2017, 2017.

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Mungall, E. L., Abbatt, J. P. D., Wentzell, J. J. B., Lee, A. K. Y., Thomas, J. L., Blais, M., Gosselin, M., Miller, L. A., Papakyriakou, T., Willis, M. D., and Liggio, J.: Microlayer source of oxygenated volatile organic compounds in the summertime marine Arctic boundary layer, Proc. Natl. Acad. Sci. U. S. A., 114, 6203–6208, https://doi.org/10.1073/pnas.1620571114, 2017.

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