

Peltola et al., 2022 represents the first measurements the composition of naturally charged ions from Baring Head, New Zealand. The paper addresses a very relevant scientific question of how aerosols are formed in a marine environment and adds context to the previous paper by the author (Peltola et al., ACP, 2022).

The manuscript introduces ion composition data from new areas of the world, which are in a key role when trying to reduce bias in aerosol formations studies, that mostly concentrate on studies in the boreal forest zone and Europe. Other than Antarctic and Bolivian measurements, these are one the first ambient observations from the Southern hemisphere. The concept is often used in aerosol formation studies but it is still rare to see actual field measurements and especially for such long time series of aerosol precursors (7 months of data). The authors characterize diurnal and seasonal cycles of air ion composition, different types of correlations and pointed out the source regions for these components. Where they could do much better is to conclude which components form molecular (ion) clusters and make more comparable correlations to nanoparticles by changing the size groups. This is something their data set is (or should) be capable of showing.

All together the paper has good scientific significance and quality and it is mostly presented in a well-structured way. In order to keep this as a scientific article I suggest more detailed analysis the results part. If you wish to keep the conclusions and results as they are now, I would suggest very minor corrections and a changing this article to a measurement report as at the current state it does not bring novel information on marine NPF to my opinion, but a lot of observations that should be published in ACP for sure. Suggestions to how to revise this scientific article are below in the more specific comments.

More specific comments:

L4: Ambient anions. You may use anions throughout the text also.

L35: Did you check your data if you can identify these compounds in your data set? I know Veres et al., 2020 used an iodine CIMS, but one can always look if they are ionized naturally.

L50-55: I suggest you add Beck et al., 2022 as citation in this section also since it introduces similar results from the area from two different sites.

L65: References within Bianchi et al., 2019 since it is a review paper, I would recommend to cite the original work if possible.

L75-76: Sulfate formation? Secondary sulfates (SA?), maybe I misunderstand this.

L80-82: Do you want to concentrate on marine NPF or both marine and land-influenced air? The introduction and your title concentrates very much on marine NPF but I think it would be valuable to include both since you have all the data you need to solve both. You could address the difference between land and marine air in the title even.

L93 / L100 and so on: Peltola et al., ACP, 2022 now, I assume. Great paper, I have to say, congratulations.

L102: What was the resolution of the device? (LTOF or HTOF?)

L104: Did you use 30 min averaging to investigate NPF events also? In clean locations, actually in most places, I use a much longer averages to increase the signal level. E.g. in Jokinen et al., 2018 paper from Antarctica, the mass defect plots are 180 min averages over the NPF event duration. I suggest you try the same to catch the possible higher SA oligomers and ammonia clusters.

L107: Increased? Did you have a different flow before?

L116: How many events (or any) did you catch during this 4.3 % of clean marine air when you had APi-TOF data?

L128: You used all data to gather the peak list in Table A1? It seems like very few peaks were present if this is the case.

L137: Is it an event day, non-event day? Since the charge is distributed to the strongest candidate, I would rather consider plotting an average night time and day time spectra since they have very specific features due to this.

L138: Can you differentiate SO_3^- from H_2ONO_3^- ? Water has a tendency in evaporating, but can be identified most of the time with nitrate ion.

L141: In Table A1 you list a peak “unknown0085” at 407.876007 Th and the exact mass of $\text{NH}_3(\text{H}_2\text{SO}_4)_3\text{HSO}_4^-$ is 407.888 Th. Is the mass accuracy sufficient to say that this peak is not ammonia-sulfuric acid-bisulfate cluster?

L145: There are multiple peaks in Table A1 that are marked as unidentified, however, I think a good amount of these peaks you can identify using the data in e.g. Ehn et al., 2012, Yan et al., 2016 PMF paper, Jokinen et al., PNAS, 2015 paper and supplementary figures that have many compositions of these peak, Bianchi et al., 2017 (<https://doi.org/10.5194/acp-17-13819-2017>) and many more if you wish. Loads of possibilities with this dataset!

L148-150: Clean air (air quality) can hold a lot of compounds in it like it is shown in Hyytiälä. Most importantly you seem to have weak sources of condensing vapours or sufficient sink for them before getting detected. Do you have an estimation of the losses in the inlet line or the transmission of the instrument? As you mention before, the APi-TOF has much lower detection threshold for ions than the one coupled with chemical ionization, so Baccharini et al., 2021 probably had the same “problem” as you, not enough production of the compounds and higher detection limit.

L160 / Schemaballs: All data? Not NPF vs. non-NPF or night vs. day? It would be useful to compare night time and daytime data separately that are unfortunately not shown at the moment. To be honest, I have difficulties in reading the schemaballs with this much data and compounds in them. Statistically all the correlations seen are significant so this seem like a good way to group the data, for future I suggest getting to know PMF, that might help grouping compounds in another way. The correlations from which the data was now grouped is not shown, please show that data also or instead of these two plots.

L164: Is H_2IO_4 an ion missing its charge? Perhaps H_2OIO_3^- ? I would also be specific in terminology when measuring ions: bisulfate (not always sulfuric acid) and so on.

L170 and Table 2: About grouping the compounds: Please correct the charge of ions (some are now neutral), e.g. NO_3^- . I would also go through the table and fix the compositions like in group 1: H_2ONO_3^- , $\text{HNO}_3\text{NO}_3^-$ (hydrogen does not have a negative charge), group 2: $\text{H}_2\text{SO}_4\text{HSO}_4^-$, $(\text{H}_2\text{SO}_4)_2\text{HSO}_4^-$ and so on, MSA: CH_3SO_3^- . I don't understand why the $\text{HIO}_3\text{IO}_3^-$ is in the different group due lower signal? It should not matter if you add these group compounds up. What is the value of having the dimer separately from the monomer and hydrated monomer? You probably also notice some similarities in the “Others”. Most masses are uneven, meaning that they may contain a certain number of nitrogen atoms. If you are interested in digging deeper to this, I suggest you start by looking at the Yan et al., 2016 PMF paper more closely on organic nitrates. “Other 4” contains a very interesting peak that was connected to NPF in Hyytiälä years back (Kulmala et al., 2013, Science).

L198: Monoterpenes and isoprene have more sources than forests, but I might say they probably do originate from vegetation. You have the means to identify more peaks since you have a mass spectrometer, Sulo et al., 2021 also helps with peak lists.

L205: and charge is always distributed according to the compound's proton affinity! This really has a large effect on what you can detect. There might be dozens of compounds in the air that you just can't detect because SA takes away all you charge.

Fig 4: I really like this illustration, clear and informative. Nicely tells a story about HOM originating from land and MSA from the ocean, you must have some nice sources around.

L213: NO_3^- or nitrate radical?

L225: Can it also be increased production, since MSA and SA have same marine source and MSA is highly abundant in your data set?

L234: Do the marine species (like Cl^- or Br^-) have correlation with higher windspeeds (sea spray)?

L245: You can give the lifetime estimation since you have condensation sink available (Peltola et al., 2022). Lifetime is proportional to the CS.

L256: I assume this is iodic acid dimer, $\text{HIO}_3\text{IO}_3^-$.

L257: Are the species clusters or sulfur and iodine containing compounds?

L293: Bisulfates increased during Austral summer months in land influenced air, so how do you connect that to increased DMS emissions? Marine air masses did not show an increase in bisulfates. When the production is higher, you should be able to see the higher clusters forming also. Did you observe those?

L313: There are long term measurements available from SMEAR I, that is not so far north as Baccharini et al., measurements from the Arctic if you want to compare to a clean continental area (Jokinen et al., 2022, <https://doi.org/10.5194/acp-22-2237-2022>).

L317: What is the temperature during winter? Lower temperature favours condensation (lower vapour pressure). CLOUD experiment has done temperature runs with HOMs if you want to have a look, e.g. Frege et al., 2018 (<https://doi.org/10.5194/acp-18-65-2018>). It would be interesting to see the meteorological data in this manuscript also.

L344: If DMS oxidation is the most important source of nss- SO_4 , then why you link bisulfates with mostly SO_2 pollution and not DMS oxidation? Can you estimate how much of bisulfate dimer would come from DMS oxidation and how much from pollution? Are the source regions same for the monomer and dimer?

L352: What is the lifetime of DMS? Can it be transported to your site and get oxidized in the vicinity of your sampling site?

Fig 8A: Could you insert more ticks to see the diameter range better? And please add number concentration of particles like you have in Fig 11.

Fig 9, 10, 12,13: I would normalize the ion signals with TIC or just a use a diurnal plot of signals in order to see the increasing or decreasing signals. How many events in total (N) are depicted as NPF and non-events?

L406: The instrument measures naturally charged ions, so in that sense it is not the limitation of the instrument but actual phenomenon in the atmosphere. Bisulfates are produced during the day and (unfortunately) take the charge and hinder the identification of processes happening in the background.

L440-450: How about correlation with formation rates? That could be better be suitable to particle numbers.

Fig 11. I don't recommend using the size class 1-10 nm (if from NAIS), since the size classes 0.8-2nm (small ions) and 2-7 nm (intermediate ions) have very different dynamics and behaviour, see Manninen et al., 2016, fig 17. Therefore, I suggest you always separate them. The ones over 7 nm (large ions, 7-20 nm) should also be in different size class than the smaller ones. Make sure you depict the instruments used for the measurement in the figure caption.

(Manninen et al., 2016, <https://amt.copernicus.org/articles/9/3577/2016/amt-9-3577-2016.pdf>)

L478: Did you have solar radiation measurements? You could show the link between the formation of precursors and radiation (or just use the daylight times)

L482-485: I suggest you take the whole NPF period where small particles are formed, from 9-12 AM, and average it in one spectrum. Make a mass defect plot to interpret further, they are extremely useful tools for this type of analysis. I don't know what you want to say with the bisulfate signal decrease in the evening, since the formation event happens in the morning-noon?

L488: If you did the analysis based on the ion classes by Manninen et al., 2016, would this conclusion be different?

L495: I recommend you to look at mass defect plots and compare e.g. events to non-events, before and during event or marine to over land air masses.

L501-505: Again, the ion size groups are selected a bit differently. 2-4 and <10 nm. I suggest using the standard operation procedure recommendations by Manninen et al., 2016 (0.8-2, 2-7 and 7-20 nm) if reporting NAIS data. This way the data will be further comparable with ACTRIS data also.

L523: Do you have values of what is the fraction of ion induced nucleation at your site? The APi-TOF should be capable of revealing clustering of iodate or bisulfates, you might need to average much longer times than 30 minutes to build up signal from NPF times and I suggest looking into mass defect plot or plotting spectra during event and non events on top of each other in order to find the differences.

L548: concentration of neutral aerosol precursors? Total concentration of gases is a wide suggestion, but naturally recommended.

Thank you for introducing the measurements to me and best of luck finishing the manuscript!