

Interactive comment on “Atmospheric VOC measurements at a High Arctic site: characteristics and source apportionment” by Jakob B. Pernov et al.

Anonymous Referee #1

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This manuscript reports on a long-term (spring through fall) Arctic VOC dataset observed at Villum Research Station at Station Nord in Greenland, and a PMF analysis performed on the dataset. The authors report the PTR-ToF-MS results for 10 detected ions, assigning 10 gas-phase molecular formulae and species/species groups to the observed ions in the PTR. A PMF analysis of the 10 species and species groups with a four-factor analysis is presented and discussed at length, including a Biomass Burning Factor, a combination Marine Cryosphere Factor, a Background Factor, and an Arctic Haze Factor. The authors give a very nice detailed analysis of the four factors, including the primary components, sources and influences and temporal variability.

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Overall this is a well-written paper, with valuable data and analysis that should be published. One of my primary concerns with the paper, and with the majority of PTR-instrument papers, is that there is a lack of accounting or explanation of the VOC specificity (or lack thereof) of the PTR technique. The authors make no effort in this paper to discuss the interfering or additional species that may comprise each observed chemical formula that make up several of their measurements – e.g., propanal's contribution to the signal attributed to acetone, isobutanal's and butanal's contribution to the signal attributed to MEK – even to justify the omission of these species from the discussion with adequate explanation and literature references. As well, the authors' treatment of methyl acetate and propionic acid is to suggest that the contributions from each species (or other species that might contribute to the $C_3H_6O_2H^+$ signal) are unknown in Section 2.2, but then they attribute the signal to methyl acetate in the Biomass Burning Factor, and propionic acid in the Marine Cryosphere Factor, with no justification as to the reasons for the identification. The authors need to add commentary for the species identification, and justify the assumed VOCs under different conditions, or simply refer to the observations as a generic $C_3H_6O_2$ VOC group. Also, as detailed below, references to VOCs that comprise the C_5H_8O observation should be clear that the measurement is not of an ion ($C_5H_8OH^+$ or $C_5H_8O^+$), but of the C_5H_8O VOC group.

My other primary concern is that the authors indicate that the data are available by contacting one of two author email addresses. I would strongly recommend that the paper not be published until the data are available in a publicly-available DOI.

The remainder of my comments are minor and detailed below.

As stated at the end of Sect. 3.2, “The different temporal patterns and correlations suggest the behavior and sources of VOCs in the Arctic are seasonally dependent. Therefore, a detailed, statistical investigation of the sources affecting VOC levels is warranted.” This is very true, and the reason why this paper should be published.

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Lines 145-152 – the authors describe the method by which “compound names” are assigned to the nine protonated masses, including Pagonis et al. and references, which is reasonable, and a priori knowledge, which is not something that can be reference checked. I would argue that there is insufficient justification given to identifying the masses which ignore contributions from additional compounds that may be included in the concentrations measured. The authors write “Another compound (C₄H₈OH⁺) was doubly assigned to propionic acid and methyl acetate.”, but they likely meant to write C₃H₆O₂H⁺, which has m/z 75.058. However, they should explain here why they don’t include ethyl formate or hydroxyacetone as possible compounds at this mass.

Lines 155-157 – The authors should be specific about how the data were quality controlled using these parameters (PSND, WD, WS, etc.), and the resulting amount (total percentage, number of time periods, etc.) of data that had to be eliminated from the useful data set.

Lines 215, 212, 467, 506, etc. – Technically the authors did not observe ambient C₅H₈O⁺ ions (or C₅H₈OH⁺ ions), but rather a compilation of [some] gas-phase C₅H₈O species, which were protonated in order to be observed by the PTR system, similar to how they did not observe atmospheric ambient C₆H₆H⁺ ions, but rather gas-phase C₆H₆ (i.e., benzene). Thus, discussion of the species or group of species with the chemical formula C₅H₈O should simply be “C₅H₈O species” or “C₅H₈O”, as in Figure 1, and should not imply the measurement of an atmospheric ion.

Lines 245-252 – The comparisons presented against literature data from similar Arctic stations make sense, for the most part, but the comparison of wintertime benzene mixing ratios from Gautrois et al. (2003) to this study are not merited, as no wintertime data is being presented here. As well, while I agree that it has been shown that benzene and acetonitrile are influenced by lower latitudes, the claim that acetonitrile is influenced by anthropogenic emissions is not backed up. Remote levels of acetonitrile are likely impacted by the significance of mid-latitude fire seasons, and are not expected to compare well from year to year.

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Line 308 – the authors state that species with $S/N < 0.2$ were excluded from the analysis, but all 10 species (or species groups) discussed in the paper are included in Table 2. Are there any other species that were measured but not included here?

Line 337 – “it is a source of methyl acetate as well. . .” – the authors recognize that methyl acetate could be contributing to the $C_3H_6O_2H^+$ signal, but by labeling it “propionic acid” in Table 2 and Figures 1, 3, 5, 7, etc., the identity of the compound is muddled. If the authors truly believe that the species is primarily propionic acid, then the presence of methyl acetate would be unimportant. If they believe that it is indeed a mixture of the two (or more) species, then this should be made clear whenever it is being referred to.

Line 445 – The back trajectories frequency map for the Marine Cryosphere Factor is interesting, but it would be more informative to highlight some of the brief periods where this factor is particularly elevated, rather than averaging over a three-month summer period. Given, as well, that all the species identified to contribute to the Marine Cryosphere Factor have atmospheric lifetimes < 5 days, it would be prudent to limit these back trajectories to 120 hours or less.

Figures – all figures in the primary manuscript and supplement should be saved at a higher resolution. There is significant pixilation when zooming in on the plots. Some of the finer details are lost as a result, and some of the axis labels are rendered illegible.

Table 1 – The table title doesn’t need to be so long. “Overview of measured protonated masses included in PMF analysis” would be sufficient. The rest is redundant with the table header, although Mean Mixing Ratio should be spelled out in the header or defined in a footnote. As well, it would be good to specify if the “Percentage below LOD” is the percentage of all data collected, or the percentage of only the data that was not removed due to the influence of local pollution. The same comment goes for the means reported.

Technical corrections

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Line 27 – “rate” would be preferable to “speed”.

Line 33 – NO_x should be defined.

Line 46 – there is a rogue hyphen/em dash that isn’t needed.

Line 46 and others – Dall’Osto is missing an apostrophe both here and in the reference list, where the reference is also missing several other diacritical marks, and the majority of C.D. O’Dowd’s last name. The references should then be rearranged for this reference to come before the more recent Dall’Osto et al. references. Be wary of automatic reference management software – references should still be verified that they were transposed and recorded properly.

Line 68 – “loss” rather than “reactions” would generate better agreement with the singular “sink”.

Lines 90-93 – “Furthermore, Boudries et al. (2002) observed emission from the snowpack to the atmosphere of acetone, acetaldehyde, and formaldehyde, which were explained by photochemical production in the snowpack and depositional fluxes of methanol was also observed, which they postulated as a source of formaldehyde.” - Consider making this two sentences: “Furthermore, Boudries et al. (2002) observed emission from the snowpack to the atmosphere of acetone, acetaldehyde, and formaldehyde, which were explained by photochemical production in the snowpack. “Depositional fluxes of methanol were also observed, which they postulated as a source of formaldehyde” Or at the very least, add a semi-colon and change “was” to “were” on line 92.

Line 94 – there should be a comma after “VOCs”.

Line 103 – It would be good to mention that Barrow, AK is now Utqiagvik, AK.

Line 104 and others – While “Alert, CA” is technically acceptable, “Alert, Canada,” or “Alert, NU,” would be less ambiguous. Also, be consistent throughout. Greenland should probably be spelled out as well.

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Line 122 – Use “s” instead of “sec” to adhere to SI units requirement.

Line 122 – Use “southwest” instead of “south-west”.

Line 131 – “5 seconds scan rate” doesn’t describe a rate, which should be something per unit of time.

Line 154 – “mixing ratios below LOD were set to”

Line 155 – “the data were time-averaged to 30-minute means.”

Line 194 – “arriving from”

Lines 199-200 – “Active fires during the period 15 August – 15 September 2018 were provided...” (you are defining the period here, not referring to it, so the commas are not needed.)

Line 259 – I recommend splitting this long sentence, “... frozen sea surface. Back trajectory...”

Line 267 – “strong negative correlation” is a little too generous for $R = -0.68$.

Lines 271-273 – It would be informative to include wind direction in addition to wind speed in Figure 2.

Line 275 – “with elevated acetone levels during ozone...” or something similar.

Line 279 – “gas-phase”

Line 303 – “species with S/N...”

Line 304 – “The uncertainties of ‘Weak’ species were tripled...”

Line 314 – “VOCs devoid of episodic influence...”, and there is a period missing at the end of the sentence.

Line 394 – The authors write “Estimated globally averaged atmospheric lifetimes against wet deposition for formic and acetic acid in the boundary layer is between 1

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and 2 days respectively (Paulot et al., 2011).” – This is not clear. Are both of the estimated atmospheric lifetimes between 1 and 2 days? If so, “respectively” isn’t needed. Either way, though, it should state “are between”...

Line 396 – “¹⁴C” (with a superscripted 14) or “carbon-14” (without a superscript).

Lines 405, 407, 410, 412, 443, 446, Figure 5, etc. etc. – sometimes “Factor” is capitalized in reference to one of the four factors, and sometimes it isn’t. This should be consistent throughout.

Line 427 – “Factor”, not “Factors”. Also, there is an extra period in this sentence: “. . . speed (Fig. S2).”

Lines 430-431 – Despite what the papers might claim, MSA is not measured in particle phase, but rather they measured the methanesulfonate ion, CH₃SO₂⁺. It would be better to simply indicate that the presence of gas-phase MSA has been indicated by the observation of methanesulfonate ion in particles.

Line 438 – “. . . Dibb and Arsenault (2002) measured levels. . .”

Line 440 – “matter, e.g.,”

Line 444 – The sentence “These trajectories and trajectory frequency maps were calculated as described in Sect. 2.4.” isn’t necessary.

Lines 460-461 – recommend: “One of the source areas identified in Fig. 6 is southeast of Villum, and a CPF analysis indicated high contributions (of what?) were observed when the winds were from south of Villum (Fig. S8a).” – this sentence needs a little clean-up for readability and clarity.

Line 469 – Recommend changing “Most of its components, particularly acetone and formaldehyde, are known. . .” to simply “Acetone and formaldehyde are known. . .”

Lines 483, 484, 487, 508, 545 – do you mean “labile [organic] carbon”?

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Line 531 – Circle should be capitalized.

References – Please format all references properly: pay attention to things like consistent journal abbreviations, consistent DOI referencing, missing or n/a information (e.g., line 680), line wrapping (e.g., line 735), and capitalization of abbreviations and proper names (e.g., lines 632; 839; 842, etc.).

Figure 4 – “red stars” – the resolution doesn’t merit calling these stars. They’re mostly just dots.

Supplement

Line 26 – Either “(5 s)” or “(5 seconds)” would be acceptable SI units.

Table S1 - The way the authors divided up the seasons here seems oddly arbitrary. Why is “summer” only two months long, while autumn is three months? And changing seasons on the 7th of a month is oddly arbitrary. As well, it would be preferable to separate the measurement and units in the first column with a comma rather than a slash. Also, use either “autumn” or “fall” but not both in the table title and header. Lastly, the start and stop dates in the title are not consistent with the dates given on Line 128 of the main text. Please make these consistent.

Tables S2-S4 – It is unclear why June, July and September are included here, but not August and October. In the text, Villum Research Station is referred to as “Villum”, not VRS. It should be the same here, or spelled out in full. The vertical alignment of these tables is off, with the numbers right justified, and the headers left-justified, making it difficult to know which values go with which headers. As well, some of the compounds listed in the left-hand column blend together. Either increase the spacing, or shorten the names (i.e., MEK, DMS, etc.) to limit the amount of word-wrapping. Formic Acid across the head is also rather unfortunately split. Finally, the “All correlations, apart from . . .” in the titles should just be included as a footnote.

Figure S1 – the text suggests that there were times when the wind speeds were < 2

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m/s, but this is not included in the figure. Please either include these, or justify their omission. Also, the resolution on the figure does not allow for the reader to discern anything > 14-18 m/s (blue). Either improve the resolution, or change the legend to eliminate the highest wind speed categories.

Figure S2 – “Time series of meteorological parameters...”; consider adding wind direction to this figure as well.

Figure S4 (and S5) – there is a lot of information shown that is repetitive and unneeded to the right of each satellite image, and as a result the majority of the important details are illegible. Remove the unnecessary parts, and make higher res and/or larger versions of the plots, and label the leads and the station in the image(s). As well, the labels a-f should be moved to the top left, or top right, or could be included inside the images in white for clarity. Lastly, here and throughout the manuscript, re: the ACP style guide, dates should be in the form dd month yyyy (or simply dd month).

Figure S6 – caption “A new trajectory was [calculated/generated] every 24 hours.” The back trajectory trace colors in the plots should have a legend or be described.

Figure S7 – The caption should include the fact that this is from the PMF analysis.

Figure S8 – plots (a) and (c) have the same size CPF scale, but different numbers of ticks and significant figures. They should be the same.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-528>, 2020.

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