Reply to *Interactive Comment* on "Atmospheric VOC measurements at a High Arctic site: characteristics and source apportionment" from anonymous Referee # 1

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.

We would like to thank referee # 1 for carefully reading the manuscript and for useful comments and feedback. We feel it improved the manuscript's readability and overall discussion of the results. As the first author is an early career scientist, they feel this exercise in the peer-review has tremendously helped them progress in critical thinking, manuscript writing, and the scientific method. We have addressed the referee's concerns and corrected errors in the manuscript below with referee's comments numbered and the author's responses in blue. New references are highlighted in yellow.

Several of the referee's concerns arose from the lack of explanation of the VOC specificity. We have group several of his comments into one and responded to them all with one reply.

1) 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 un- known 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.

2) 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 ($C_4H_8OH^+$) 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.

3) Line 337 – "it is a source of methyl acetate as well. . ." – the authors recognize that methyl acetate could be contributing to the C3H6O2H+ signal, but by labeling it "propionic acid" in Table 2 and Figures 1, 3, 5, 7, etc., the identity of the compound is muddied. 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.

We recognize that the points made by the referee are correct and have thus modified the manuscript, accordingly, adding a more detailed discussion of the possible and most likely assignments of the detected masses to chemical species:

Line 160: "The PTR-MS technique allows to observe species with a proton-affinity higher than water, this encompasses most VOCs found in the atmosphere with the important exception of alkanes. It does not allow for the distinction between isomers to be made. Compound names were assigned based on comparison with the libraries from the PTR-MS Viewer and Pagonis et al. (2019), and references therein. Inspection of the mass spectrum yielded ten protonated masses from which an empirical formula was calculated, and compound names were assigned for nine masses, as discussed in Sect. 3.1."

The following paragraph has been added at the beginning of Sect. 3.1:

Line 252: "The ten selected masses monitored by the PTR-TOF-MS and their assignments to species names are presented in Table 1. Assignments are made by choosing the most plausible contributions to an observed mass but each measured ion may have contributions from several different isomeric molecules. The assignment of masses in the table to protonated molecules of formaldehyde, acetonitrile, formic acid, acetic acid, and benzene appears to be unproblematic as no meaningful alternatives are found. For the remaining molecules, alternative assignments are possible. The mass assigned to acetone could be propanal as well, but propanal has a shorter atmospheric residence time and acetone is known to be one of the dominating VOCs observed in the atmosphere (Jacob et al., 2002), further, it has been found to have sources in the Arctic (Guimbaud et al., 2002). The mass assigned to DMS could be ethanethiol as well, but the large marine source of DMS makes it the most plausible assignment. Methyl ethyl ketone is isomeric with butenal, but being the second most abundant ketone in the atmosphere with, among others, apparently an oceanic source (Brewer et al., 2020) it appears to be the best assignment. $C_3H_6O_2$ may stem from propionic acid but also hydroxyacetone, methyl acetate, and ethyl formate. While it seems unlikely that ethyl formate could give a major contribution to this signal, the other three species are all plausible candidates: Low molecular weight organic acids are commonly found in the atmosphere (Lee et al., 2009), methyl acetate has been found in emissions from biomass burning (Andreae, 2019) and hydroxyacetone is known to be formed by the atmospheric degradation of isoprene (Karl et al., 2009). For what concerns the $C_5H_8OH^+$ ion we prefer not to make an assignment, possible isomers include, among others, pentenals and pentenones."

The references Jacob et al., 2002, Brewer et al., 2020, Lee et al., 2009 and Karl et al., 2009 are new and have been added to the list of references.

Line 271 and lines 282–284: Sentences have been deleted.

Line 286: ‘propionic acid’ has been replaced by “$C_3H_6O_2$”.

Lines 297–298: ‘an oxidation product of n-butane’ has been deleted.

Line 404–405: “one of the $C_3H_6O_2$ isomers” has been added to the sentence.

Line 462: ‘propionic acid’ has been replaced by “$C_3H_6O_2$”.

Line 469–471: “The $C_3H_6O_2$ is in this case assigned to propionic acid as the alternative isomers seem less probable, considering their typical origins (biomass burning for methyl acetate and isoprene oxidation for hydroxyacetone).”

Line 564: ‘propionic acid’ has been replaced by “$C_3H_6O_2$”.

The following sentence has been added:

Line 564–565: “$C_3H_6O_2$ may in this case result from all three of the isomers: propionic acid, methyl acetate, and hydroxyacetone.”

Throughout the manuscript, and specifically in Figure 1, 2, 4, 5, 8, and 10 as well as Table 2, S2, S3, S4 and S5, ‘propionic acid’ has been replaced by “$C_3H_6O_2$”.

4) 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 data for this manuscript including VOC mixing ratios and their associated uncertainty can be found in a publicly-available DOI. The Data Availability section has been amended to now read:

Line 673–675: All data used in this publication are available at https://doi.org/10.5281/zenodo.4299817 or by request to the corresponding authors Jakob Boyd Pernov (jbp@envs.au.dk) and Rossana Bossi (rbo@envs.au.dk).

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.

We have added Section 2 “Quality Control Procedure” in the Supplement which describes how local pollution was identified and removed (see text below). We have also a column in Table 1 which lists the total percentage of data removed due to QC (see an updated Table 1 below).

SI Line 35–52: “**Quality Control Procedure**

Data were quality controlled by analysis of PNSD, ozone, wind direction and speed, and internal activity logs. Local pollution at Villum can arise from activity around the measurement site (e.g., passenger vehicles, all-terrain vehicles, snowmobiles, and heavy machinery) as well as from activities from Station Nord (e.g., waste incineration, vehicular activity, and aircraft landing, idling, and take off). Internal activity logs of visits to the measurement building were used to highlight periods when human activity could affect the measurements, periods where VOC levels were elevated over background levels for the duration of the visit to the station were removed. Measurements of PNSD and ozone were analyzed, in tandem, for sharp and sudden increases in the ultrafine mode (< 100 nm) aerosol particles and concurrent sharp and sudden decreases in ozone, increases in ultrafine mode particles are indications of vehicular emissions while decreases in ozone results from its titration with nitrogen oxides. These periods were further inspected for wind direction and speed, with winds coming from due north at low speeds indicative of local pollution from Station Nord. All periods where local pollution was suspected of influencing the measurements were visually inspected by a panel of three persons, a consensus was required before data were removed. Data were also quality controlled for abnormal levels of instrumental parameters (i.e., E/N ratio, drift tube temperature, pressure, and voltage), periods with large deviations from nominal values were removed. Certain compounds (DMS, formic acid, and acetic acid) exhibited a slow return to nominal values after a blank than before, this issue was especially evident in the summer, these periods were removed. All quality control was performed on VOCs at a 5 s time resolution, data was removed before averaging to 30-minute means."

Table 1. Overview of measured protonated masses included in PMF analysis. Mean refers to the arithmetic average of the mixing ratio for each compound. Mean, Mean LOD, and % < LOD were calculated after quality control of data influenced by local pollution. % QC represents the percentage of data removed due to the Quality Control Procedure (Sect. S2).

Measured mass (*m/z*)	Empirical Formula	Assigned Compound	Mean (ppbv)	Mean LOD (ppbv)	% < LOD	Mean Relative Uncertainty (%)	% QC
30.997	CH_2OH^+	Formaldehyde	0.220	0.176	0.6	41	5
42.019	$C_2H_3NH^+$	Acetonitrile	0.067	0.045	0	46	5
47.011	$CH_2O_2H^+$	Formic Acid	0.454	0.250	17	37	7
59.062	$C_3H_6OH^+$	Acetone	0.608	0.037	0	32	0
61.047	$C_2H_4O_2H^+$	Acetic Acid	0.201	0.096	5	39	8
63.034	$C_2H_6SH^+$	Dimethyl Sulfide	0.046	0.043	4	57	25
73.068	$C_4H_8OH^+$	Methyl Ethyl Ketone	0.031	0.023	0.1	56	0
75.058	$C_3H_6O_2H^+$	Propionic Acid / Hydroxyacetone/ Methyl Acetate	0.025	0.031	0.1	61	2
79.057	$C_6H_6H^+$	Benzene	0.027	0.031	0.5	64	0
85.066	$C_5H_8OH^+$	N/A	0.027	0.030	0.03	61	0

5) 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.

The group of species identified at m/z 85.066 is now referred to as simply “C_5H_8O” throughout the text.

6) 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 winter time 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.

The referee is correct no wintertime data was collected. We compared our spring period measurements to Gautrois et al. (2003) wintertime data. The authors agree this comparison could create some confusion as it was not indicated in the text that we compared springtime to wintertime data. The text had been amended to reflect only comparisons during summer.

Line 305–308: “Benzene has shown a seasonal pattern at Alert, NU with a higher mixing ratio in winter due to no or limited photochemistry and long-range transport from lower latitudes (Gautrois et al., 2003). They reported mean winter and summer mixing ratios of 0.200 and 0.034 ppbv, respectively; when compared to the present study there is good agreement during the summer.”

The authors interpreted the similar pattern as benzene during spring to be indicative of anthropogenic influence, although the referee is correct, year to year variability from fires could hinder the proper interpretation of this pattern. The text has been amended as follows:

Line 309–310: “Acetonitrile followed a similar pattern to benzene during the spring with decreasing values, as well as exhibiting minima in the summer and maxima during the autumn (Fig. 1b).”

We have added the following sentence:

Line 314: The main source of acetonitrile in the atmosphere has been found to be biomass burning (Singh et al., 2003).

The reference Singh et al., 2003 is new and has thus been added to the list of references.

The discussion of acetonitrile during spring in Sect. 3.3.1 has also been changed:

Lines 407-412: “The decrease in the spring is reflective of decreasing concentrations of benzene and acetonitrile; in the case of benzene this can be ascribed to anthropogenic emissions during this period as the polar dome is expanded during winter and spring allowing for emissions to be entrained from the mid-latitudes. In the case of acetonitrile, the reason is more uncertain, there are anthropogenic sources of acetonitrile, particularly wood burning for residential heating and solvent use (Languille et al., 2020), but they appear to be of very minor importance compared to forest fires (de Gouw et al., 2003).”

Languille et al., 2020 is a new reference that has been added to the list of references.

We have also added the following text in the Arctic Haze section when we compare our Arctic Haze Factor to other Haze factors from previous literature.

Line 617–620: “It is worth noting that the Arctic Haze Factor from this study is only for spring, while the other studies present data from the winter/spring, therefore any comparisons we make are from our spring Arctic Haze Factor to other Haze factors during winter and spring. While this is not a perfect comparison, it is one worth making, as Arctic Haze is the main source of anthropogenic pollution in the Arctic.”

7) 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?

The species listed in Table 1 and 2 were the compounds identified that could be reasonably identified with an empirical formula with a proton affinity greater than water, without interference from neighboring ions, and exhibited a meaningful temporal profile.

The PTR measures ions with a m/z ratio up to 430 Da, so there are hundreds of ions measured by the instrument, but the ions reported here are the only those the authors could be confident were real signals from ambient VOCs. To answer the referee’s question, no there was not.

8) 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.

The second referee has asked for a potential source contribution function (PSCF) for source region analysis of the Marine Cryosphere Factor. The authors agree this would be the appropriate method for determining source regions for the Marine Cryosphere Factor. Therefore, the authors have become familiar with the programming language R and the R package Openair (Carslaw and Ropkins, 2012). Using this package, the authors were able to produce a (PSCF) for source region analysis of the Marine Cryosphere Factor. We have replaced the trajectory frequency map for the summer season with a PSCF map for the entire campaign. A PSCF for the summer period was also produced and compared to the entire campaign which produced similar results. Inclusion of the entire campaign data provides a more robust statistical calculation of the PSCF; therefore, we have chosen to perform the PSCF for the entire campaign.

We have replaced the trajectory frequency map in Fig. 7 (previously Fig. 6, we have added a figure showing the diurnal profile of the four factors in as the new Fig. 6 thus making this Fig. 7) with the PCSF as seen below, and updated the figure caption accordingly.

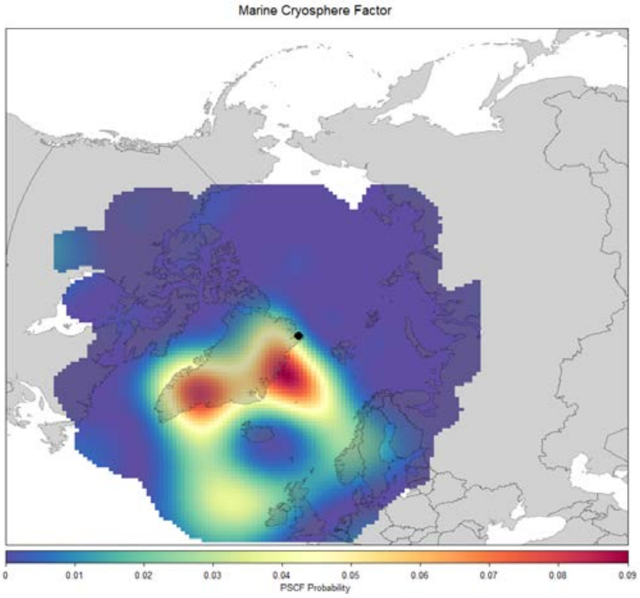


Fig. 7. PSCF for the Marine Cryosphere Factor and air mass back trajectories arriving at 100 m altitude, extending backward 120 hours in time. This plot and analysis method were produced in R and R Studio programs (R Foundation for Statistical Computing, Vienna, Austria, and R Studio Inc, MA, USA) and the OpenAir suite of analysis tools (Carslaw and Ropkins, 2012).

We have also updated Sect. 2.5 Back Trajectory Analysis to describe the PSCF:

Line 232–250: "To investigate source regions, the R package Openair (Carslaw and Ropkins, 2012) was utilized to produce a potential source contribution function (PSCF). Trajectories in Openair were calculated using the HYSPLIT model (Draxler and Hess, 1998; Rolph et al., 2017) at 100 m altitude and 120 hours backwards in time using Global NOAA-NCEP/NCAR reanalysis data archives on a 2.5° resolution. A PSCF, shown in Eq. (3), calculates the probability that an emission source is located in a grid cell of latitude *i* and longitude *j*, on the basis that emitted material in the gird cell *ij* can be transported along the trajectory and reach the receptor site.

$$PSCF = \frac{m_{ij}}{n_{ij}} \tag{3}$$

Where n_{ij} is the number of times a trajectory has passed through grid cell *ij* and m_{ij} is the number of times that a concentration was above a certain threshold value, in this case the 90th percentile. To account for uncertainty in cells with a small number of trajectories passing through, a weighting function was applied (Carslaw and Ropkins, 2012)."

We have also added the following text in the Marine Cryosphere Factor section discussing the results.

Line 527–541: "The spatial origin of the Marine Cryosphere Factor was investigated via a PSCF, calculated with the R package Openair (Carslaw and Ropkins, 2012). Figure 7 displays the PSCF for air masses arriving every hour during the measurement campaign, which provides increased statistical robustness to the results over calculating a PSCF just for the summer period. From Fig. 7, two areas with a high probability of being a source region for the Marine Cryosphere Factor can be discerned, the coast around Southeastern and Northeastern

Greenland. This analysis is supported by the CPF for the Marine Cryosphere Factor (Fig. S8b), which shows the dominant wind direction for this factor to be the south and south-south-east. Lee et al. (2020) used monthly chlorophyll-*a* derived from the MODIS satellite to demonstrate the coasts around Northeastern Greenland to contain high chlorophyll-*a* concentrations during June, which has been supported by previous studies (Degerlund and Eilertsen, 2010; Galí and Simó, 2010). Lee et al. (2020) also used a PSCF to determine this area to be the source regions for total particle number concentrations in the nucleation size range (3–25 nm). This area has been demonstrated to be a source region for MSA during the summer months (Heintzenberg et al., 2017). Thus, we propose the biologically active coasts around Eastern Greenland to be the source region for the Marine Cryosphere Factor."

The references Carslaw and Ropkins, 2012, Degerlund and Eilertsen, 2010, Galí and Simó, 2010, Lee et al. (2020), and Heintzenberg et al., 2017 are new and thus have been added to the reference list.

9) 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.

All figures included in the manuscript have been saved at a resolution of 600 DPI. This is an excellent suggestion and in the future the authors will be more attentive to this matter.

10) 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.

The table title has been shortened with redundant information removed and the following text added:

Table 1: "Overview of measured protonated masses included in PMF analysis. Mean refers to the arithmetic average of the mixing ratio for each compound. Mean, Mean LOD, and % < LOD were calculated after quality control of data influenced by local pollution. % QC represents the percentage of data removed due to the Quality Control Procedure (Sect. S2)."

11) Line 27 – "rate" would be preferable to "speed".

Line 29: "Speed" has been replaced with "rate".

12) Line 33 – NOx should be defined.

Line 35 and 36: "NO_x" has been defined as "nitrogen oxides" and "VOCs" have been defined as "volatile organic compounds".

Line 52: "DMS" has been defined as "dimethyl sulfide".

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

Line 48: The rouge em dash has been removed.

14) Line 46 and others – Dall’Osto is missing an apostrophe both here and in the refer- ence 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.

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.).

This is an excellent catch by the referee. The Dall’Osto reference has been corrected and the entire reference list has been checked for accuracy and updated where appropriate. This is excellent advice from the referee. We believe the problem arose from importing references from PDFs using the “Import” function in Endnote. We have now imported references either form Web of Science or the respective journal website. The authors were unaware of such pitfalls when working with automatic referencing software and will be more vigilant in the future.

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

Line 70: “reactions” has been replaced with “loss”.

16) Lines 90-93 – “Furthermore, Boudries et al. (2002) observed emission from the snow- pack 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: This sentence has been made into two sentence following the referee’s suggestions and “was” is now “were”.

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

Line 96: A comma has been added after VOCs.

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

Throughout the text “Barrow” has been replaced with “Utqiagvik”.

On line 105, it is mentioned that Utqiagvik is formerly known as Barrow.

19) 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.

Throughout the text "Alert, CA" has been replaced with "Alert, NU".

20) Line 122 – Use "s" instead of "sec" to adhere to SI units requirement.

Line 133: "sec" has been replaced with "s". The entire manuscript and SI has also been checked for proper use of SI units were appropriate.

21) Line 122 – Use "southwest" instead of "south-west".

Line 133: The hyphen has been removed.

22) Line 131 – "5 seconds scan rate" doesn't describe a rate, which should be something per unit of time.

Line 142: "5 seconds scan rate" has been replaced with "5 second single spectra integration time" as specified in the PTR software.

23) Line 154 – "mixing ratios below LOD were set to"

Line 173: "was" has been replaced with "were".

24) Line 155 – "the data were time-averaged to 30-minute means."

Line 173: "was" has been replaced with "were" and "mean" was made plural.

25) Line 194 – "arriving from"

Line 222: "form" has been replaced with "from".

26) 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.)

This sentence has been removed from this section and moved to the Biomass Burning section (Line 424), where the commas have been removed.

27) Line 259 – I recommend splitting this long sentence, ". . . frozen sea surface. Back trajectory. . ."

Line 324–325: The sentence has been split into two following the referee's suggestion.

28) Line 267 – "strong negative correlation" is a little too generous for R = -0.68.

Line 332–333: "strong" has been replaced with "moderate".

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

Wind direction has been added to Figure 3, which is the old Figure 2 after addition of a figure showing the diurnal profile of certain VOCs during the summer as suggested by the second referee. Wind direction has also been added to Fig. S2. The effect of wind direction has been included in the text:

Line 338: These changes in mixing ratios are accompanied by a change in meteorological conditions, illustrated here by changes in wind speed and to a less extent wind direction (Fig. 3).

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

The text has been amended following the referee’s suggestion.

Line 339–341: Guimbaud et al. (2002) found a similar relationship between acetone and ozone during different field campaigns at Alert, Canada with elevated acetone levels during ozone depletion episodes accompanied by a concomitant decrease in the propane mixing ratios.

31) Line 279 – “gas-phase”

Line 342: A hyphen has been added to “gas-phase”.

32) Line 303 – “species with S/N. . .”

Line 369: “Signal-to-noise” has been removed.

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

Line 370: “Uncertainty” has been made plural to “uncertainties” and “was” replaced with “were”.

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

Line 381: “void” has been replaced with “devoid” and a period has been added to the end of this sentence.

35) 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 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”. . .

The text has been amended in the following manner:

Line 476–478: “Estimated globally averaged atmospheric lifetimes against deposition for both formic and acetic acid in the boundary layer are between 1 and 2 days (Paulot et al., 2011).”

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

Line 479: A superscripted 14 has been added to the front of C, the text now reads “^{14}C”.

37) 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.

The text has been amended throughout, when referring to a specific factor, “Factor” is now capitalized.

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

Line 510: “Factors” is now singular “Factor” and the extra period has been removed and reference to Fig. S2 has been removed and replaced with the correlation coefficient between the Marine Cryosphere Factor and wind speed (as requested by the second referee).

39) 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.

The text has been amended in the following manner:

Line 513–515: “The presence of gas-phase MSA has been indicated by the observation of the methanesulfonate ion, which has been previously measured in the particle phase at Villum in February–May 2015 (Dall'Osto et al., 2018; Nielsen et al., 2019).”

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

Line 522: The word “had” has been removed.

41) Line 440 – “matter, e.g.,”

Line 524: A comma has been added after “matter”.

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

Line 529–530: This sentence has been removed.

43) 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.

This sentence has been amended in the following manner:

Line 554–556: “One of the source areas identified in Fig. 7 is southeast of Villum, and a CPF analysis indicated high contributions of the Marine Cryosphere Factor were observed when the wind direction was south of Villum (Fig. S5b).”

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

Line 565: The sentence has been amended following the referee’s suggestion.

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

Throughout the text “liable carbon” has been replaced with “labile organic carbon”.

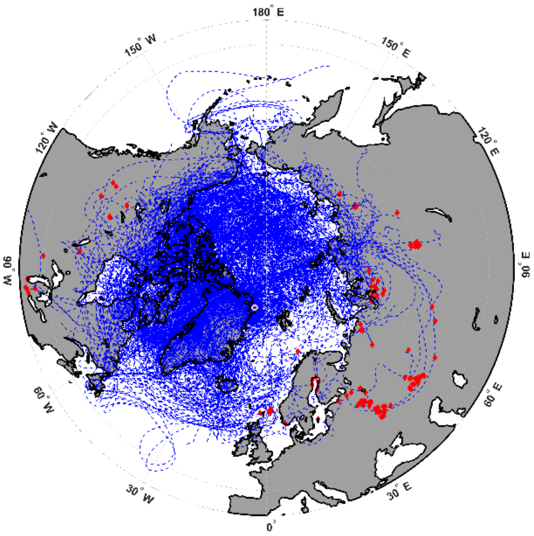
46) Line 531 – Circle should be capitalized.

Line 632: Circle is now capitalized.

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

This figure has been removed from the manuscript. The second referee asked for a more statistical analysis of the back trajectories with the active fires. We collocated back trajectory endpoints with active fires with 1° latitude/longitude and temporally within one hour. While there was evidence of active fires in North America and Eurasia occurring when an endpoint was near, the uncertainty in individual trajectories at 336 hours is too great to draw meaningful conclusions from this analysis.

We have included the figure in our response, this figure will not be included in the manuscript. Individual trajectories are indicated in the dashed blue lines and active fires occurring within 1° lat/lon and within one hour of trajectory endpoints are indicated in red.



We have amended the text for the Biomass Burning section.

Line 413: To examine the geographical origin of this factor, air mass back trajectories from the HYSPLIT model were calculated every hour during the peak of the Biomass Burning Factor (15 August–15 September 2018) and extending 336 hours (two weeks) backward in time. The trajectory length of two weeks was selected to account for the long lifetime of acetonitrile. Active fires during the period 15 August–15 September 2018 was provided by NASA's Fire Information for Resource Management System (FIRMS) (Schroeder et al., 2014). Active fires occurring with one hour and one-degree latitude/longitude of a trajectory endpoint was used to access the influence of active fires on the Biomass Burning Factor. While there was evidence of active fires in North America and Eurasia occurring near a trajectory endpoint with one hour, the uncertainty of a trajectory with a length of 336 hours is quite large (Stohl, 1998). Therefore, no meaningful conclusions can be drawn from this analysis other than the transport time of emissions influencing the Biomass Burning Factor is greater than two weeks, and that we are unable to capture these emissions with the current trajectory models with any confidence.

Supplement

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

SI Line 27: “sec” has been changed to “s”.

49) 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.

The authors admit this is an unusual set of dates for dividing seasons. This is because the data is split into three periods by interruptions (mainly due to power failure) as seen in Figure 1. Therefore, the authors divided the seasons according to these groups. “Fall” in the table has been changed to “Autumn”, the manuscript has also been checked throughout for consistency regarding this naming. The slashes between measurement and unit has been removed and replaced with a comma. The dates have been made consistent with the dates listed in the manuscript. See the updated Table 1 below.

Table S1. Statistics for meteorological parameters (mean ± s.d.) for all seasons, spring (April 4 – June 8), summer (June 9 – August 6), and autumn (August 7 – October 25). During the campaign, there were several large gaps in the data, most noticeably one in July and one in August, as seen in Fig. 1. The seasons are therefore divided based on the continuous collection of data uninterrupted by large missing gaps. The seasons roughly correspond to the conventional definition of seasons.

	All Seasons	Spring	Summer	Autumn
Wind Direction, °	207.5 ± 89.0	202.4 ± 91.8	189.3 ± 2.6	223.8 ± 81.2
Wind Speed, m s^{-1}	3.3 ± 2.6	3.1 ± 2.4	3.5 ± 2.4	3.4 ± 2.7
Temperature, °C	-6.5 ± 9.6	-13.8 ± 9.0	2.2 ± 4.1	-7.0 ± 7.9
RH, %	77.4 ± 12.6	74.6 ± 10.6	78.0 ± 15.6	79.1 ± 11.4
Radiation, W m^{-2}	174.9 ± 163.9	222.3 ± 146.3	295.9 ± 4.2	57.0 ± 97.4
Pressure, hPa	1010.6 ± 9.0	1014.8 ± 8.6	1007.5 ± 6.5	1009.6 ± 9.5
Snow Depth, m	0.9 ± 0.6	1.4 ± 0.1	1.1 ± 0.4	0.3 ± 0.4

50) 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.

The correlation analysis was performed for one month from each season which had a good data coverage for the parameters being compared. We have added Table S2, which details the number of measurement hours for each compound for each month that displays this. VRS has been changed to Villum in the table headers. The columns of Tables S3, S4, and S5 are all now left aligned. DMS and MEK are now used in the left column and top row, which eliminated all word-wrapping. The text “All correlations…” has been made a footnote. Please see the updated tables in the SI, considering the length of the tables they are not included here.

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

The figure has been remade to include all wind speeds and the intervals of the color bar have been changed to allow the relative wind speeds to be discerned. The figure has been expanded for individual wind roses for each season. The figure was also saved at a higher resolution (300 vs 600 DPI). See the updated Fig. S1 below.

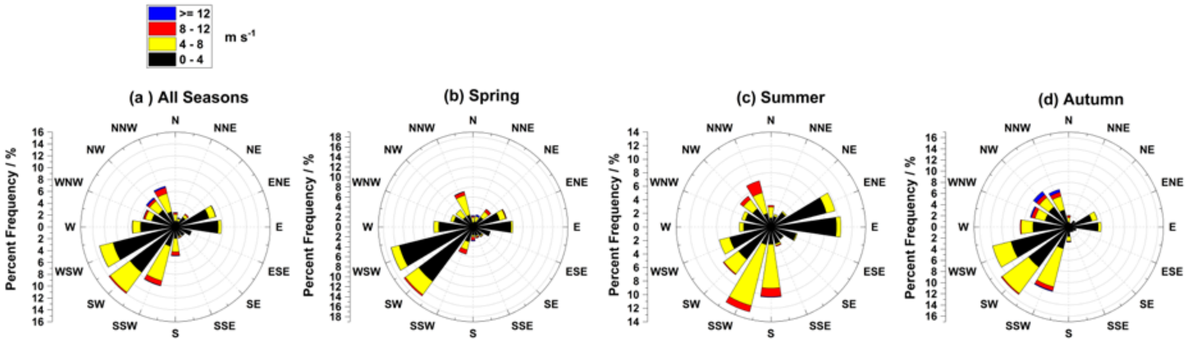


Fig. S1. Wind Rose for mean wind speed at 5 min time resolution for (a) all seasons, (b) spring, (c) summer, and (d) autumn. The y-axis represents the percent frequency of wind direction in percent and the colors indicate mean wind speed in m s^{-1}. The seasons follow the selection outlined in Table 1.

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

Wind direction has been added to this figure. The figure was also saved at a higher resolution (300 vs 600 DPI). Please see the updated Fig. S2 in the Supplement.

53) 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 de- tails 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).

The old Figures S4 and S5 have been removed from the manuscript. Both referees raised concerns about the legibility of these two figures, therefore, we have removed them and directed the reader to the website where they were obtained (Line 324). We feel they add valuable information about the origin of the elevated DMS periods but displaying them in a meaningful manner proved problematic.

Throughout the manuscript, texts and figures have been amended to display the correct date format for ACP.

54) 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.

The Fig. S6 caption now reads:

“**Fig. S6.** HYSPLIT back trajectory analysis for **(a)** May 2st – 6th **(b)** May 16th–20th arriving at 100 m above ground level extending 72 hours backward in time. The colored trajectories represent a new trajectory started every 24 hours after the last day of each period until the first day, in descending order the trajectories are red (last day), blue (fourth day), green (third day), light blue (second day), and purple (first day).”

The figure was also remade at a higher resolution and with panel labels ((a) and (b)) located at the top left of each panel.

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

The caption for Fig. S7 now reads:

“The ratio of Q_{true} to Q_{theo} versus the number of factors for the PMF analysis.”

The caption for Fig. S8 now reads:

“Conditional probability function roses for **(a)** Biomass Burning Factor, **(b)** Marine Cryosphere Factor, **(c)** Background Factor, and **(d)** Arctic Haze Factor.”

56) 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.

Figure S8 has been updated to include all factors. The Biomass Burning, Background, and Arctic Haze Factors now all have the same scale, and all panels now have the same number of significant figures for the scale.

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Reply to *Interactive Comment* on "Atmospheric VOC measurements at a High Arctic site: characteristics and source apportionment" from anonymous Referee # 2

This manuscript by Pernov et al. reports atmospheric non-methane volatile organic compounds (VOCs) measurements at Villum Research Station at Station Nord, Green- land, from April to October 2018. Given the scarcity of VOC measurements in the Arctic and the significance of VOCs in the background atmosphere (formation of ozone, CO, and aerosols), this study will make a valuable contribution to the body of literature. The manuscript is overall well written and structured. My main concern is that the figures do not support the discussion and conclusions (see comments below). Additionally, the introduction could be more succinct.

We would like to thank referee # 1 for carefully reading the manuscript and for useful comments and feedback. We feel it improved the manuscript's readability and overall discussion of the results. As the first author is an early career scientist, they feel this exercise in the peer-review has tremendously helped them progress in critical thinking, manuscript writing, and the scientific method. We have addressed the referee's concerns and corrected errors in the manuscript below with referee's comments numbered and the author's responses in blue. New references are highlighted in yellow.

Several of the reviewer's comment address the same concerns, where appropriate we have grouped these comments together and responded to them all with one reply.

The referee suggested the Introduction could be more succinct. We have removed the following lines from the introduction in order to reduce the wordiness:

Lines 40–44

Lines 64–65

Lines 73–75

1) Diurnal variation

The authors say that certain compounds (e.g. DMS and OVOCs) follow a diurnal cycle. This is not shown in Figure 1 and I would like to see a Figure describing, for each compound of interest, the mean diurnal cycle per season.

Line 217: "certain compounds (DMS and OVOCs) revealed a diurnal cycle that closely follows radiation". Please make a Figure to prove this.

Line 219: "summer when a diurnal pattern following sunlight was observed". Same as above, please demonstrate this.

Lines 225-227: "a clear diurnal variation was observed in the period July-August, with peak mixing ratios occurring around midday (Fig. 1 a, c, d, e). The diurnal variation was less pronounced in April-May and September-October, highlighting the dependence on sunlight". None of this is shown in Figure 1.

Line 255: "DMS showed a clear diurnal cycle during sea ice melt in the summer months correlating with sunlight intensity". Prove/illustrate it.

Lines 259-261: see comment above. As is, Figures S4-S6 do not do a good job at showing this.

Lines 286-287: “In addition to the previously mentioned dependence on the diurnal variations of sunlight, providing strong evidence of a local photochemical source”. Again, this has not been demonstrated.

Lines 383-384: “This factor shows an enhanced diurnal variation with a clear correlation to sunlight during the summer months (Fig. 5, Top)”. Again, Figure 5 does not illustrate this.

Lines 406-407: “Periods of high contributions and clear diurnal pattern by the Marine Cryosphere factors starts on June 23”. I don’t see the “clear diurnal pattern”.

We agree with the referee’s concern about a lack of the diurnal nature being illustrated properly. We have therefore added two figures in the main text (Fig. 2 and 6) to display diurnal profile for each of the relevant compounds and the four factors, respectively, during the summer months, as well as the diurnal profiles for each season (as requested by the referee) in the Supplement (Fig. S3, S4, and S5). We have amended the text throughout to reference these two figures and removed references to a diurnal profile when they do not pertain to these figures.

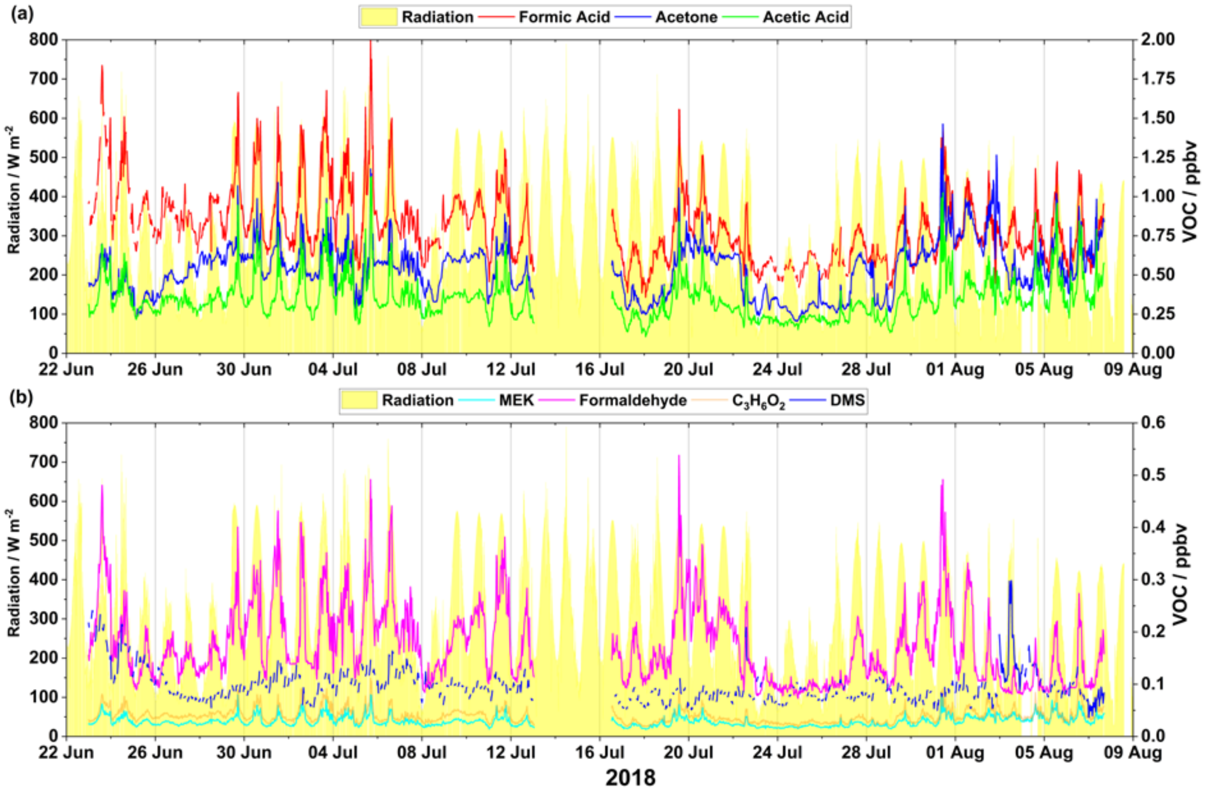


Fig. 2. Diurnal profile for (a) formic acid, acetone, acetic acid, and radiation and (b) MEK, formaldehyde, $C_3H_6O_2$, DMS, and radiation during the period 22 June–09 August.

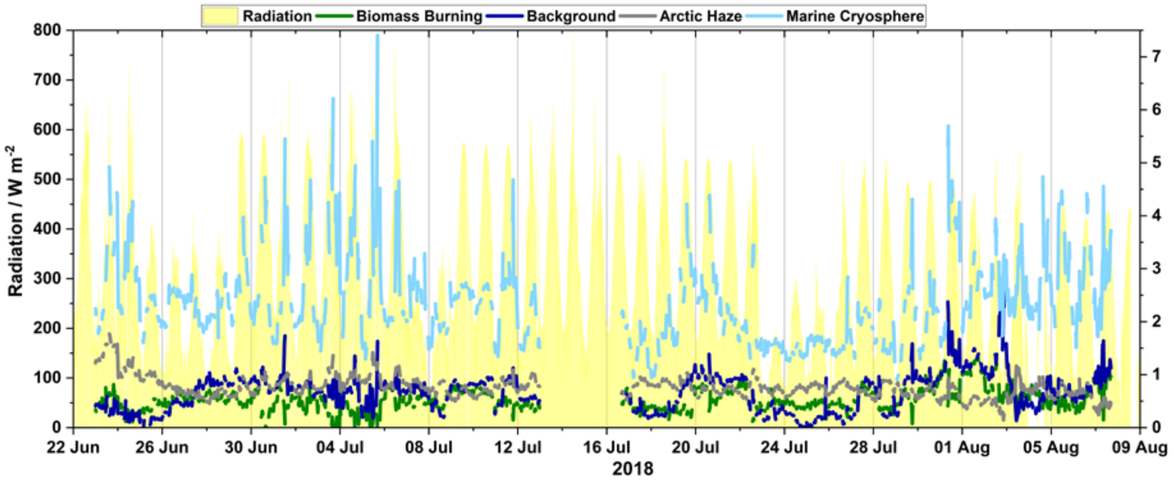


Fig. 6. Time series of the four factors from 22 June–09 August displaying the diurnal profile together with radiation.

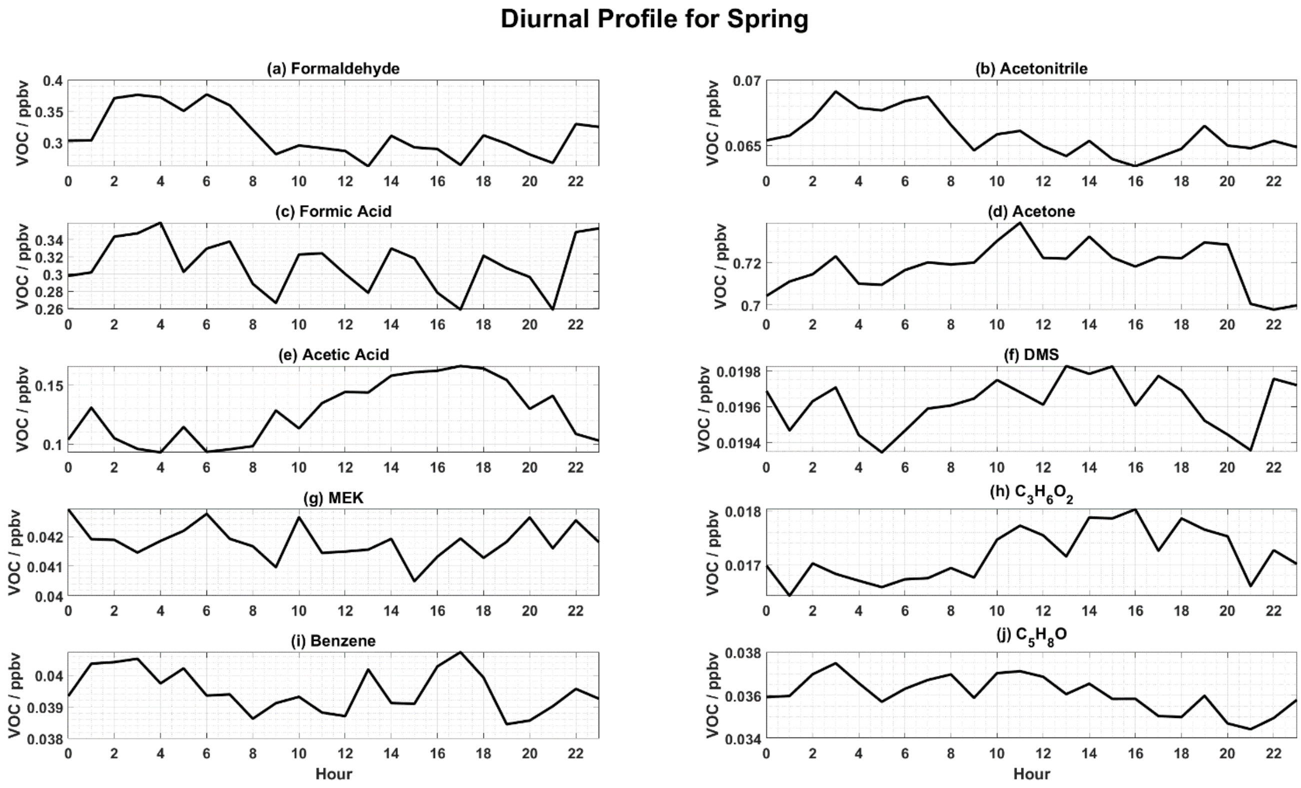


Fig. S3. Diurnal profile for the spring (April–May) of **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid, **(d)** acetone, **(e)** acetic acid, **(f)** DMS, **(g)** MEK, **(h)** $C_3H_6O_2$, **(i)** benzene, **(j)** C_5H_8O. Data were averaged to hourly medians.

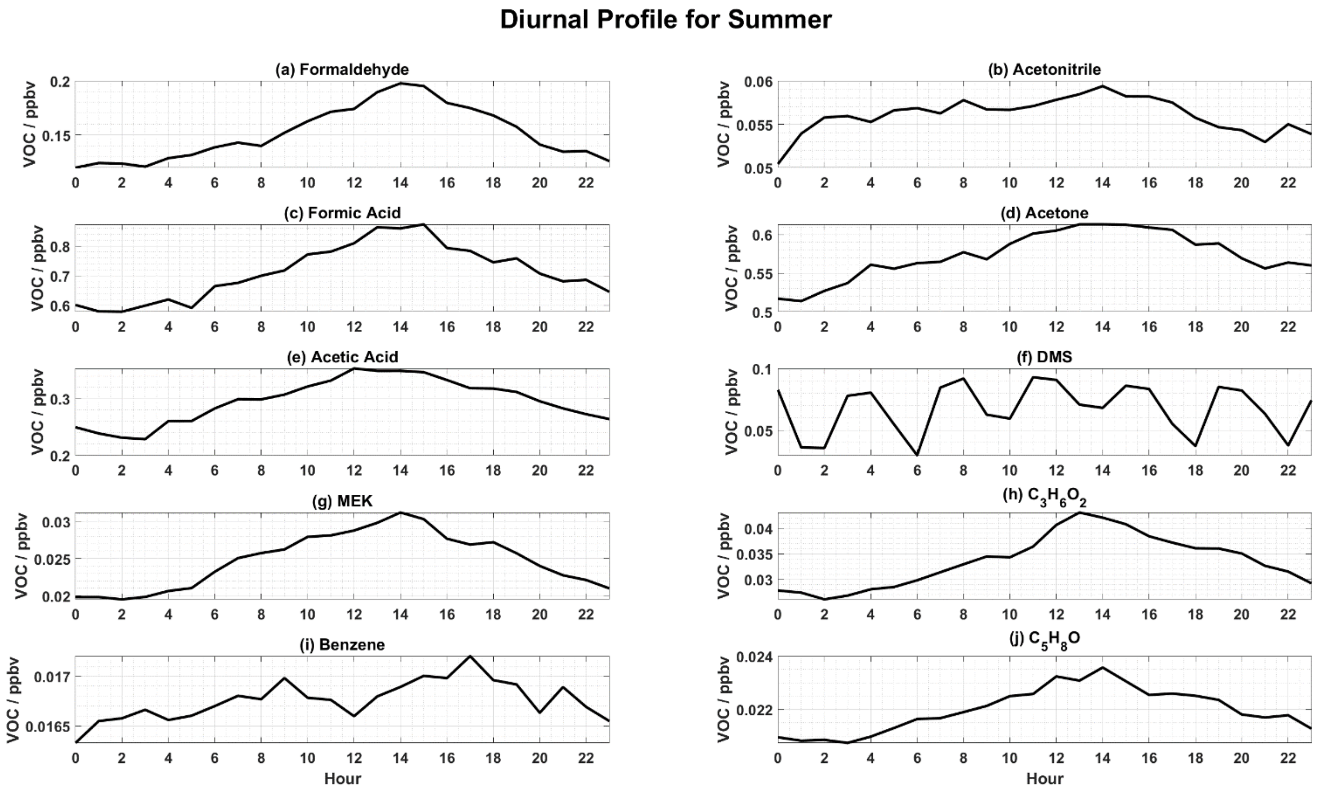


Fig. S4. Diurnal profile for the summer (June–August) of **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid, **(d)** acetone, **(e)** acetic acid, **(f)** DMS, **(g)** MEK, **(h)** $C_3H_6O_2$, **(i)** benzene, **(j)** C_5H_8O. Data were averaged to hourly medians.

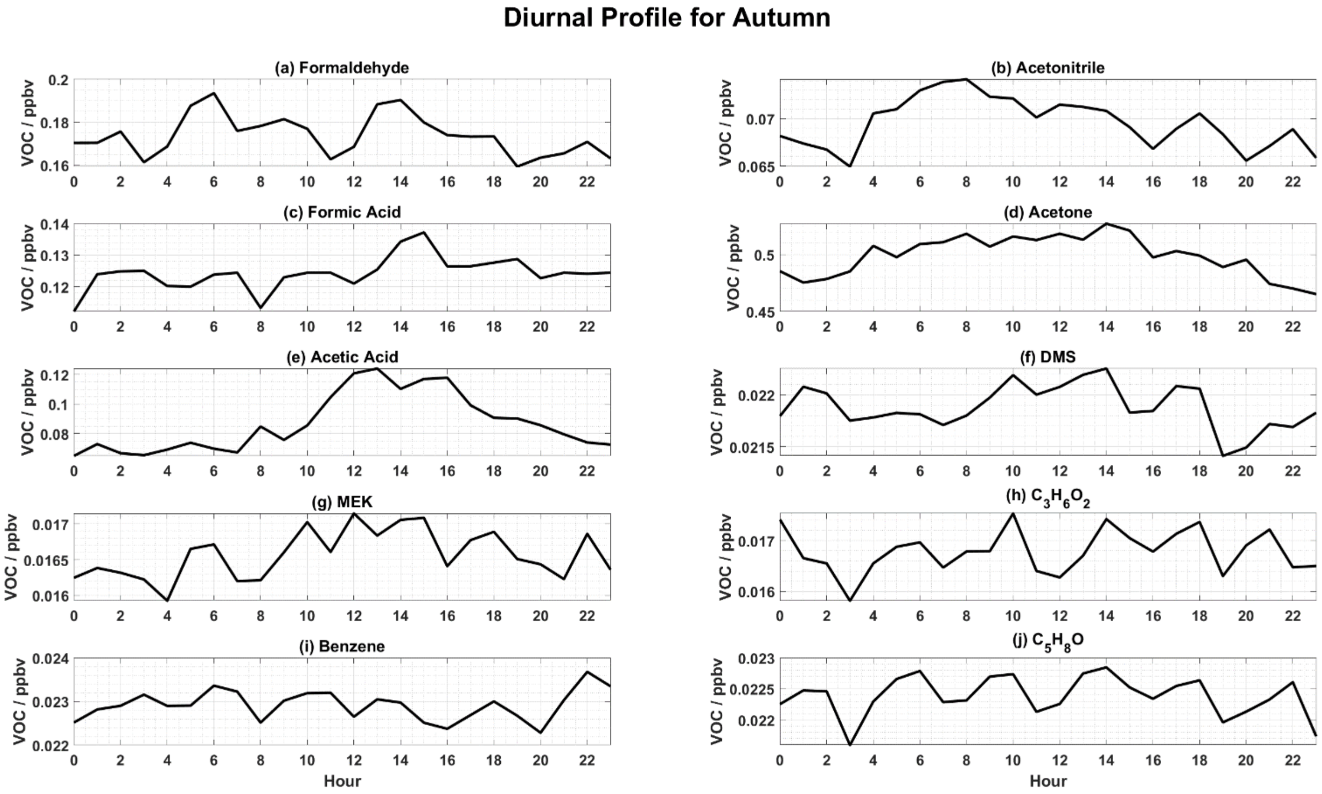


Fig. S5. Diurnal profile for the autumn (September–October) of **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid, **(d)** acetone, **(e)** acetic acid, **(f)** DMS, **(g)** MEK, **(h)** $C_3H_6O_2$, **(i)** benzene, **(j)** C_5H_8O. Data were averaged to hourly medians.

We have amended the text to mention the diurnal profiles for relative compound in the relative season:

Line 269–280: "For the ten selected VOCs, time series of mixing ratios during the entire measurement period are displayed in Fig. 1a-f. During the spring (April–May), certain compounds (benzene and C_5H_8O) exhibited a maximum and thereafter a decreasing pattern, similar to the timing and profile of the Arctic Haze phenomena. During the spring, compounds did not display a diurnal profile except for acetic acid (Fig. S3) Whilst in summer (June–August), OVOCs revealed a diurnal cycle that closely follows radiation (Fig. 2 and S4). Compounds of non-photochemical origin (benzene and acetonitrile) also displayed a slight diurnal pattern, which could possibly be due to entrainment from aloft (Fig. S4). Interestingly, several compounds (formaldehyde, formic acid, and acetone) peaked in the spring with decreasing levels until the summer when a diurnal pattern following sunlight was observed (Fig. 1, 2, S4). During the autumn (September–October), all compounds were low except for acetone and acetonitrile (Fig. 1) and only acetic acid displayed a diurnal profile (Fig. S5). The levels, seasonal patterns, and comparison with other studies of these compounds will be discussed below."

2) Springtime DMS

I have difficulties reading satellite images (Figures S4 and S5). The caption says that the presence of open leads can be seen southwest of the station but I don't even know where the station is. Then, according to the authors, "the back-trajectory calculations confirmed that, during the DMS emission episodes, the air masses (. . .) traversed over the open leads before reaching the station". First of all, what is the meaning of the different colors? I do not understand Figure S6. Then, this Figure does not show that air masses traversed over the open leads. If you want to show this, then please consider combining satellite images and back-trajectories on a single Figure.

Figures S4 and S5 have been removed from the manuscript. Both reviewers raised concerns about the legibility of these two figures, therefore, we have removed them and directed the reader to the website where they were obtained (http://ocean.dmi.dk/arctic/nord.php). We feel they add valuable information about the origin of the elevated DMS periods but displaying them in a meaningful manner proved problematic. We have left the HYSPLIT back trajectories in Fig. S6 in and updated the figure caption to indicate the meaning of the different trajectories, the text now reads :

"HYSPLIT back trajectory analysis for **(a)** May 2nd– 6th **(b)** May 16th–20th arriving at 100 m above ground level extending 72 hours backward in time. The colored trajectories represent a new trajectory started every 24 hours after the last day of each period until the first day, in descending order the trajectories are red (last day), blue (fourth day), green (third day), light blue (second day), and purple (first day)."

3) Biomass burning

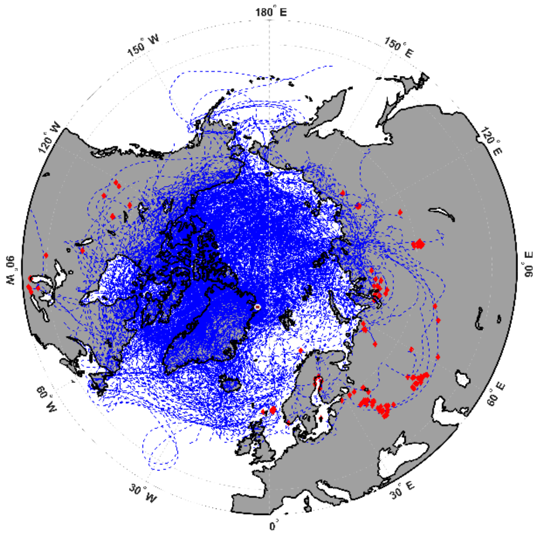
Contrary to what the authors say, Figure 4 does not show “evidence of overlap between air mass history and active fires during this period”. Figure 4 shows all fires from mid- August to mid-September and all back-trajectories. This does not prove that a given fire existed at the time an air mass traveled in the area. I expect a more thorough statistical analysis here. In order to link the fires up with back trajectories, you could for instance cross check the latitudes and longitudes to a, let’s say, 1-degree accuracy. If a longitude and latitude match exists between a fire and a back-trajectory, then check if the time of the fire product and the back-trajectory were within, let’s say, 1 hour. Thus, a match is completely defined as a back-trajectory crossing over a fire within 1 hour and within 1-degree difference.

Lines 206-207: “The trajectory length was varied between 240 and 336 hours”. Why did you use two different trajectory lengths? Additionally, I would recommend the use of shorter back trajectories (typically 5-7 days max) as uncertainties increase with time along the way (Stohl, 1998). I would also like to see a more critical discussion on back trajectories; they only give a general indication of source regions.

Line 351: “336 hours backward in time”. That’s too long to my point of view. Use max 5-7 days.

We collocated back trajectory endpoints with active fires with 1° latitude/longitude and temporally within one hour as the reviewer requested. While there was evidence of active fires in North America and Eurasia occurring when an endpoint was near (see figure below), as the reviewer pointed out the uncertainty in individual trajectories at 336 hours is too great to draw meaningful conclusions from this analysis. Therefore, this figure has been removed from the manuscript.

We have included the figure in our response, this figure will not be included in the manuscript. Individual trajectories are indicated in the dashed blue lines and active fires occurring within 1° lat/lon and within one hour of trajectory endpoints are indicated in red.



We have amended the text for the Biomass Burning section.

Line 420–431: “To examine the geographical origin of this factor, air mass back trajectories from the HYSPLIT model were calculated every hour during the peak of the Biomass Burning Factor (15 August–15 September 2018) and extending 336 hours (two weeks) backward in time. The trajectory length of two weeks was selected to account for the long lifetime of acetonitrile. Active fires during the period 15 August–15 September 2018 were provided by NASA's Fire Information for Resource Management System (FIRMS) (Schroeder et al., 2014). Active fires occurring with one hour and one-degree latitude/longitude of a trajectory endpoint was used to access the influence of active fires on the Biomass Burning Factor. While there was evidence of active fires in North America and Eurasia occurring near a trajectory endpoint within one hour, the uncertainty of a trajectory with a length of 336 hours is quite large (Stohl, 1998). Therefore, no meaningful conclusions can be drawn from this analysis other than the transport time of emissions influencing the Biomass Burning Factor is greater than two weeks, and that we are unable to capture these emissions with the current trajectory models with any confidence.”

4) Spatial origin of the Marine Cryosphere factor

Figure 6 (trajectory frequency) shows more frequent air masses from coastal regions but does not show that these areas are responsible for enhanced marine cryosphere factor. It does not support this sentence in the conclusion “Back trajectory analysis yielded MIZs around the coasts of Greenland and the Arctic Ocean as source regions”. I suggest a Potential Source Contribution Function (PSCF) analysis to determine probable locations of emission sources.

Lines 443-454: see comment above on Figure 6 and the fact that it does not show that coastal regions are responsible for enhanced marine cryosphere factor.

At the time of preparation of this manuscript, the authors did not possess the tools or knowledge about how to perform a PSCF. The authors agree this would be the appropriate method for determining source regions for the Marine Cryosphere Factor. Therefore, the authors have become familiar with the programming language R and the R package Openair (Carslaw and Ropkins, 2012). Using this package, the authors were able to produce a (PSCF) for source region analysis of the Marine Cryosphere Factor. We have replaced the trajectory frequency map for the summer season with a PSCF map using data from the entire campaign. A PSCF for the summer period was also produced and compared to the entire campaign which produced similar results. Inclusion of the entire campaign data provides a more robust statistical calculation of the PSCF; therefore, we have chosen to perform the PSCF for the entire campaign.

We have replaced the trajectory frequency map in Fig. 7 (previously Fig. 6, we have added a figure showing the diurnal profile of the four factors in as the new Fig. 6 thus making this Fig. 7) with the PCSF as seen below and updated the figure caption accordingly.

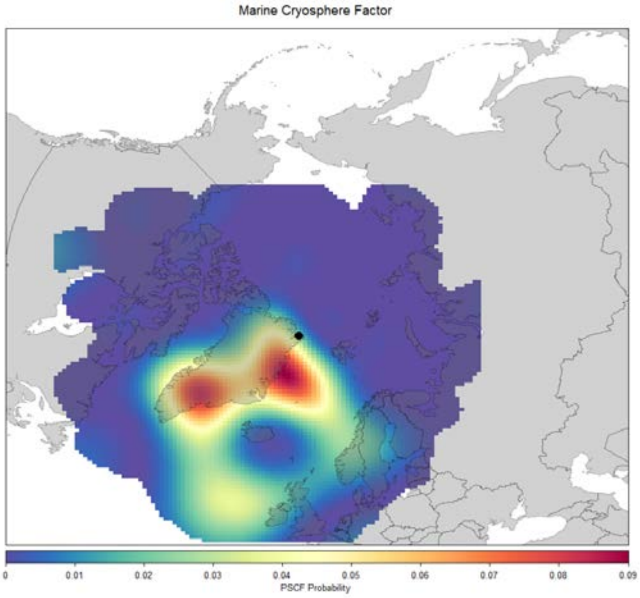


Fig. 7. PSCF for the Marine Cryosphere Factor and air mass back trajectories arriving at 100 m altitude, extending backward 120 hours in time. This plot and analysis method were produced in R and R Studio programs (R Foundation for Statistical Computing, Vienna, Austria, and R Studio Inc, MA, USA) and the OpenAir suite of analysis tools (Carslaw and Ropkins, 2012).

We have also updated Sect. 2.5 Back Trajectory Analysis to describe the PSCF:

Line 223–250: "To investigate source regions, the R package Openair (Carslaw and Ropkins, 2012) was utilized to produce a potential source contribution function (PSCF). Trajectories in Openair were calculated using the HYSPLIT model (Draxler and Hess, 1998; Rolph et al., 2017) at 100 m altitude and 120 hours backward in time using Global NOAA-NCEP/NCAR reanalysis data archives on a 2.5° resolution. A PSCF, shown in Eq. (3), calculates the probability that an emission source is located in a grid cell of latitude *i* and longitude *j*, on the basis that emitted material in the gird cell *ij* can be transported along the trajectory and reach the receptor site.

$$PSCF = \frac{m_{ij}}{n_{ij}} \qquad (3)$$

Where n_{ij} is the number of times a trajectory has passed through grid cell *ij* and m_{ij} is the number of times that a concentration was above a certain threshold value, in this case, the 90th percentile. To account for uncertainty in cells with a small number of trajectories passing through, a weighting function was applied (Carslaw and Ropkins, 2012).

We have amended the text in the Marine Cryosphere Factor section to reflect his new analysis method:

Line 527–541: "The spatial origin of the Marine Cryosphere Factor was investigated via a PSCF, calculated with the R package Openair (Carslaw and Ropkins, 2012). Figure 7 displays the PSCF for air masses arriving every hour during the measurement campaign, which provides increased statistical robustness to the results over calculating a PSCF just for the summer period. From Fig. 7, two areas with a high probability of being a source region for the Marine Cryosphere Factor can be discerned, the coast around Southeastern and Northeastern

Greenland. This analysis is supported by the CPF for the Marine Cryosphere Factor (Fig. S8b), which shows the dominant wind direction for this factor to be the south and south-south-east. Lee et al. (2020) used monthly chlorophyll-*a* derived from the MODIS satellite to demonstrate the coasts around Northeastern Greenland to contain high chlorophyll-*a* concentrations during June, which has been supported by previous studies (Degerlund and Eilertsen, 2010; Galí and Simó, 2010). Lee et al. (2020) also used a PSCF to determine this area to be the source regions for total particle number concentrations in the nucleation size range (3–25 nm). This area has been demonstrated to be a source region for MSA during the summer months (Heintzenberg et al., 2017). Thus, we propose the biologically active coasts around Eastern Greenland to be the source region for the Marine Cryosphere Factor."

Line-by-line comments:

5) Line 10: "we report a long-term dataset". The authors report measurement from April to October 2018, i.e., less than a year. This is not what I would call a "long-term dataset". Please edit this sentence.

We have replaced "long-term" with "multi-season" throughout the text to better reflect the duration of the dataset.

6) Line 33: Define VOCs and NOx.

Line 35 and 36: "NO_x" has been defined as "nitrogen oxides" and "VOCs" have been defined as "volatile organic compounds".

7) Line 49: Define DMS.

Line 52: "DMS" has been defined as "dimethyl sulfide".

8) Line 108-109: "with low time resolution". Be more specific here. Gautrois et al. (2003) collected about one sample every 9 days. Additionally, the authors did not use a GC- MS, but a combination of GC-FID and GC-ECD.

The text has been amended to read:

Line 109–112: "Gautrois et al. (2003) reported long-term VOC concentrations for Alert, NU, where a seven-year time-series of VOCs mixing ratios has been generated, although with a 9 day time resolution, using off-line techniques (GC coupled to flame ionization and electron capture detectors)."

9) Line 110: You don't really explain why we need high time-resolved measurements of VOCs. Do you expect a high temporal variability? How about the global atmospheric watch reactive gases measurement network (Schultz et al., 2015) – Aren't these measurements enough?

   Line 111: Same comment as above. In the previous sentence, you highlight the need for long-term measurements of VOCs in the Arctic. While a substantial contribution to the literature, you "only" report several months of data. You could perhaps emphasize more the high temporal frequency of your measurements.

The reviewer is correct in pointing out the lack of explanation for the need of high-time resolved measurement. We do expect a high temporal variability, especially in the summer when meteorological conditions can change rapidly. Schultz et al. (2015) is an important piece of literature, which highlights the need for high-time resolved measurements, therefore we have highlighted the need for high-time resolved measurements with the addition of the following paragraph:

Line 112–120: "High time resolution measurements are of vital importance for the study of Arctic atmospheric chemistry. For instance, diurnal studies can only be accomplished with a fast response instrument, as grab samples and time-integrated samples (i.e., adsorbent tubes) will not capture the variability on short enough time scales (de Gouw and Warneke, 2007). Understanding the effects of meteorological parameters on VOCs levels requires an instrument response which is shorter than the transient event being observed. Also, flux measurements can only be achieved through fast responding instrumentation (Müller et al., 2010). The study of short-lived compounds, such as reactive halogen species, and their interactions with VOCs is only possible on short timescales. Finally, global networks have highlighted the need for a quick turnaround in the delivery of atmospheric species for the validation of global atmospheric composition forecasting systems (Schultz et al., 2015)."

The reference de Gouw and Warneke, 2007, Müller et al., 2010, and Schultz et al., 2015 are new and have been added to the reference list.

10) Line 123: Did you filter data for local contamination? If so, how?

Line 157: How exactly did you remove the influence of local pollution. What criteria did you use for wind speed and direction?

We have added Section 2 "Quality Control Procedure" in the Supplement, which describes how local pollution was identified and removed, as seen below.

SI Line 35– 52: **"Quality Control Procedure**

Data were quality controlled by analysis of PNSD, ozone, wind direction and speed, and internal activity logs. Local pollution at Villum can arise from activity around the measurement site (e.g., passenger vehicles, all-terrain vehicles, snowmobiles, and heavy machinery) as well as from activities from Station Nord (e.g., waste incineration, vehicular activity, and aircraft landing, idling, and take off). Internal activity logs of visits to the measurement building were used to highlight periods when human activity could affect the measurements, periods where VOC levels were elevated over background levels for the duration of the visit to the station were removed. Measurements of PNSD and ozone were analyzed, in tandem, for sharp and sudden increases in the ultrafine mode (< 100 nm) aerosol particles and concurrent sharp and sudden decreases in ozone, increases in ultrafine mode particles are indications of vehicular emissions while decreases in ozone results from its titration with nitrogen oxides. These periods were further inspected for wind direction and speed, with winds coming from due north at low speeds indicative of local pollution from Station Nord. All periods where local pollution was suspected of influencing the measurements were visually inspected by a panel of three persons, a consensus was required before data were removed. Data were also quality controlled for abnormal levels of instrumental parameters (i.e., E/N ratio, drift tube temperature, pressure, and voltage), periods with large deviations from nominal values were removed. Certain compounds (DMS, formic acid, and acetic acid) exhibited a slow return to nominal values after a blank than before, this issue was especially evident in the summer, these periods were removed. All quality control was performed on VOCs at a 5 s time resolution, data was removed before averaging to 30-minute means.”

11) Line 125, Table S1: I have a hard time understanding how the seasons were defined. Skov et al. (2020) recently used a different (and more straightforward) definition: winter from December to February, spring from March to May, summer from June to August, and fall from September to November.

The authors admit this is an unusual set of dates for dividing seasons. This is because the data is split into three periods by interruptions (mainly due to power failure) as seen in Figure 1. Therefore, the authors divided the seasons according to these groups to include uninterrupted collected data. Additionally, “Fall” in the table has been changed to “Autumn”, the manuscript has also been checked throughout for consistency regarding this naming. The slashes between measurement and unit has been removed and replaced with a comma. The dates have been made consistent with the dates listed in the manuscript. An updated Table 1 along with its caption is presented below:

Table S1. Statistics for meteorological parameters (mean ± s.d.) for all seasons, spring (April 4 – June 8), summer (June 9 – August 6), and autumn (August 7 – October 25). During the campaign, there were several large gaps in the data, most noticeably one in July and one in August, as seen in Fig. 1. The seasons are therefore divided based on the continuous collection of data uninterrupted by large missing gaps. The seasons roughly correspond to the conventional definition of seasons.

	All Seasons	Spring	Summer	Autumn
Wind Direction, °	207.5 ± 89.0	202.4 ± 91.8	189.3 ± 2.6	223.8 ± 81.2
Wind Speed, m s^{-1}	3.3 ± 2.6	3.1 ± 2.4	3.5 ± 2.4	3.4 ± 2.7
Temperature, °C	-6.5 ± 9.6	-13.8 ± 9.0	2.2 ± 4.1	-7.0 ± 7.9
RH, %	77.4 ± 12.6	74.6 ± 10.6	78.0 ± 15.6	79.1 ± 11.4
Radiation, W m^{-2}	174.9 ± 163.9	222.3 ± 146.3	295.9 ± 4.2	57.0 ± 97.4
Pressure, hPa	1010.6 ± 9.0	1014.8 ± 8.6	1007.5 ± 6.5	1009.6 ± 9.5
Snow Depth, m	0.9 ± 0.6	1.4 ± 0.1	1.1 ± 0.4	0.3 ± 0.4

12) Line 137-138: “measurements were interrupted for short periods ranging from days to weeks”. Could you please add a Table summarizing, for each month, the number of hours of operation?

Table S2 has been added to the Supplement summarizing the number of hours the instrument was in operation for each compound for each month of the campaign. The following text has been added:

Line 151–152: “Table S2 summarizes the total number of operational hours for each compound for each month of the campaign.” See Table 2 below.

Table S2. Total hours of operation of the PTR-ToF-MS for each month of the campaign and for each compound. Periods removed through the QC procedure are not included.

	April	May	June	July	August	September	October

Formaldehyde	374	601	288	661	417	443	403
Acetonitrile	229	601	288	661	417	443	403
Formic Acid	349	601	288	641	417	443	403
Acetone	376	601	288	661	417	443	403
Acetic Acid	375	577	288	661	417	411	359
DMS	300	577	169	391	357	443	377
MEK	376	601	288	661	417	443	403
$C_3H_6O_2$	327	601	288	661	417	443	403
Benzene	376	601	288	661	417	443	403
C_5H_8O	376	601	288	661	417	443	403

13) Line 144: “within the analytical uncertainties”. Please refer to Table 1 here. Additionally, how often did you perform a calibration?

VOC mixing ratios were quantified using the kinetic rate reaction method (Supplement Sect. 1) and were validated against a certified reference standard at the beginning of the campaign. We have added a reference to (Holzinger et al., 2019) in the sentence, which refers to the quantification method and the reference standard. The phrase “using the reaction kinetics quantification method.” has been added to the Supplement on Line 2. Table 1 has been referred to in the sentence. The main text was amended to:

Line 153: “Data generated by the PTR-ToF-MS instrument were processed with the PTR-MS Viewer software v. 3.2.12 (Ionicon Analytik). Mass calibrations and VOC mixing ratios were calculated by the PTR-MS Viewer, based on the reaction kinetics quantification method (Sect. S1). The instrument quantification was validated against an external gas-phase calibration standard (Apel-Riemer Environmental), a comparison between standard and instrument mixing ratios yielded percent errors that were within the analytical uncertainties (Table 1), therefore we are confident in the quantification method (Holzinger et al., 2019).”

14) Lines 179-181: Did you perform a sensitivity test? How does changing concentrations below LOD and missing concentrations influence the PMF results?

The authors performed an innumerable amount of PMF runs, varying treatment of data below the LOD, treatment of missing values (either removing the sample or replacing with median for the dataset), treatment of the uncertainty matrix, number of species included in the model (species were systematically removed and added), threshold values for species categorization, and number of factors. While each model run, produced unique results, the overall shape of the factor time series and species profile for each factor was consistent with the final reported model setup. The optimal model solution (as configured in the study) was deemed robust to these different variations of the dataset.

The text has been amended to include this description of model robustness.

Line 203–211: “Numerous sensitivity runs were performed to evaluate the validity of this data preparation protocol including varying the treatment of data below the LOD (replacing with half of the LOD or leaving as is), treatment of missing values (removing the sample or replacing missing species with the median), treatment of the uncertainty matrix, number of species included in the model (species were systematically removed or added to observe their influence on the model solution), threshold values for species categorization, and the number of factors. Each variation of the input data, of course, produced a unique solution, however, the overall shape of the time series and factor contributions profile was consistent with the solution present in this study. The optimal model solution, for the configuration present here, was therefore deemed robust to these variations of the input data and provided acceptable diagnostics."

15) Line 191: "automatic weather station placed close to the measurement site". How close? Be more specific.

The text now states the distance of the automatic weather station from the measurement site.

Line 218–219: "Meteorological data including temperature, relative humidity, wind speed, wind direction, pressure, radiation, and snow depth were generated by an automatic weather station placed ~44 meters away from the measurement site."

16) Line 257: "Elevated DMS mixing ratios". What do you mean by "elevated"? Be more specific.

The text has been amended to better describe the elevated mixing ratios of DMS during these periods. The main text now reads:

Line 321: "Elevated DMS mixing ratios were observed for two short periods of a few days' duration in May (1–5 May and 16–19 May), where DMS mixing ratios increased an order of magnitude from ~0.02 to >0.2 ppbv (Fig. 3a and b)."

17) Line 273: "illustrated here by changes in wind speed". I would expect changes in wind direction to be a more useful tracer of change in meteorological conditions.

The authors also expected wind direction to be more useful tracer of meteorological conditions, however, for the two episodes of elevated DMS, changes in wind speed appear to be a better indicator than wind direction. To reflect this, we have added wind direction to Fig. 3 in the manuscript (see below). For the first episode, the wind direction is quite variable while increased wind speeds are observed during depletions in acetone and elevations of DMS, and it is unfortunate meteorological data are missing on 3rd and 4th of May. For the second episode, the wind direction does change concurrently with an increase in wind speed, although throughout the episode wind direction is also variable with contributions from the north and the east. We have mentioned this in the text:

Line 338–339: "These changes in mixing ratios are accompanied by a change in meteorological conditions, illustrated here by changes in wind speed and to a less extent wind direction (Fig. 3)."

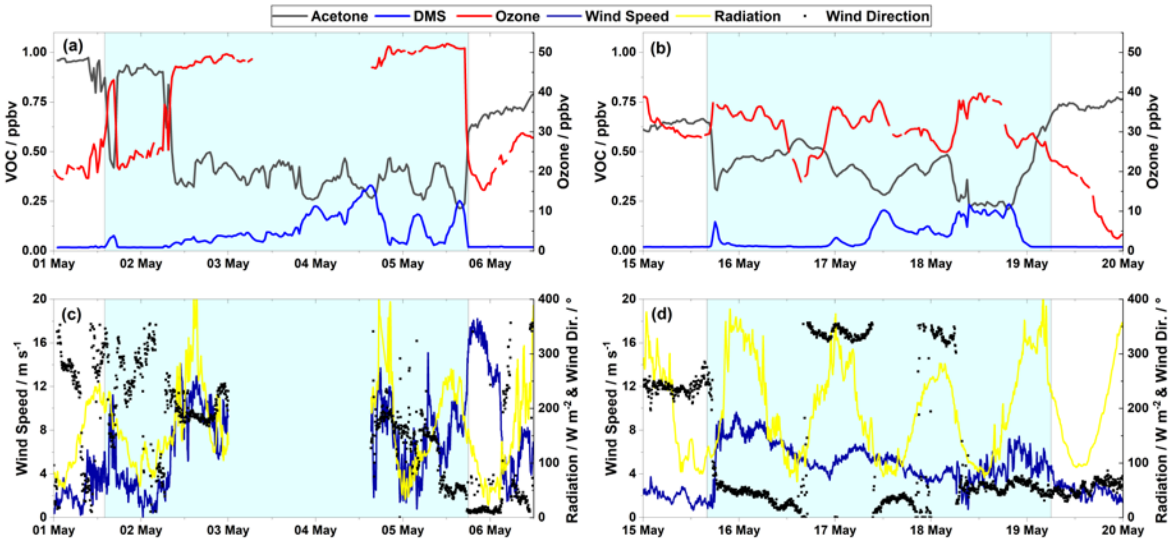


Fig. 3. Left: The first period of elevated DMS mixing ratios (May 1–5). Right: The second period of elevated DMS mixing ratios (May 15– 19); (a) and (b) mixing ratios of acetone, DMS (left axis), and ozone (right axis); (c) and (d) wind speed (left axis) and radiation and wind direction (right axis). The shaded area represents episodes of elevated DMS mixing ratios.

18) Line 344: “a sink during the summer”. A sink of what?

Line 414: “Increased areas of open water in the Arctic also act as a sink for acetonitrile during the summer (de Gouw et al., 2003).”

19) Lines 426-427: “Although, the variation of the Marine Cryosphere Factors seems not to be driven mainly by the dependence on horizontal wind speed (Fig. S2)”. Figure S2 does not illustrate this. What is the correlation coefficient between the Marine Cryosphere Factor and wind speed?

The reference to Fig. S2 has been removed and replaced with the correlation coefficient between the Marine Cryosphere Factor and wind speed (R=-0.04) to better illustrate the lack of dependence between the two.

Line 509–510: “Although, the variation of the Marine Cryosphere Factor seems not to be driven mainly by the dependence on horizontal wind speed (R=-0.04).”

20) Lines 428-429: “given the distance of the measuring site from open water”. What is the distance between the station and open water?

The fjord immediate to the station is located ~1.7 km away, during the summer this is mostly ice free, although is prone to freeze-ups when the temperature drops below zero for several hours. The station is located on a peninsula which is surrounded by sea ice throughout the year, taking this sea ice into account, open water is ~25 km away. The following text has been added:

Line 510–513: “Marine microorganisms produce DMS (Stefels et al., 2007; Levasseur, 2013), and given the distance of the measuring site from open water (taking sea ice into account the, station is approx. 25 km distance from open water), it is proposed that the majority of DMS produced is already oxidized to MSA and other products when reaching the station.”

21) Section on Arctic Haze: please mention/discuss more clearly that you do not have data in wintertime, when Arctic Haze is expected to be at its maximum.

It has been made clear to the reader that our Arctic Haze Factor is only from spring and other studies present data from winter and spring. The following text has been added.

Line 617–620: "It is worth noting that the Arctic Haze Factor from this study is only for spring, while the other studies present data from the winter/spring, therefore any comparisons we make are from our spring Arctic Haze Factor to other Haze factors during winter and spring. While this is not a perfect comparison, it is one worth making, as Arctic Haze is the main source of anthropogenic pollution in the Arctic."

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Atmospheric VOC measurements at a High Arctic site: characteristics and source apportionment

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Abstract. There are few long-term datasets of volatile organic compounds (VOCs) in the High Arctic. Furthermore, knowledge about their source regions remains lacking. To address this matter, we report a ~~long-term~~multi-season dataset of highly time-resolved VOC measurements in the High Arctic from April to October 2018. We have utilized a combination of measurement and modeling techniques to characterize the mixing ratios, temporal patterns, and sources of VOCs at Villum Research Station at Station Nord, in Northeastern Greenland. Atmospheric VOCs were measured using Proton Transfer-Time of Flight-Mass Spectrometry (PTR-ToF-MS). Ten ions were selected for source apportionment with the receptor model, positive matrix factorization (PMF). A four-factor solution to the PMF model was deemed optimal. The factors identified were Biomass Burning, Marine Cryosphere, Background, and Arctic Haze. The Biomass Burning F~~f~~actor described the variation of acetonitrile and benzene and peaked during August and September.~~ Back trajectory analysis indicated the influence of active fires in North America and Eurasia.~~ The Marine Cryosphere ~~factor~~Factor was comprised of carboxylic acids (formic, acetic, and $C_3H_6O_2$~~propionic acid~~) as well as dimethyl sulfide (DMS). This factor displayed ~~a~~peak contributions ~~clear diurnal profile~~ during periods of snow and sea ice melt. ~~Back trajectories~~A potential source contribution function (PSCF) showed that the source regions for this factor were the coasts around Southeastern and Northeastern ~~North~~ Greenland~~ and the Arctic Ocean~~. The Background ~~factor~~Factor was temporally ubiquitous, with a slight decrease in the summer. This factor was not driven by any individual chemical species. The Arctic Haze ~~factor~~Factor was dominated by benzene with contributions from oxygenated VOCs. This factor exhibited a maximum in the spring and minima during the summer and autumn. This temporal pattern and species profile are indicative of anthropogenic sources in the mid-latitudes. This study provides seasonal characteristics and sources of VOCs and can help elucidate the processes affecting the atmospheric chemistry and biogeochemical feedback mechanisms in the High Arctic.

1 Introduction

The temperature in the Arctic has increased at twice the ~~speed~~ rate of the global average (IPCC, 2019), a phenomenon known as Arctic amplification. Increased CO_2 concentration and sea ice loss are responsible for the majority of this temperature increase (Dai et al., 2019). However, short-lived climate forcers (SLCFs; methane, ozone, black carbon (BC), and aerosol particles) are together responsible for half of the present temperature increase observed in the Arctic (Quinn et al., 2008). Atmospheric aerosol particles are the most important SLCF (due to their scattering, absorbing, and cloud modification properties) but their climate forcing is associated with the largest uncertainty, especially in the Arctic (Pörtner, 2019). Ozone is an important photochemical oxidant in the Arctic troposphere. Ozone precursors, e.g., volatile organic compounds (VOCs), nitrogen oxides (NO_x), and peroxyacetyl nitrate (PAN), remained poorly characterized in the High Arctic (AMAP, 2015). Photochemical reactions including ozone and VOCs have important implications for the lifetime of methane, a major greenhouse gas. The identification and characterization of processes leading to precursor emissions of aerosols and ozone are therefore needed to improve the assessments of biosphere-aerosol-climate feedback mechanisms.

~~In the Arctic, there are strong seasonal variations in aerosol size and concentrations, with long-range transport of accumulation mode particles in late winter and spring and local production of ultra-fine particles in the summer and autumn season (Flyger et al., 1980; Barrie et al., 1981; Heidam et al., 2004; Nguyen et al., 2016). Expansion of the polar dome and inefficient wet removal in the winter and spring allows for the transport of anthropogenic pollution (sulfate aerosols with acidic and toxic components, BC, and VOCs) to the Arctic (Klonecki et al., 2003; Heidam et al., 2004; Nielsen et al., 2019).~~ Several studies have reported on new particle formation (NPF) events, involving naturally emitted biogenic VOCs during the summer in the High Arctic. Dall'Osto et al. (2018b) recently demonstrated a negative correlation of NPF events at Villum Research Station, Station Nord, in Northeastern Greenland with sea ice extent. The authors suggested that ultrafine aerosol formation is likely to increase in the future,~~–~~ given the projected increased melting of sea ice (Boe et al., 2009; Bi et al., 2018). Dall'Osto et al. (2017) hypothesized that NPF events during summer on Svalbard were linked to marine biological activities within the open leads and between the pack ice and/or along the marginal sea-ice zones. Further confirming the same processes are occurring for Northeastern Greenland (Dall'Osto et al., 2018a; Nielsen et al., 2019). Open leads and open pack ice emit dimethyl sulfide (DMS) that undergoes atmospheric oxidation leading to methanesulfonic acid (MSA), sulfur dioxide, and ultimately sulfuric acid, which helps form and grow particles (Nielsen et al., 2019). After formation, aerosols grow to sizes where they can act as cloud condensation nuclei (CCN) (Ramanathan et al., 2001). VOCs of marine biogenic origin greatly contribute to CCN activity during summer (Lange et al., 2018; Lange et al., 2019). The sources of NPF in the Arctic and its corresponding precursors are a topic of intense research, as uncertainty remains regarding the mechanism of aerosol production. For example, Burkart et al. (2017) found that the condensable vapors responsible for particle growth were more semi-volatile than previously observed in mid-latitudes, although they could not identify a source area for these vapors. Aerosol formation is one of the most important factors in determining the surface energy balance in the Arctic. Recently, it was estimated that NPF events could increase CCN concentrations by 2–5 fold over background concentrations (Kecorius et al., 2019). However, parametrization of the processes leading to aerosol formation is still a large source of uncertainty in global radiative forcing predictions (Haywood and Boucher, 2000). The characterization of these gas-phase precursors to particle formation is a key factor for understanding the dynamics of the Arctic troposphere and the corresponding effects on climate.

~~Ozone has a distinct seasonality in the Arctic, with maximum mixing ratios in the winter, depletion events in the spring, and a minimum in the summer (Bottenheim and Chan, 2006).~~ Ozone is an important pollutant at the surface and greenhouse gas in the mid to upper troposphere. Ozone can perturb radiation fluxes and modify heat transport to the Arctic (Shindell, 2007). In the Arctic, sources of ozone include long-range transport and photochemical production. Ozone and its precursors (VOCs, NO_x, CO, and PAN) can be transported from anthropogenic sources in the mid-latitudes (Hirdman et al., 2009) and natural boreal forest fire emissions (Arnold et al., 2015), which have been increasing in recent years (Parrish et al., 2012). The major sink for ozone in the Arctic is photochemical ~~reactions~~loss, followed by minor contributions from dry deposition. Ozone largely controls the oxidative capacity of the atmosphere, as a chief precursor for OH, an oxidant for many compounds, and a major prerequisite for halogen explosion event (Simpson et al., 2007). Halogen explosion events can affect the lifetime and reaction rates for organic gases and the deposition of mercury ~~to~~ in the Arctic ecosystem.~~, Formaldehyde, a~~

~~product of photochemical degradation and ozonolysis of VOCs, is also an important photolytic source of OH radicals particularly at high solar zenith angles, i.e., Arctic summer (Cooke et al., 2010).~~ Photochemical reactions involving VOCs can be a sink (by reactions with ozone) and a source (through reactions with NO_x) of ozone. Increased anthropogenic activity in the Arctic (shipping and resource extraction) is expected to increase emissions of both NO_x and VOCs (Law et al., 2017). Biomass burning emissions, which are expected to increase in the future, have been shown to increase ozone production by as high as 22 % in the Arctic (Arnold et al., 2015). Ozone levels have consequences for OH radical production, which is the main oxidant of methane, thus largely controlling its lifetime in the atmosphere. Therefore, the characterization of the interactions of ozone and VOCs have implications for climate effects and atmospheric chemistry.

Several factors, including chemical lifetime, local emissions, and long-range transport, govern the mixing ratios of VOCs in the Arctic atmosphere. The chemical lifetime of most VOCs in the Arctic is dependent on the oxidative capacity of the atmosphere, thus there is a strong seasonality (Gautrois et al., 2003). However, due to the low humidity in the Arctic atmosphere, the concentration of OH is low (Spivakovsky et al., 2000). Therefore, halogen and ozone chemistry plays an active role during the spring in the atmospheric chemistry of VOCs in Arctic regions (Simpson et al., 2015). However, atmospheric reactions alone seem unable to explain the VOCs mixing ratios and dynamics observed at Arctic sites (Grannas et al., 2002; Guimbaud et al., 2002; Sumner et al., 2002), indicating missing sources other than photochemical production. Two potential local sources are the snowpack and the sea surface microlayer. The snowpack also has a major impact on ambient VOCs by uptake/release mechanisms and acts as a matrix for many photochemical and biological processes (Guimbaud et al., 2002; Grannas et al., 2004; Kos et al., 2014). For example, Dibb and Arsenault (2002) demonstrated that the snowpack is a source of formic and acetic acid through the oxidation of ubiquitous organic matter. 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 d~~Depositional fluxes of methanol ~~was~~ were also observed, which they postulated as a source of formaldehyde. These observed gas-phase fluxes had a diurnal cycle following polar sunrise that correlated with the solar zenith angle. Sea surface microlayer emissions are important local sources of atmospheric VOCs, e.g. DMS, formic acid, and acetic acid (Mungall et al., 2017). Sea emissions have a pronounced seasonality because of sea ice preventing air-sea exchange during most of the year in the Arctic. The sea surface microlayer could play a role in the emission of VOCs due to photochemical processes (Chiu et al., 2017; Bruggemann et al., 2018) or heterogenic oxidation (Zhou et al., 2014). For highly water-soluble compounds, the ocean could also be an important sink (Sjostedt et al., 2012). Finally, transport of VOCs, such as benzene, methane, ethane, propane, and chlorofluorocarbons, has been observed from the mid-latitudes to the High Arctic (Stohl, 2006; Harrigan et al., 2011; Willis et al., 2018).

Few studies have reported VOCs in ambient air from Arctic sites with on-line techniques, usually during short-term campaigns. Hornbrook et al. (2016) utilized non-methane hydrocarbons measurements to derive time-integrated halogen mixing ratios during the OASIS-2009 campaign at Utqiagvik~~Barrow~~, AK (formerly known as Barrow, AK). Mungall et al. (2018) studied the sources of formic and acetic acid at Alert~~, CA~~, NU during the summer of 2016. Sjostedt et al. (2012) and (Mungall et al., 2017) performed VOC measurements onboard the CCGS *Amundsen* in the Canadian Archipelago during the summer of 2008 and 2014, respectively. There have been several campaigns exploring snowpack emissions of VOCs (Boudries et al., 2002; Dibb and Arsenault, 2002; Guimbaud et al., 2002; Barret et al., 2011; Gao et al., 2012). Gautrois et al. (2003) reported long-term VOC concentrations for Alert~~, CA~~, NU, where a seven-year time-series of VOCs mixing ratios has been generated, although with ~~low~~ a 9-day time resolution, using off-line techniques (GC~~-MS~~ coupled to flame ionization and electron capture detectors). High time resolution measurements are of vital importance for the study of Arctic atmospheric chemistry. For instance, diurnal studies can only be accomplished with a fast response instrument, as grab samples and time-integrated samples (i.e., adsorbent tubes) will not capture the variability on short enough time scales (de Gouw and Warneke, 2007). Understanding the effects of meteorological parameters on VOCs levels requires an instrument response which is shorter than the transient event being observed. Also, flux measurements can only be achieved through fast responding instrumentation (Müller et al., 2010). The study of short-lived compounds, such as reactive halogen species, and their interactions with VOCs is only possible on short timescales. Finally, global networks have highlighted the need for a quick turnaround in the delivery of atmospheric species for the validation of global atmospheric composition forecasting systems (Schultz et al., 2015). These previous studies call for higher time resolved and longer measurement campaigns, thus highlighting the importance of long-term high time-resolved measurements of VOCs in the Arctic.

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In this study, we report several months of high time-resolved mixing ratios of selected VOCs measured at the high Arctic site Villum Research Station (Villum) at Station Nord (Northeastern Greenland). This study aims to provide a better insight into the dynamics, seasonal behavior, and potential sources of VOCs in the high Arctic. We accomplish this by combining VOC mixing ratios with meteorological data, air mass back trajectories, and the receptor model, positive matrix factorization (PMF). In Sect. 2, we describe our analytical instrumentation and models in detail. In Sect. 3, we cover the seasonal dynamics of VOC as well as each factor from the PMF model.

2 Methods

2.1 Field site

The sampling campaign took place at Villum Research Station (Villum), which is situated on the Danish military base, Station Nord, in Northeastern Greenland (81° 36’ N, 16° 40’ W, 24 m above mean sea level). Villum is situated in a region with a dry and cold climate where the annual precipitation is 188 mm and the annual mean temperature is -16 °C. The dominating wind direction is southwestern with an average wind speed of 4 m s~~ec~~$^{-1}$. The sampling took place about 2.5 km south~~-~~west of the main facilities of the Station Nord military camp. The sampling location is upwind from the Station most of the time for all seasons (Fig. S1). An overview of the meteorological data is presented in Fig. S2. Statistics for meteorological data over the sampling campaign can be found in Table S1.

2.2 Gas-phase measurements and data processing

Gas-phase measurements of VOCs were obtained using a PTR-ToF-MS 1000 (Ionicon Analytik GmbH). The measurement campaign commenced after polar sunrise on April 4 and concluded before polar sunset on October 28, 2018. The PTR-ToF-MS was operated with hydronium ion (H_3O^+) as a reagent ion, a drift tube temperature of 70 °C, a drift pressure of 2.80 mbar, a drift tube voltage of 650 V leading to an *E/N* (Electric field/density of the buffer gas in the drift tube) value of around 120 Townsend (Td). Mass spectra up to *m/z*=430 Da were collected at 5 second single spectra integration time~~s scan rate~~. The instrument inlet consisted of a PEEK capillary tube heated at 70 °C and a built-in permeation unit (PerMasCal; Ionicon Analytik) which emitted 1,3-diiodobenzene, used for mass scale calibration. The inlet of the sampling line consisted of ¼" Teflon tubing extending through an insulated opening in the roof with a sampling cone at the tip to prevent water and debris from blocking the orifice. Ambient outdoor air was aspirated into the instrument at a rate of 100 ml min^{-1}. Blank measurements were obtained every 4 hours for 15 minutes by automatic switching from the ambient outdoor air to indoor air pumped through a Zero Air Generator (Parker-Balston, Part #75–83). Due to technical issues (mainly electrical power failure), measurements were interrupted for short periods ranging from days to weeks in April, June, August, and September. Instrument parameters (E/N ratio, drift tube temperature, pressure, and voltage) were inspected before and after power failures to ensure proper instrument functionality. Periods with abnormal parameter values were removed. Table S2 summarizes the total number of operational hours for each compound for each month of the campaign.

Data generated by the PTR-ToF-MS instrument were processed with the PTR-MS Viewer software v. 3.2.12 (Ionicon Analytik). Mass calibrations and VOC mixing ratios were calculated by the PTR-MS Viewer, based on the reaction kinetics quantification method (Sect. S1). The instrument quantification was validated against an external gas-phase calibration standard (Apel-Riemer Environmental), a comparison between standard and instrument mixing ratios yielded percent errors that were within the analytical uncertainties (Table 1), therefore we are confident in the quantification method (Holzinger et al., 2019). ~~Inspection of the mass spectrum yielded nine protonated masses from which an empirical formula was calculated, and a compound name assigned. Compound names were assigned based on comparison with the libraries from the PTR-MS Viewer and Pagonis et al. (2019), and references therein, as well as *a priori* knowledge.~~ The PTR-MS technique allows to observe species with a proton-affinity higher than water, this ~~comprehends~~encompasses most VOCs found in the atmosphere with the important exception of alkanes. It does not allow ~~to~~for the distin~~guish~~ction between isomers to be made. Compound names were assigned based on comparison with the libraries from the PTR-MS Viewer and Pagonis et al. (2019), and references therein~~, as well as *a priori* knowledge~~. Inspection of the mass spectrum yielded ten protonated masses from which an empirical formula was calculated, and compound names were assigned for nine masses, as discussed in ~~Chapter~~Sect. 3.1. ~~For one compound, an empirical formula was calculated ($C_5H_8OH^+$) but a compound name could not be assigned due to the inability of PTR-MS to distinguish isomers. Another compound ($C_4H_8OH^+$) was doubly assigned to propionic acid and methyl acetate. Methyl acetate has the same protonated m/z ratio as propionic acid; thus, contributions of methyl acetate to the signal at 75.058 m/z cannot be ruled out. Due to a proton affinity below water, saturated hydrocarbons (alkanes) are unable to be~~

~~detected via PTR-ToF-MS. See Table 1 for a detailed list of selected masses.~~ Output files were further processed with MATLAB R2018B for time averaging and blank ~~values~~ subtraction. The limit of detection (LOD) for each identified species was calculated as three times the standard deviation (s.d.) of the blank values for each day. For calculation of statistics, mixing ratios below LOD ~~was~~ were set to ½ the LOD. The data ~~was~~ were time-averaged to a 30-minute means. Uncertainty in VOC measurements accounted for the reaction rate coefficient as well as primary ion counts and blank corrected ion counts, for a detailed description see the Sect. S1.The data set has been rigorously quality controlled, through analysis of particle number size distributions (PNSD), meteorological data (wind direction and speed), and internal activity logs, to remove the influence of local pollution, for a detailed description see Sect. S2. ~~Uncertainty in VOC measurements accounted for the reaction rate coefficient as well as primary ion counts and blank corrected ion counts, for a detailed description see the Supplement.~~ Ozone (O_3) was measured using an API photometric O_3 analyzer M400, data is quality assured and controlled via standard EN14625:2012, with calibrations every six months (Skov et al., 2004; Skov et al., 2020).

2.3 Positive Matrix Factorization (PMF) analysis

The PMF model was operated using the US EPA PMF version 5.0 software, which uses the second version of the multilinear-engine 2 (ME-2) platform (Paatero and Tapper, 1994). The goal of PMF is to identify the number of factors or sources *p*, the species profile *f*, and the mass contributed by each factor to each sample. PMF accomplishes this by decomposing a data matrix *X* into two matrices *G* and *F*. The input data matrix *X* consists of dimensions *i* and *j*, where *i* is the number of samples and *j* is the measured chemical species. The source profile matrix *f* is of dimensions *p* and *j*. The source contribution matrix *g* is composed of *p* and *i* dimensions. This is expressed in Eq. (1), below.

$$X_{ij} = \sum_{k=1}^{p} g_{ik} \times f_{kj} + e_{ij} \quad (1)$$

Where e_{ij} is the residual matrix and *k* ~~are~~ is the individual sources. PMF uses measurement uncertainties u_{ij} and the residual matrix to minimize the Objective Function *Q*, Eq. (2) below:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} [\frac{e_{ij}}{u_{ij}}]^2 \quad (2)$$

Where *n* is the total number of samples and m is the total number of species. There are three versions of the objective function: Q_{true} that includes all data points, Q_{robust} that excludes outliers, and Q_{theo} that is approximately equal to the number of degrees of freedom. The ME-2 platform performs iterations via the conjugate gradient method until convergence to minimize *Q*. Each good data point contributes a value of approximately one to the value of *Q*; therefore, *Q* and the ratio of Q_{true} to Q_{theo} are the goodness of fit parameters for the appropriate number of factors (Paatero et al., 2014).

The following data preparation protocol was developed according to standard practice in the field (Polissar et al., 1998; Reff et al., 2007; Hopke, 2016) which allows PMF analysis to be performed effectively. In certain cases, discussed here, the data set was modified before modeling via PMF. Data with concentrations below the LOD were replaced with a value equal to half of the LOD. The associated uncertainty was set to 5/6 of the LOD. Missing concentrations from a sample were replaced with the median concentration of the data set and the uncertainty was set as a multiple (3) of median concentration (Polissar et al., 1998; Reff et al., 2007). It is worth noting that the operational protocols used to estimate the uncertainties and treatment of data are based on extensive testing to find an approach that provided useful results (Hopke, 2016). Numerous sensitivity runs were performed to evaluate the validity of this data preparation protocol including varying the treatment of data below the LOD (replacing with half of the LOD or leaving as is), treatment of missing values (removing the sample or replacing missing species with the median), treatment of the uncertainty matrix, number of species included in the model (species were systematically removed or added to observe their influence on the model solution), threshold values for species categorization, and the number of factors. Each variation of the input data, of course, produced a unique solution, however, the overall shape of the time series and factor contributions profile was consistent with the solution present in this study. The optimal model solution, for the configuration present here, was therefore deemed robust to these variations of the input data and provided acceptable diagnostics.

Two methods for evaluating modeling uncertainty in PMF were performed: bootstrapping (BS) and displacement of factor elements (DISP) (for a description see Paatero et al. (2014)). BS uncertainty includes effects from random errors and partially includes the effects of rotational ambiguity. DISP explicitly captures uncertainty from rotational ambiguity (Brown et al., 2015). Another method of estimating rotational ambiguity is the Fpeak function. Fpeak evaluates *Q* under different rotational strengths, in this study Fpeak strengths from -5 to 5 in intervals of 1 and from -1 to 1 in intervals of 0.1.

2.4 Ancillary data

Meteorological data including temperature, relative humidity, wind speed, wind direction, pressure, radiation, and snow depth were generated by an automatic weather station placed ~44 meters away from~~close to~~ the measurement site. Using the local wind direction and wind speed, a conditional probability function (CPF) was calculated using the source contributions for each factor. CPF is defined as CPF $=m_\theta/n_\theta$, where m_θ is the number of occurrences that a source contribution exceeds a predetermined threshold criterion (75th percentile) while arriving fro~~or~~m a wind sector and n_θ is the total number of occurrences wind arrived from the same wind sector. A wind sector was defined as 30° and wind speeds below 0.5 m s^{-1} were excluded to account for uncertainty in wind direction at low wind speeds. Daily polar gridded sea ice concentrations for the measurement period were obtained through the Nimbus–7 SMMR and DMSP SSM/I-SSMIS Passive Microwave Data (Cavalieri et al., 1996). Time series of local sea ice concentrations were calculated from the gridded daily average sea ice concentrations (%) by masking an area of ± 2° longitude and +8°/-4° latitude around Villum (Greene et al., 2017; Greene, 2020). ~~Active fires during the period, August 15–September 15, 2018, was provided by NASA's Fire Information for Resource Management System (FIRMS) which distributes Near Real-Time (NRT) active fire data from NASA's Moderate Resolution Imaging Spectroradiometer (MODIS) and NASA's Visible Infrared Imaging Radiometer Suite (VIIRS) (Schroeder et al., 2014).~~

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2.5 Back Trajectory Analysis

To investigate source regions, the R package Openair (Carslaw and Ropkins, 2012) was utilized to produce a potential source contribution function (PSCF). Trajectories in Openair were calculated using the HYSPLIT model (Draxler and Hess, 1998; Rolph et al., 2017) at 100 m altitude and 120 hours backward in time using Global NOAA-NCEP/NCAR reanalysis data archives on a 2.5° resolution. A PSCF, shown in Eq. (3), calculates the probability that an emission source is located in a grid cell of latitude *i* and longitude *j*, on the basis that emitted material in the gird cell *ij* can be transported along the trajectory and reach the receptor site.~~The back trajectory model HYSPLIT (Draxler and Hess, 1998; Rolph et al., 2017) calculated air mass back trajectories arriving at Villum, incorporating Global Data Assimilation System (GDAS) meteorological data with 1° spatial resolution, and employing modeled vertical velocity. Air mass back trajectories were calculated at 100 m arrival altitude. The trajectory length was varied between 240 and 336 hours. For a synoptic view of air mass history, trajectory frequency maps were calculated following a similar methodology utilized by Tunved et al. (2013) and Freud et al. (2017). Grids of 1° × 1° cells were centered concentrically on Villum; the number of individual trajectories passing over each grid cell was summed, normalized by the total number of trajectories, and multiplied by 100 % to give a trajectory frequency map. The large number of trajectories included in the frequency maps provide statistical robustness to their interpretation and reduces their associated uncertainty.~~

$$PSCF = \frac{m_{ij}}{n_{ij}} \quad (3)$$

Where n_{ij} is the number of times a trajectory has passed through grid cell *ij* and m_{ij} is the number of times that a concentration was above a certain threshold value, in this case, the 90th percentile. To account for uncertainty in cells with a small number of trajectories passing through, a weighting function was applied (Carslaw and Ropkins, 2012). ~~(de Gouw et al., 2003; Singh et al., 2003)~~

3 Results and discussion

3.1 VOC temporal patterns and mixing ratios

The ten selected masses monitored by the PTR-TOF-MS and their assignments to species names are presented in Table 1. Assignments are made by choosing the most plausible contributions to an observed mass but ~~obviously~~ each measured ion may have contributions from several different isomeric molecules. The assignment of masses in the table to protonated molecules of formaldehyde, acetonitrile, formic acid, acetic acid, and benzene appears to be unproblematic as no meaningful alternatives are found. For the remaining molecules, alternative assignments are possible. T~~: T~~he mass assigned to acetone could be propanal as well, but propanal has a shorter atmospheric residence time and acetone is known to be one of the dominating VOCs observed in the atmosphere (Jacob et al., 2002), further, it has been found to have sources in the Arctic (Guimbaud et al., 2002). The mass assigned to DMS could be ethanethiol as well, but the large marine source of DMS makes

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it ~~clearly~~ the most plausible assignment. Methyl ethyl ketone is isomeric with butenal, but being the second most abundant ketone in the atmosphere with, among others, apparently an oceanic source (Brewer et al., 2020) it appears to be the best assignment. $C_3H_6O_2$ may stem from propionic acid but also ~~from~~ hydroxyacetone, methyl acetate, and ethyl formate. While it seems unlikely that ethyl formate could give a major contribution to this signal, the other three species are all plausible candidates: Low molecular weight organic acids are commonly found in the atmosphere (Lee et al., 2009), methyl acetate has been found in emissions from biomass burning (Andreae, 2019) and hydroxyacetone is known to be formed by the atmospheric degradation of isoprene (Karl et al., 2009). For what concerns the $C_5H_8OH^+$ ion we prefer not to make an assignment, possible isomers include, among others, pentenals and pentenones.

For the ~~-~~ t~~t~~en selected VOCs, time series of mixing ratios during the entire measurement~~ing~~ period are displayed in Fig. 1 ~~(~~a-f~~)~~. ~~Details for each compound are presented in Table 1.~~ During the spring (April–May), certain compounds (benzene and ~~$C_5H_8O^+$~~ C_5H_8O) exhibited a maximum and thereafter a decreasing pattern, similar to the timing and profile of the Arctic Haze phenomena. During the spring, compounds did not display a diurnal profile except for acetic acid (Fig. S3) ~~; w~~Whilst in summer (June–August), OVOCs~~certain compounds (DMS and OVOCs)~~ revealed a diurnal cycle that closely follows radiation (Fig. 2 and S4). Compounds of non-photochemical origin (benzene and acetonitrile) also displayed a slight diurnal pattern, which could possibly be due to entrainment from aloft (Fig. S4). Interestingly, several compounds (formaldehyde, formic acid, and acetone) peaked in the spring with decreasing levels until the summer when a diurnal pattern following sunlight was observed (Fig. 1, 2, S4). During the autumn (September–October), all compounds were low except for acetone and acetonitrile (Fig. 1) and only acetic acid displayed a diurnal profile (Fig. S5). The levels, seasonal patterns, and comparison with other studies of these compounds will be discussed below.

~~Oxygenated volatile organic compounds (OVOCs) selected for this study included formaldehyde, formic acid, acetic acid, propionic acid, MEK (methyl ethyl ketone) and an ion with empirical formula $C_5H_8OH^+$ (possible isomers for this compound include, among others, methyl butenal, pentenal, methyl butanone).~~ Formaldehyde, formic acid, MEK, and acetone, and to a lesser extent acetic acid and C_5H_8O~~H^+~~, displayed a decreasing pattern in the spring. For formaldehyde, formic acid, acetic acid, acetone, MEK, and ~~p~~ $C_3H_6O_2$ ~~ropionic acid~~ a ~~clear~~ diurnal variation was observed in the period July–August, with peak mixing ratios occurring around midday (Fig. 2 and S4), highlighting their dependence on sunlight. ~~(Fig. 1 a, c, d, e). The diurnal variation was less pronounced in April–May and September–October, highlighting the dependence on sunlight.~~ Acetone showed the highest mean mixing ratio ± s.d. (0.608 ± 0.196 ppbv). Mean mixing ratios of acetone measured at ~~Barrow~~Utqiagvik, AK during the OASIS-2009 field campaign (March–April 2009) were 0.900 ± 0.300 ppbv (range of 0.364–2.21 ppbv) (Hornbrook et al., 2016), and in the Canadian Archipelago in August–October was 0.424 ppbv (Sjostedt et al., 2012), which is within the same range observed at Villum (0.608 ± 0.196 ppbv, Table 1). The average mixing ratio of formaldehyde in the present study (0.220 ± 0.128 ppbv) is similar to those measured at ~~Barrow~~Utqiagvik, AK (0.204 ppbv)

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The two main non-oxygenated compounds measured were acetonitrile and benzene. Benzene mixing ratios followed the expansion of the polar dome with high mixing ratios in the spring period and lowest in the summer period (Fig. 1~~-~~f), similar to sulfate and BC measured (Massling et al., 2015; Skov et al., 2016) and accumulation mode aerosols (Lange et al., 2018). The mean mixing ratio of benzene measured at Villum was 0.027 ± 0.016 ppbv, which is a factor of two higher than those measured in the Canadian Archipelago (0.013 ppbv) by Sjostedt et al. (2012). Benzene has shown a seasonal pattern at Alert~~, CA~~, NU with a higher mixing ratio in winter due to no or limited photochemistry and long-range transport from lower latitudes (Gautrois et al., 2003). They reported mean winter and summer mixing ratios of 0.200 and 0.034 ppbv, respectively; when compared to the present study ~~is a factor of two higher in the winter but in~~there is good agreement during the summer. Acetonitrile followed a similar pattern to benzene during the spring ~~indicating a slight influence from anthropogenic emissions~~with decreasing values, as well as exhibiting minima in the summer and maxima during the autumn (Fig. 1~~-~~b). The mean mixing ratio of acetonitrile observed at Villum is 0.067 ± 0.025 ppbv, which is a factor of two higher than reported by Sjostedt et al. (2012) (0.030 ppb). The range of acetonitrile mixing ratios (0.023–0.156 ppbv) corresponds to the upper and lower limits of background levels over the Atlantic Ocean (0.10–0.15 ppbv) reported by Hamm et al. (1984) and Hamm and Warneck (1990). The main source of acetonitrile in the atmosphere has been found to be biomass burning (Singh et al., 2003).

DMS was the only sulfur-containing compound detected, with a mean ± s.d. of 0.046 ± 0.043 ppbv. The mixing ratios of DMS observed in this study are a factor of two lower than those reported by Sjostedt et al. (2012) (0.093 ppbv). DMS mixing ratios were near LOD during the spring and autumn, however, were significantly elevated levels during the summer periods of sea ice melt (Fig. 1~~-~~e and 2). ~~DMS showed a clear diurnal cycle during sea ice melt in the summer months correlating with sunlight intensity.~~

3.2 Springtime VOC correlations

Elevated DMS mixing ratios were observed for two short periods of a few days' duration in May (1–5 May ~~1–5~~ and 16–19 May~~ 16–19~~), where DMS mixing ratios increased an order of magnitude from ~0.02 to >0.2 ppbv~~.~~ (~~See~~ Fig. ~~2~~ 3~~Left~~ a and ~~Right~~b ~~below~~). In May, most of the ocean surrounding Villum is still frozen. However, satellite images from the area (available at http://ocean.dmi.dk/arctic/nord.php)~~Fig. S4 a-f and S5 a-e)~~ showed that there were open leads in the frozen sea surface. ~~and b~~Back trajectory calculations (Fig. S6~~-~~a and b) confirmed that, during the DMS emission episodes, the air masses experienced extensive surface contact, traversed ~~over the open leads~~near areas containing open leads (as identified from satellite images)

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before reaching the station. During DMS emission episodes, the acetone mixing ratios decreased correspondingly. Sjostedt et al. (2012) found moderate anti-correlation (R=0.37, $p<10^{-4}$) for DMS with acetone. Minimum values of acetone were observed when DMS reached its maximum values, and the short photochemical lifetime of DMS suggests a localized biological sink for acetone associated with the production of DMS. Certain microorganisms can consume acetone as well as produce DMS from DMSP (Taylor et al., 1980; Kiene et al., 2000). At Villum, the relationship between acetone and DMS showed seasonal changes with a moderate negative correlation in April (R=-0.55), a weak positive correlation in July (R=0.23), and a ~~strong~~ moderate negative correlation in September (R=-0.68). Possible reasons for these variations may be changes in the biological conditions of the seawater, photochemical activity, and source~~s~~ regions. Pearson correlation coefficients for chemical species, radiation, and temperature for April, July, and September are tabulated in Table S3~~2~~, S4~~3~~, and S5~~4~~, respectively.

As illustrated in Fig. ~~2~~ 3a and b, acetone is anti-correlated with ozone during periods of elevated DMS. This relationship is particularly ~~clear~~ evident during situations with abrupt changes in the mixing ratios of the species as on 1, 2, and 5 May~~ 1, 2, and 5~~. These changes in mixing ratios are accompanied by a change in meteorological conditions, illustrated here by changes in wind speed and to a less extent wind direction (Fig. 3). Guimbaud et al. (2002) found a similar relationship between acetone and ozone during different field campaigns at Alert, Canada with elevated acetone levels ~~increased~~ during ozone depletion episodes accompanied by a concomitant decrease in the propane mixing ratios. However, it was found that the increase in acetone could not be explained by gas~~-~~ phase chemistry but possibly by photochemically induced emissions from the snowpack. This phenomenon was also observed by Boudries et al. (2002). The anti-correlation between ozone and acetone observed at Villum may also be explained by a similar influence of photochemistry that causes destruction of ozone as well as the formation of acetone by gas phase and surface reactions. Also, the possible influence of vertical air exchange must be considered as well. During pristine atmospheric conditions at Villum, ozone is destroyed but not produced within the boundary layer, due to low NO_x concentrations (Nguyen et al., 2016). Exchange with the free troposphere will lead to increases in the ozone concentrations and possibly a reduction of acetone concentrations at ground level due to dilution by air from aloft with a lower acetone concentration. The anti-correlation between ozone and acetone supports the hypothesis that acetone is not brought down from aloft to a significant extent but has surface or boundary layer chemistry as its main source.

During the summer, the behavior of acetone is different. In addition to the previously mentioned dependence on the diurnal variations of sunlight (Fig. 2 and S4), providing strong evidence of a local photochemical source, a positive correlation with ozone was observed. In June, an anti-correlation is still seen, but in July and August, the two species are correlated (R=0.69 for July and R=0.46 for August). The fact that ozone is also positively correlated to other OVOCs (particularly formaldehyde, R=0.86 for July) suggests that the correlation is due to the influence of transport of air containing ozone and acetone formed by the photochemical degradation of air pollutants. During the summer period, acetone is correlated with acetonitrile (R=0.73 for June–August), in September and October this correlation becomes very strong (R=0.96). Acetonitrile is considered an atmospheric tracer of biomass burning as the global budget of this compound, as previously mentioned, is dominated by emissions from biomass burning (Holzinger et al., 2001). Thus, biomass burning and atmospheric degradation of biomass burning products seem to be an important source of acetonitrile and acetone during this period. The correlation with ozone is also positive during these months, most likely because the photochemistry of biomass burning emissions is also a source of ozone brought to Villum. 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.

3.3 Source Apportionment via PMF

VOCs exhibited distinct temporal patterns that are seasonally dependent and suggest different processes contributing to ambient mixing ratios. Therefore, the source apportionment model, PMF, was employed to provide an in-depth examination of these VOC sources. The base model was executed 100 times with a random start seed. Species were categorized based on their ~~signal-to-noise ratio (~~S/N~~)~~, species with an $S/N \geq 1$, $0.2 < S/N < 1$, $S/N < 0.2$ were categorized a ‘Strong’, ‘Weak’, and ‘Bad’, respectively. The uncertainties~~y~~ of ‘Weak’ species ~~was~~ were tripled, and ‘Bad’ species were excluded from the analysis. Two species deviated from this categorization; benzene ($S/N = 0.3$) was classified as ‘Strong’ since it serves as a tracer for anthropogenic emissions from fossil fuel combustion and formic acid ($S/N = 1.0$) was classified as ‘Weak’ since there was substantial variability of blank measurements in the spring. Rather than down-weighting spring samples, the entire dataset for formic acid was down-weighted to minimize bias for the spring period. The species included in the analysis were those shown in Table 2. Expanded uncertainties for model input were estimated as described in the Sect. S1~~ of the Supplemental Information~~. The two periods of elevated DMS mixing ratios were removed from the model input matrix since these periods were considered an anomaly compared to the rest of the measurement period (appearance of open leads, wind direction directly from these leads, and air masses with extensive surface contact). Therefore, these periods violated one of the assumptions of PMF; that sources do not change significantly over time or do so in a reproducible manner. The inclusion of these two periods did not improve model performance. Instead, we argue that their exclusion allows us to model the ambient behavior of VOCs devoid of episodic influence due to certain meteorological conditions.

A four-factor solution was deemed optimal based on Q_{true}/Q_{theo} ratios, R^2 values between modeled and measured mixing ratios, and physical interpretation of the factor time series and profiles. Figure S7 displays the Q_{true}/Q_{theo} ratios against the factor number. Increasing the factor number from two to three produces the largest decrease in the Q_{true}/Q_{theo} ratio, which is often taken as the optimal solution for the number of factors. However, the mean R^2 values for the 3-factor solution (0.8) were lower than for the four-factor solution (0.85) and the physical interpretation of the four-factor solution yielded more robust analysis. Therefore, a four-factor solution was deemed optimal. The large discrepancy between Q_{true} and Q_{theo} can be explained by the large analytical uncertainties (32–64 %, Table 1), which is due to the extremely low mixing ratios observed, causing Q_{true} to be small, the large number of samples which produces a large Q_{theo}, as well as co-variation in the species (see Sect. 3.1). While these uncertainties are high, they are reasonable for a kinetic quantification of organics at these instrument parameters and extremely low mixing ratios based on Holzinger et al. (2019).

Displacement on the four-factor solution yielded no errors in the model and zero factor swaps, illustrating the solution is valid and free of rotational ambiguity. Bootstrapping was performed for 100 runs and mapped >85 % of the boot factors to the base factor. This high percentage indicates the model solution is free of random error. Variations of the Fpeak strength consistently returned the lowest change in *Q* at Fpeak = 0, indicating the model is free of rotational ambiguity. The inspection of G-space plots produced no visible correlations between factors. Together these error estimation methods show the model solution is robust, valid, and free of random errors and rotational ambiguity.

Based on their chemical composition and their temporal variation the four factors were assigned to likely sources including Biomass Burning, Marine Cryosphere, Background, and Arctic Haze, which will be explained in detail below.

3.3.1 Biomass Burning Factor

The most prominent species in the profile of the Biomass Burning ~~factor~~Factor is acetonitrile, explaining 63 % of the variation, and benzene, explaining 33 % of the variation (Fig. ~~3~~4b). As mentioned above, acetonitrile is a characteristic tracer for biomass burning emissions. Biomass burning is also an important source of benzene, with an estimated global strength of about half of the anthropogenic sources (Lewis et al., 2013) and it is a source of methyl acetate as well (Andreae, 2019), one of the $C_3H_6O_2$ isomers~~-~~. The chemical species profile (Fig. ~~3~~4~~, ~~b~~ottom~~) of this factor, therefore, points to a biomass-burning source. The time series (Fig. ~~3~~4~~, top~~a), shows this factor to decrease in the spring to a minimum in the summer, and slowly increase to a maximum at the beginning of September. The decrease in the spring is reflective of decreasing concentrations of benzene and acetonitrile; in the case of benzene this can be ascribed to anthropogenic emissions ~~of acetonitrile and benzene~~ during this period as the polar dome is expanded during winter and spring allowing for emissions to be entrained from the mid-latitudes. In the case of acetonitrile, the reason is more uncertain, there are anthropogenic sources of acetonitrile, particularly wood burning for residential heating and solvent use (Languille et al., 2020), but they appear to be of very minor importance compared to forest fires (de Gouw et al., 2003). The height of the biomass burning season in North America and Northern Eurasia is July (Lavoue et al., 2000), although due to the contraction of the polar dome during summer, minimum contributions from this factor are observed. Increased areas of open water in the Arctic also act as a sink for acetonitrile during the summer (de Gouw et al., 2003). The Biomass Burning ~~factor~~Factor peaks in August/September when the polar dome starts to expand thus allowing biomass burning emissions to reach the High Arctic.

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~~While the species profile and temporal nature indicate biomass burning emissions as the source of this factor, where do these emissions originate from? Stohl (2006) revealed three major pathways for transport of air masses into the Arctic: low-level transport followed by ascent, low-level transport, and ascent outside the Arctic followed by descent into the Arctic. Emissions from North America and Asia only enter the Arctic through the last pathway.~~ To examine the geographical origin of this factor, air mass back trajectories from the HYSPLIT model were calculated every hour during the peak of the Biomass Burning ~~factor~~Factor (15 August~~ 15~~–15 September~~ 15,~~ 2018) ~~for 100 meter arrival altitude~~ and extending 336 hours (two weeks) backward in time. The trajectory length of two weeks was selected to account for the long lifetime of acetonitrile ~~backward in time~~. ~~This analysis combined with a~~Active fires during the period 15 August–15 September 2018 were provided by NASA's Fire Information for Resource Management System (FIRMS) (Schroeder et al., 2014). Active fires occurring with one hour and one-degree latitude/longitude of a trajectory endpoint was used to access the influence of active fires on the

Biomass Burning Factor. While there was evidence of active fires in North America and Eurasia occurring near a trajectory endpoint within one hour, the uncertainty of a trajectory with a length of 336 hours is quite large (Stohl, 1998). Therefore, no meaningful conclusions can be drawn from this analysis other than the transport time of emissions influencing the Biomass Burning Factor is greater than two weeks, and that we are unable to capture these emissions with the current trajectory models with any confidence.~~ctive fire data from the FIRMS database indicates the influence of active fires in North America and Eurasia (Fig. 4).~~

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~~While most air masses stayed within the Arctic, there is evidence of overlap between air mass history and active fires during this period in North America and Eurasia (Fig. 4).~~ The influence of biomass burning was observed at other High Arctic sites during this period. (Lutsch et al., 2020) used fourier-transform infrared spectroscopy (FTIR) measurements of CO, HCN, and ethane at several High Arctic sites coupled with aerosol optical depth data and the GEOS-Chem model to detect the influence of wildfires and attribute their sources. They observed fire-affected enhancements in the tropospheric CO column at Eureka~~, CA~~, NU from September 9 to the 25, 2018, and at Thule, Greenland~~L~~ from 24 August~~ 24~~ through 26 September~~ 26,~~ 2018. The GEOS-Chem simulated the source regions for the ~~fire ~~fire-affected enhancements in the tropospheric CO column measurements to be boreal forests in North America and Asia at both sites (Lutsch et al., 2020). These observations of biomass burning at other High Arctic sites are in good agreement with the Biomass Burning ~~factor~~Factor presented here, adding robustness to this factor assignment and can offer insight into the geographical origins of the Biomass Burning Factor.

Biomass burning is known to be an important source of BC, and it has been estimated to account for about 35 % of the BC emissions in the Northern Hemisphere (Qi and Wang, 2019). Despite this, the observed time profile of BC (not shown) at Villum did not show an increase during the autumn of 2018. This is likely to be explained by the fact that the emissions from biomass burning sources have been transported over long distances with corresponding long transport time (> two weeks), as BC is removed much faster from the atmosphere than acetonitrile due to wet deposition. The atmospheric residence time of BC is below 5.5 days, according to a recent estimate (Lund et al., 2018), while that of acetonitrile is several months (de Gouw et al., 2003). Using meteorological parameters calculated along the trajectory path using HYSPLIT (see above)~~, for air masses arriving at 100 m altitude~~, the mean accumulated precipitation for the peak of the Biomass Burning ~~factor~~Factor was 14 millimeters (mm). Raut et al. (2017) used a combination of in situ observations from aircraft, satellite remote sensing, and modeling simulations to calculate the transport efficiency of BC during 2012. They concluded that the transport efficiency of BC was low (<30 %) when accumulated precipitation was large (5–10 mm). These previous observations combined with the accumulated precipitation data along each trajectory during the peak of the Biomass Burning ~~factor~~Factor support the lack of BC loading during this time. While biomass burning is a source of BC globally, which is expected to increase in the future (Westerling et al., 2006), the results presented here indicate meteorological parameters encountered during transport can play a role in the levels observed in the High Arctic atmosphere. While biomass-burning emissions may increase in the future, increased precipitation patterns might counterbalance this increase although more research is needed to elucidate the relationship between these feedback mechanisms.

3.3.2 Marine Cryosphere Factor

The Marine Cryosphere ~~factor~~Factor was characterized by formic acid, acetic acid, $C_3H_6O_2$~~propionic acid~~, and DMS, explaining over 50 % of the variability of each of these compounds (Fig. 5~~, Bottom~~b). The contribution of this factor is near zero in the spring and autumn and maxima during the summer months (Fig. 5a). This factor shows an enhanced diurnal variation with a ~~clear~~ correlation to sunlight during the summer months (Fig. 6~~5, Top~~). The high content of DMS points to a marine origin of this factor, while carboxylic acids have been demonstrated to be emitted from the snowpack (Dibb and Arsenault, 2002). Analysis of snow depth and sea ice concentrations (± 2° longitude and +8°/-4° latitude area around Villum) illustrate the onset of this factor coincides with the snowmelt and sea ice decline. Therefore, a combination of marine and cryosphere sources appears to contribute to the species observed in this factor. The $C_3H_6O_2$ is in this case assigned to propionic acid as the alternative isomers seem less probable, considering their typical origins (biomass burning for methyl acetate and isoprene oxidation for hydroxyacetone).

The sources of the organic acids are much less well characterized than those of DMS; in fact, model simulations have not been able to reproduce the mixing ratios of formic and acetic acid, particularly in the Arctic and northern mid-latitudes (Paulot et al., 2011; Mungall et al., 2018). As the lifetimes of formic acid and acetic acid against photochemical oxidation by reaction with the OH radical are relatively long (about 25 and 10 days, respectively, for $[OH]=10^6$ molecules/cm^3), dry and wet deposition ~~are~~ is thought to be the main removal pathways (Seinfeld and Pandis, 2016). Estimated globally averaged atmospheric lifetimes against ~~wet~~ deposition for both formic and acetic acid in the boundary layer ~~is~~ are between 1 and 2 days~~, respectively~~ (Paulot et al., 2011). Thus, it is unlikely that direct long-range transport plays a relevant role in determining the mixing ratios of these species at Villum. Analysis of ~~C~~^{14}C isotopes in formic and acetic acid in air and rainwater have shown that outside of urban and semi-urban areas the dominating (>80 %) source is modern carbon (Glasius et al., 2001). This analysis is consistent with model simulations showing that atmospheric oxidation of biogenic hydrocarbons is the largest source (Paulot et al., 2011; Millet et al., 2015). Even though vegetation in the High Arctic is sparse, contributions from precursor emissions or direct emissions of formic acid and acetic acid from vegetation cannot be excluded, as discussed by Mungall et al. (2018). Emissions from the soil ~~is~~ are also a possible but highly uncertain source of these species (Mungall et al., 2018). However, the Marine Cryosphere ~~factor~~Factor is largely absent when snow is completely melted, exposing the bare ground and vegetation to the atmosphere, thus soil emissions and vegetation are improbable sources of these compounds. Instead, enhancements in these species and this factor is observed during periods of snowmelt and sea ice melt.

A comparison of the contribution of the Marine Cryosphere Factor to sea ice concentration, calculated as described in Sect. 2.3, and snow depth can further shed light on the origin of this factor (Fig. 5~~, top~~a). Periods of high contributions and ~~clear~~ diurnal pattern by the Marine Cryosphere ~~factor~~Factor starts on 22 June (Fig. 6) ~~23~~, where the local sea ice concentration and snow depth are starting to decline. Diurnal patterns were observed during this period of melting (Fig. 5a and 6). This continues until 9 August ~~7~~, when the measurements were interrupted due to technical issues. When measurements resumed on 16 August ~~16~~, the contribution from the Marine Cryosphere ~~factor~~Factor had returned to the low levels found during

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springtime. Note that instrument parameters were monitored before and after interruptions to ensure proper functionality of the instrument, and periods that deviated from nominal values were removed. The Marine Cryosphere Factor appears not to be strongly dependent on the extension of the open sea, as sea ice concentrations/extensions reach a minimum, and consequently, the open sea area reaches a maximum by the beginning of September, but rather depends on active melting of snow and sea ice. Thus, it seems that emissions of VOCs from melting snowpacks and newly exposed sea ice areas could offer a viable explanation for the observed dependence of this source.

Previous work has shown that emissions from the sea in the Arctic area can be caused by a surface microlayer enriched in organic substances that acts as a source of formic acid and other oxidized VOCs (Mungall et al., 2017). This occurs either via heterogeneous chemistry or by photochemically driven reactions within the surface layer (Vlasenko et al., 2010; Chiu et al., 2017). Mungall et al. (2017) performed factor analysis of VOCs in the Canadian Archipelago finding four factors. One factor (Ocean ~~factor~~Factor; containing formic acid, isocyanic acid, and oxo-acids) was highly correlated with dissolved organic carbon (DOC), fluorescent chromophoric dissolved organic matter (fCDOM), and radiation. However, DMS was poorly correlated with this factor. They concluded the source to be photochemical or heterogeneous oxidation from sources on the sea surface microlayer. While formic and acetic acid, as well as the carbonyl compounds, show ~~clear~~ daily variations correlating with radiation, as mentioned above, DMS shows a less clear correlation. The emission of DMS from the open ocean has been demonstrated to be dependent on horizontal wind speed (Bell et al., 2013). Although, the variation of the Marine Cryosphere Factor~~s~~ seems not to be driven mainly by the dependence on horizontal wind speed (R=-0.04~~Fig. S2.~~). Marine microorganisms produce DMS (Stefels et al., 2007; Levasseur, 2013), and given the distance of the measuring site from open water (taking sea ice into account the, station is approx. 25 km distance from open water), it is proposed that the majority of DMS produced is already oxidized to MSA and other products when reaching the station. The presence of gas-phase MSA has been indicated by the observation of the methanesulfonate ion,~~MSA~~ which has been previously measured in the particle phase at Villum in February–May 2015 (Dall'Osto et al., 2018b; Nielsen et al., 2019).

Several studies have demonstrated the emission of VOCs from the snowpack; Gao et al. (2012) observed photo enhanced release of VOCs from both Arctic and mid-latitude snow; Grannas et al. (2002) obtained similar results by applying a box model to simulate observed emissions of carbonyl compounds from an Arctic surface layer at Alert. They found that diel cycles of carbonyl compounds are impacted by snowpack exchange characterized by nighttime adsorptive uptake from the snowpack and the largest release around noon, similar to the observations in this study. Anderson et al. (2008) found a high concentration of water-soluble organic compounds (presumably mainly formic and acetic acid) in the surface layer of polar snow, and Dibb and Arsenault (2002) ~~had~~ measured levels well above 1 ppbv of formic and acetic acid in firn air. Gao et al. (2012) also observed enhanced release of acetone, formic acid, and acetic acid from snow coinciding with radiation, which they explained by oxidation of organic matter, e.g., humic substances present within the snowpack, perhaps by photochemically produced OH radicals (Nguyen et al., 2014). This experimental evidence that Arctic snow and areas of open sea are a relevant source of VOC emissions adds credence to this factor assignment.

The spatial origin of the Marine Cryosphere ~~factor~~Factor was investigated via a PSCF, calculated with the R package Openair (Carslaw and Ropkins, 2012)~~using 240-hour HYSPLIT air mass back trajectories arriving at 100 m altitude~~. ~~These trajectories and trajectory frequency maps were calculated as described in Sect. 2.4.~~ Figure ~~6~~ 7 displays the ~~trajectory frequency map~~PSCF for air masses arriving every hour ~~from June to August, corresponding to the period of maximum contribution from the Marine Cryosphere factor and diurnal variation~~during the measurement campaign, which provides increased statistical robustness to the results over calculating a PSCF just for the summer period. From Fig. ~~6~~7, ~~three~~ two areas with~~of~~ a ~~air-mass origin~~high probability of being a source region for the Marine Cryosphere Factor can be discerned, the coast around Southeastern and Northeastern Greenland. This analysis is supported by the CPF for the Marine Cryosphere Factor (Fig. S8b), which shows the dominant wind direction for this factor to be the south and south-south-east. Lee et al. (2020) used monthly chlorophyll-*a* derived from the MODIS satellite to demonstrate the coasts around Northeastern Greenland to contain high chlorophyll-*a* concentrations during June, which has been supported by previous studies (Degerlund and Eilertsen, 2010; Galí and Simó, 2010). Lee et al. (2020) also used a PSCF to determine this area to be the source regions for total particle number concentrations in the nucleation size range (3–25 nm). This area has been demonstrated to be a source region for MSA during the summer months (Heintzenberg et al., 2017). Thus, we propose the biologically active coasts around Eastern Greenland to be the source region for the Marine Cryosphere Factor. ~~Air masses arrived from regions along the eastern and northern coast of Greenland as well as from the Arctic Ocean.~~

~~Marginal ice zones (MIZ), defined as areas where fragmented sea ice encounters land, have been identified as a source region of biogenic activity leading to new particle production (Dall'Osto et al., 2017). Kecorius et al. (2019) recently identified two types of NPF events on a cruise in the waters surrounding Svalbard; one being more hygroscopic, which they hypothesized to arise from sulfuric acid, while another was less hygroscopic, likely with higher contributions from organic species. Both types of NPF events were observed to have originated from both MIZs around the northern coast of Greenland and the Arctic Ocean north of Svalbard. MIZs are therefore proposed as a major source area for the Marine Cryosphere factor.~~

The properties of the Marine Cryosphere ~~factor~~Factor (composition, temporal variation, and spatial origins) helps confirm the work of previous studies in the High Arctic. We propose this factor (although not necessarily these exact species) as responsible for the biogenic precursor emissions of particles observed in other studies (Nguyen et al., 2016; Burkart et al., 2017; Dall'Osto et al., 2017; Freud et al., 2017; Dall'Osto et al., 2018a; Dall'Osto et al., 2018b; Dall'Osto et al., 2019; Nielsen et al., 2019). For example, Nguyen et al. (2016) identified the area southeast of Villum as having a high probability of observing an NPF event when air masses originating from this sector. One of the source areas identified in Fig. ~~6~~ 7 is southeast of Villum, and a CPF analysis~~,~~ indicated high contributions of the Marine Cryosphere Factor were observed when the wind direction was south of Villum (Fig. S~~8~~8b ~~a~~). While the species identified using this analytical technique might not be responsible for particle formation and growth, other high molecular weight compounds originating from the same sources could well be. Therefore, this factor has important climatic implications, as sea ice and snowmelt are expected to start earlier due to warming temperatures. Increased contributions from this factor can be expected, which will alter the CCN budget and occurrence in the summer and thus alter the radiative balance.

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3.3.3 Background Factor

The Background ~~factor~~Factor explains the majority (>50 %) of the variation of acetone and ~~the ion $C_5H_8O^+$~~C_5H_8O as well as 37 % of formaldehyde (Fig. 8a). It explains approximately 30 % of the variation of acetonitrile and MEK, followed by minor (< 20 %) variations of acetic acid, benzene, and ~~propionic acid~~$C_3H_6O_2$. $C_3H_6O_2$ may in this case result from all three of the ~~three~~ isomers:~~,~~ propionic acid, methyl acetate, and hydroxyacetone. ~~Most of its components, particularly a~~Acetone and formaldehyde ~~,~~ are known to have photochemical oxidation of precursor compounds in the atmosphere as an important source. The chemical profile of this factor does not point to a specific, known source (Fig. ~~7~~8~~, bottom~~b). Its contributions start increasing in the middle of April and reach a maximum by the end of the month ~~(Fig. 7, top). The contributions~~, then decrease until the summer period (Fig. 8a). ~~, where a slight diurnal profile, albeit weaker in magnitude when compared to the Marine Cryosphere factor, can be recognized.~~ During the autumn, contribution~~s~~ levels are similar to the summer ~~period,~~period; however, the temporal pattern is quite similar to the one observed for the Biomass Burning ~~factor~~Factor. The temporal correlations of the Background ~~factor~~Factor to the Marine Cryosphere and Biomass Burning ~~factor~~Factor during their respective periods of peak contributions indicate this factor does not arise from one identifiable source but rather from a myriad of sources, hence the assignment as a background factor. The species profile for the Background Factor corresponds to mixing ratios of 0.355 ppbv for acetone, 0.090 ppbv for formaldehyde, and less than 0.050 ppbv for all other compounds. These mixing ratios can be interpreted as the background mixing ratios for these compounds in the High Arctic.

The Background ~~factor~~Factor has its highest period of mean contributions during the spring when solar intensity increases but before the emissions related to open sea or melting snow become relevant. This factor likely represents a source of VOCs caused by the increasing rate of photochemical oxidation of labile~~liable~~ organic carbon naturally present in the air and on surfaces. Photo-oxidation of alkanes present in the air and deposited during the winter is a possible source of ~~liable~~labile organic carbon (Boudries et al., 2002; Guimbaud et al., 2002; Gao et al., 2012). For example, acetone (~~(~~a major component of the Background Factor) is primarily formed from reactions of OH and Cl with propane, isobutane, and pentane (Hornbrook et al., 2016). This slow decrease during the spring could be due to the decreasing supply of ~~liable~~labile organic carbon in the snowpack. The weak diurnal pattern of this factor in the summer (Fig. 6) could be due to increased available organic matter for oxidation from the open ocean and melting snowpack. Further measurements, especially during the polar night to day transition, are required to test this hypothesis.

Given the lack of a peak period for contributions from this factor, we were unable to locate the source regions of this factor through air mass back trajectory ~~frequency~~ analysis ~~(as described above)~~. Therefore, local wind direction and normalized contributions for this factor were used to create a conditional probability function (see Sect. 2.3). During the spring and autumn, the dominant wind direction at Villum is from the southwest, while during the summer it is from the east (Nguyen et al., 2016). The CPF can give information regarding the directional dependence of a factor or compound. Figure ~~8~~ 9 shows the CPF for the Background ~~factor~~Factor. There is a lack of directional dependence for this factor, indicating this factor does not arise from one specific source area, but rather it is spatially ubiquitous.

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The Background Factor likely represents natural processes occurring in the Arctic. This factor can serve as a baseline for comparison with future VOC measurements and source apportionment analysis. These comparisons can help expound upon the effects of climate change on the natural processes occurring in this pristine and sensitive region. This, however, requires more long-term VOC measurements, especially across all seasons.

3.3.4 Arctic Haze Factor

The Arctic Haze ~~factor~~Factor exhibits high contributions at the beginning of April and it rapidly decreases until the middle of May where it remains low and stable for the remaining of the measurement campaign (Fig. ~~9~~10~~, top~~a). This factor accounts for 56 % of the variation of benzene and zero percent of acetonitrile, which suggests fossil fuel combustion processes as the source of this factor (Liu et al., 2008) (Fig. ~~9~~10~~, bottom~~b). Interestingly, the other species apportioned to this factor with significant contributions, i.e., MEK, formic acid, formaldehyde, and ~~$C_5H_8O^+$~~ C_5H_8O (Fig. ~~9~~10~~, bottom~~b) are all oxygenated compounds that exhibit decreasing patterns in the spring as well as diurnal variation in the summer (Fig. ~~1 a, c, d, and f~~2). Much like for the Background ~~factor~~Factor, the source of these OVOCs is the oxidation of ~~liable~~labile organic carbon transported from the mid-latitudes.

The high levels of anthropogenic pollutants transported to the High Arctic during this period give the well-known ‘Arctic Haze’ phenomenon (Barrie et al., 1981). The decrease in mixing ratio during the spring is characteristic of the seasonality for long-range transport for this region (Willis et al., 2018). The mixing ratio of compounds emitted from sources outside the Polar dome is drastically reduced in the summer (Klonecki et al., 2003). Also, the faster oxidation rates due to higher OH radical concentrations as well as increased wet scavenging during transport in summer will reduce VOC and BC mixing ratios (Browse et al., 2012). Gautrois et al. (2003) reported benzene mixing ratios for 7 years at Alert~~, CA~~, NU, and found an annual variation similar to observations for the Arctic Haze Factor in this study. The enhanced levels of BC (not shown) during this period (and lack thereof during summer and autumn) supports the assignment of this factor to anthropogenic combustion sources.

The Arctic Haze ~~factor~~Factor presented in this study can be compared to other Arctic Haze ~~factor~~Factors previously found using factor analysis or clustering of either aerosol composition or PNSD data. It is worth noting that the Arctic Haze Factor from this study is only for spring, while the other studies present data from the winter/spring, therefore any comparisons we make are from our spring Arctic Haze Factor to other Haze factors during winter and spring. While this is not a perfect comparison, it is one worth making, as Arctic Haze is the main source of anthropogenic pollution in the Arctic. Lange et al. (2018) used k-means clustering of aerosol size distribution to classify the accumulation mode aerosol population from Villum. The authors found three accumulation mode clusters, one of which they named ‘Haze’ occurred predominately in the winter/spring and was largely absent in the summer. The Haze cluster contained the largest amounts of refractory BC, sulfate, and organics as well as the highest concentrations of CCN. Extending this analysis into the chemical composition of aerosols, Nielsen et al. (2019) utilized PMF to find three factors. The factor deemed ‘Arctic Haze Organic Aerosol’ was closely correlated with sulfate and temporally followed the pattern exhibited by the Haze cluster from Lange et al. (2018) and the

Arctic Haze Factor (this study), due to the contraction of the Polar Dome in spring. These similar factors/clusters resolved from different data sources (PNSD, aerosol chemical composition, and VOCs) and different statistical methods (k-means and PMF) highlight the extent ~~of~~ to how anthropogenic pollution can influence the characteristics of the High Arctic atmosphere. Given recent trends in emission reductions across Europe and Eurasia, these factors/clusters are expected to decrease in magnitude, although the extent and occurrence of this anthropogenic pollution will ultimately be governed by several factors including transport patterns, precipitation patterns, and expansion of anthropogenic pollution sources within the Arctic C~~c~~ircle (resource extraction and shipping) (Law et al., 2017).

4 Conclusions

VOC~~s~~ mixing ratios were measured during April–October 2018 at the High Arctic station Villum Research Station, located at Station Nord in Northeast Greenland. We identified 10 compounds by PTR-ToF-MS and provided time series of VOCs in the High Arctic covering several months. Generally, the mixing ratios observed in the present study are in accordance with other VOC measurements carried out in Arctic locations. We apportioned sources of these VOCs using PMF, finding four factors: Biomass Burning, Marine Cryosphere, Background, and Arctic Haze. The Biomass Burning Factor exhibited maxima during the autumn and the chemical profile was dominated by acetonitrile with contributions from benzene.~~ Back trajectory analysis reveals the influence of fires in North America and Eurasia.~~ Interestingly, BC did not show enhancements during the peak of the Biomass Burning Factor, which we show is due to washout during transport. The Marine Cryosphere Factor was described by carboxylic acids (formic and ~~,~~ acetic acid~~,~~ and possibly propionic acid from $C_3H_6O_2$~~propionic acid~~) and DMS. This factor displayed maxima in the summer during periods of snow and sea ice melt. ~~Back trajectory~~A PSCF analysis yielded ~~MIZs around~~ the coasts of Southeastern and Northeastern Greenland ~~and the Arctic Ocean~~ as source regions for this factor. The Background Factor showed maxima in the spring and~~,~~ autumn, and minima during the summer. While acetone was the dominating species in this factor, the chemical profile did not resemble any known processes or sources. Oxidation of labile ~~liable~~ organic carbon is proposed as the source of the OVOCs present in this factor. The Arctic Haze Factor peaked in April, decreased until mid-May, and was absent during the summer. This factor was driven by ~~levels of~~ benzene as well as OVOCs. The source of OVOCs present in this factor is postulated to be the oxidation of precursor emissions during transport from the mid-latitudes to the Arctic.

This study has several important results that have implications for the Arctic climate. Recent studies have highlighted the importance of natural emissions to aerosol formation and their contribution to CCN concentrations in the summer (Leaitch et al., 2016; Lange et al., 2019; Nielsen et al., 2019). The Marine Cryosphere Factor presents an important source of condensable vapors necessary for this formation and growth to CCN sizes. Due to increasing temperatures in the Arctic, the snowpack and sea ice are expected to experience increased melting in the coming years, which could increase the flux of DMS and carboxylic acids from the surface to the atmosphere. With the onset of the melt season in the Arctic expected to begin earlier in the future, we also expect that the timing of this onset can also affect NPF events and their subsequent growth as well as ozone photochemistry. While biomass burning is expected to increase in the future, the year-to-year variability is still highly uncertain. The Biomass Burning Factor was characterized by acetonitrile, benzene, and correlated temporally with ozone. Due to washout during transport, there were no enhancements in BC during the peak of the Biomass Burning Factor. The inter-annual variability of biomass burning events and meteorological conditions can, therefore, have a substantial impact on atmospheric pollution levels at ground level.

While this research provides valuable insight into the atmospheric chemistry and sources of VOCs in the High Arctic, future work is still needed. While calculated mixing ratios using a kinetic quantification are reliable, they are inherently uncertain, therefore external calibration with gas-phase standards would greatly improve the accuracy and reduce the analytical uncertainty. This work presents a ~~long time~~multi-season time series of VOC mixing ratios; however, these measurements are only during polar day. A full seasonal cycle including polar night, dark to light transition periods, and polar day would help elucidate the importance of transport of anthropogenic emissions in the absence of photochemical reactions. This work expounds on the understanding of the atmospheric chemistry and sources of VOCs in the High Arctic; however, future research is needed to fully understand the biogeochemical feedback mechanisms and their implications for a changing Arctic.

Data availability. All data used in this publication are available at https://doi.org/10.5281/zenodo.4299817 ~~to the community and can be accessed~~or by request to the corresponding authors Jakob Boyd Pernov (jbp@envs.au.dk) and Rossana Bossi (rbo@envs.au.dk).

Author contributions. JBP, RB, and RH collected the measurements. JBP and RB processed the data. JBP, JH, RB, and TL analyzed the data. JBP, JKN, and TL performed the PMF analysis. JBP and JH wrote the manuscript. HSK provided initial project funding and idea for VOC measurements at Villum. All co-authors proofread and commented on the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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Table 1. Overview of measured protonated masses included in PMF analysis. ~~including mass to charge ratio of measured protonated mass, empirical formula, assigned compound name, mean volume mixing ratio in ppbv, mean LOD in ppbv, percentage below LOD, and mean relative uncertainty.~~Mean refers to the arithmetic average of the mixing ratio for each compound. Mean, Mean LOD, and % < LOD were calculated after quality control of data influenced by local pollution. % QC represents the percentage of data removed due to the Quality Control Procedure (Sect. S2).

Measured mass (*m/z*)	Empirical Formula	Assigned Compound	Mean (ppbv)	Mean LOD (ppbv)	% < LOD	Mean Relative Uncertainty (%)	% QC
30.997	CH_2OH^+	Formaldehyde	0.220	0.176	0.6	41	5
42.019	$C_2H_3NH^+$	Acetonitrile	0.067	0.045	0	46	5
47.011	$CH_2O_2H^+$	Formic Acid	0.454	0.250	17	37	7
59.062	$C_3H_6OH^+$	Acetone	0.608	0.037	0	32	0
61.047	$C_2H_4O_2H^+$	Acetic Acid	0.201	0.096	5	39	8
63.034	$C_2H_6SH^+$	Dimethyl Sulfide	0.046	0.043	4	57	25
73.068	$C_4H_8OH^+$	Methyl Ethyl Ketone	0.031	0.023	0.1	56	0
75.058	$C_3H_6O_2H^+$	Propionic Acid / Hydroxyacetone/ Methyl Acetate	0.025	0.031	0.1	61	2
79.057	$C_6H_6H^+$	Benzene	0.027	0.031	0.5	64	0
85.066	$C_5H_8OH^+$	N/A	0.027	0.030	0.03	61	0

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Table 2. Input species for PMF model along with species categorization, S/N, and R^2 value for modeled versus measured values.

Species	Categorization	S/N	R^2 (Modelled vs Measured)
Formaldehyde	Weak	0.9	0.83
Acetonitrile	Strong	1.1	0.97
Formic Acid	Weak	1.0	0.67
Acetone	Strong	2.2	1.00
Acetic Acid	Strong	1.0	0.67
Dimethyl Sulfide	Weak	0.4	0.62
Methyl Ethyl Ketone	Weak	0.5	0.95
$C_3H_6O_2$~~Propionic Acid~~	Weak	0.2	0.91
C_5H_8O	Weak	0.2	0.62
Benzene	Strong	0.3	0.96

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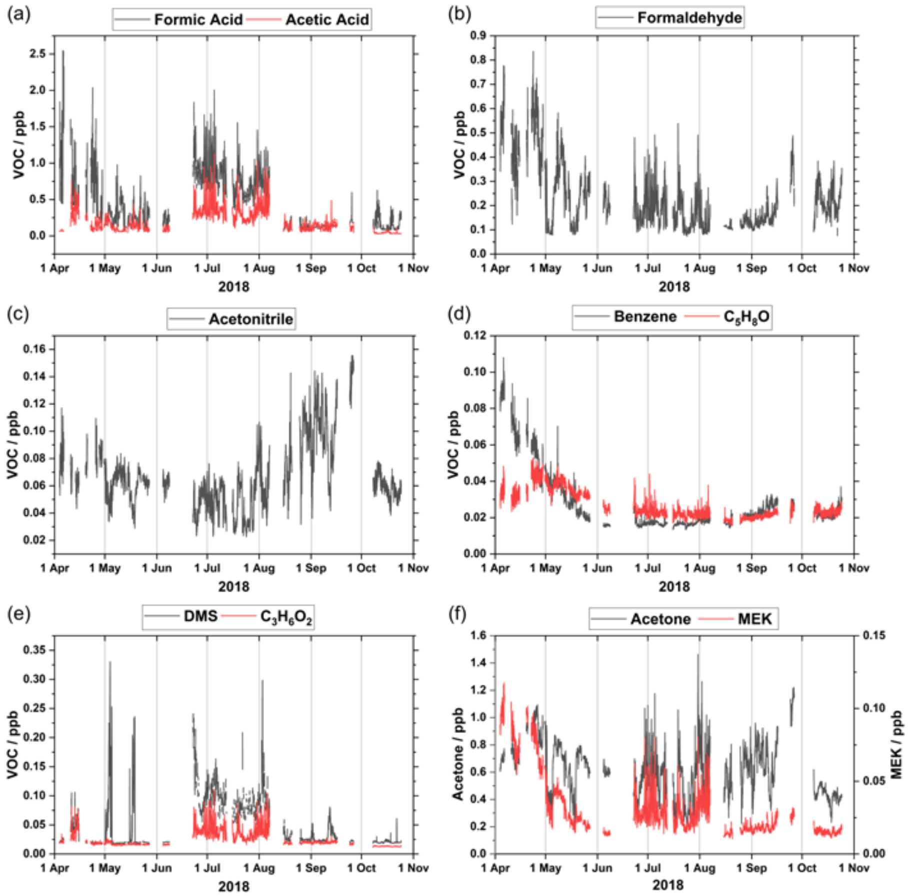

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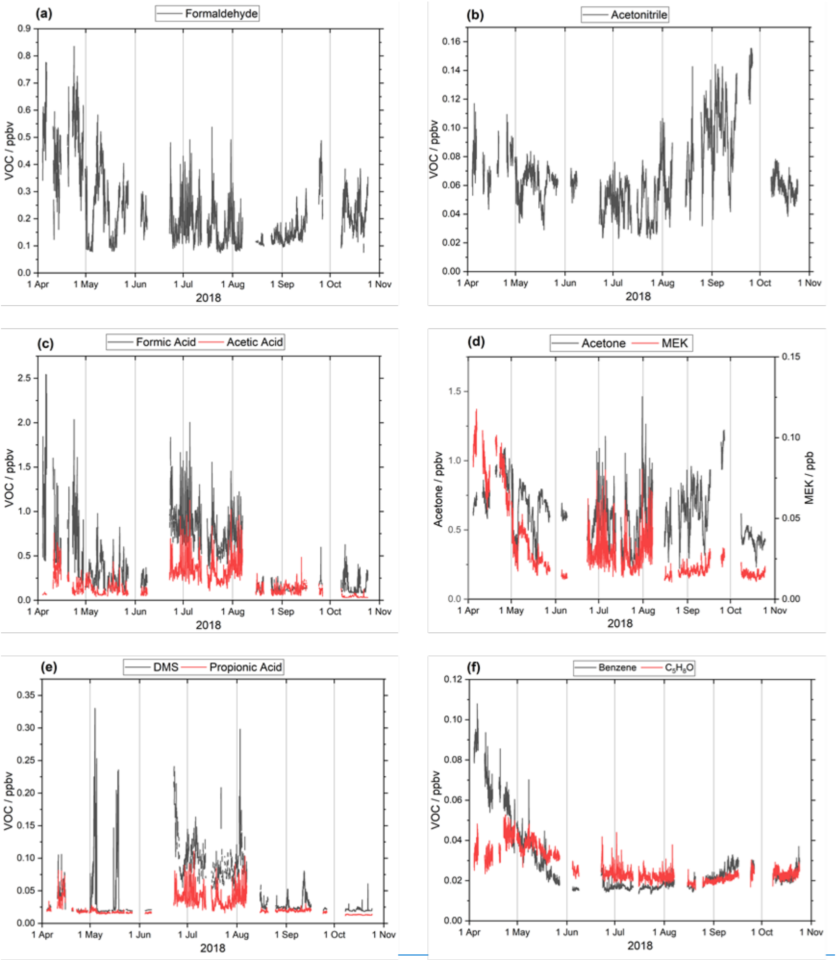

Fig. 1. Time series of mixing ratios (ppbv) for **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid and acetic acid, **(d)** acetone and MEK, **(e)** DMS and $C_3H_6O_2$~~propionic acid~~, and **(f)** benzene and C_5H_8O during the entire measurement period.

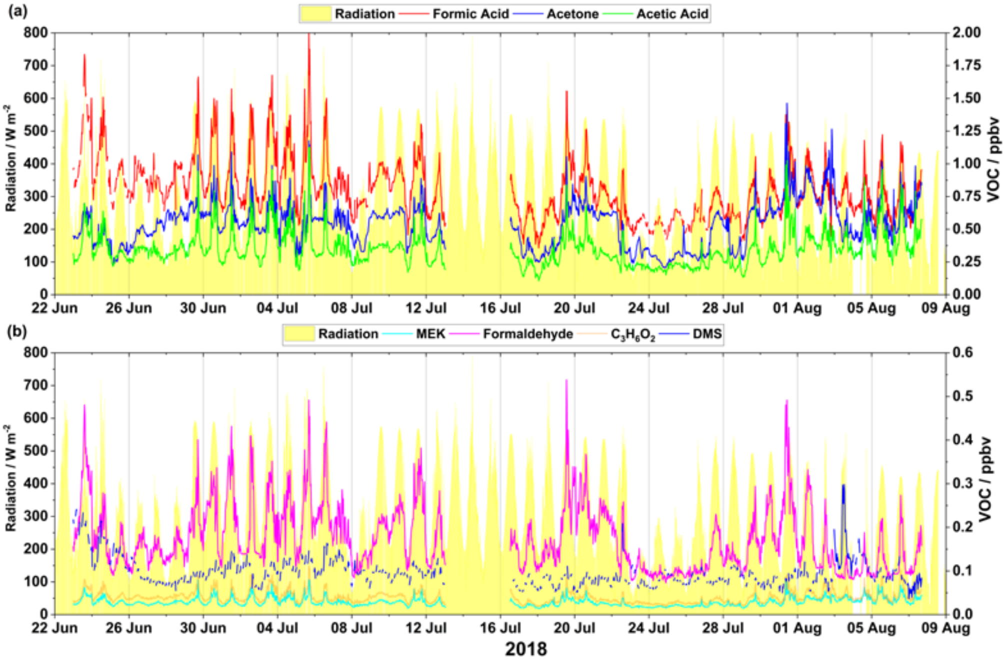

Fig. 2. Time series for (a) formic acid, acetone, acetic acid, and radiation and (b) MEK, formaldehyde, $C_3H_6O_2$, DMS, and radiation during the period 22 June–09 August displaying the diurnal profile for each species.

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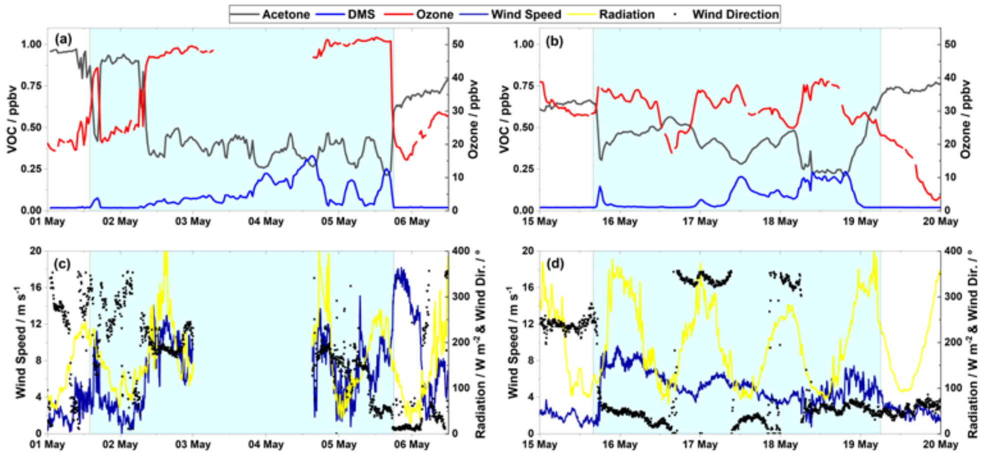

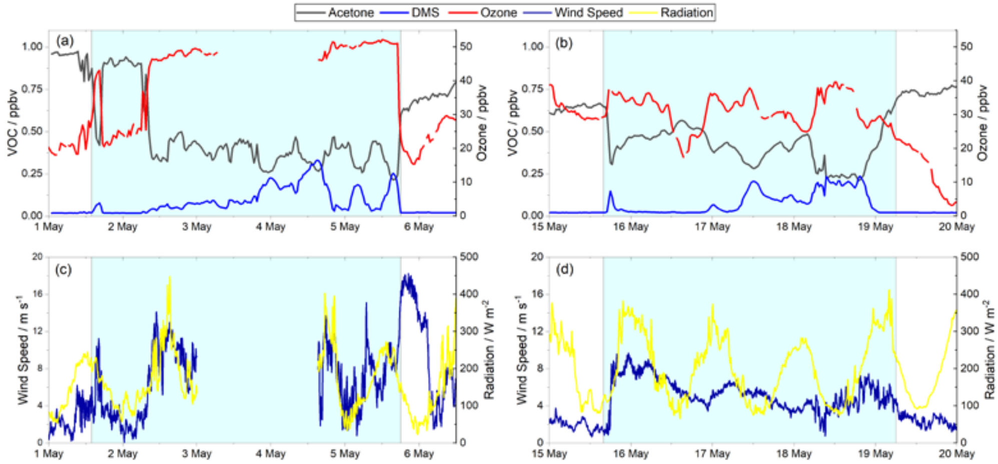

Fig. ~~2~~3. Left: The first period of elevated DMS mixing ratios (May 1–5). Right: The second period of elevated DMS mixing ratios (May 15– 19); (a) and (b) mixing ratios of acetone, DMS (left axis), and ozone (right axis); (c) and (d) wind speed ~~radiation~~ (left axis) and radiation and wind direction ~~wind speed~~ (right axis). The shaded area represents episodes of elevated DMS mixing ratios.

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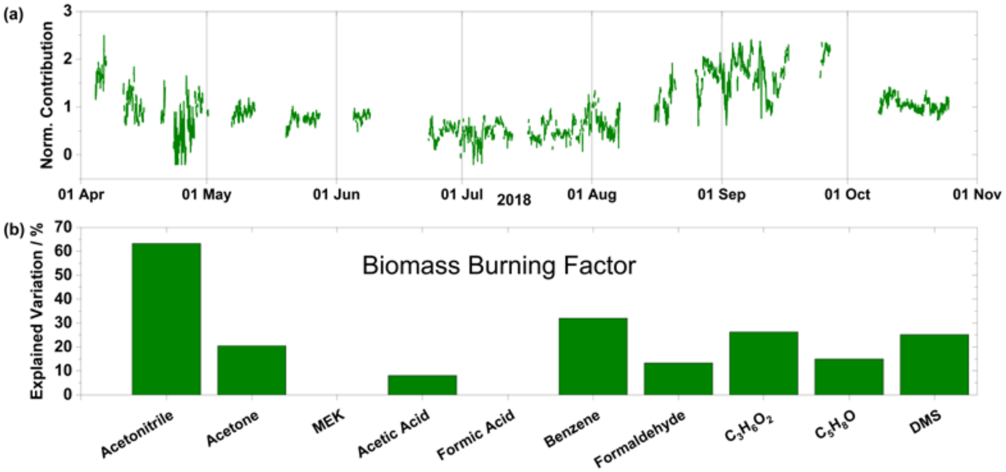

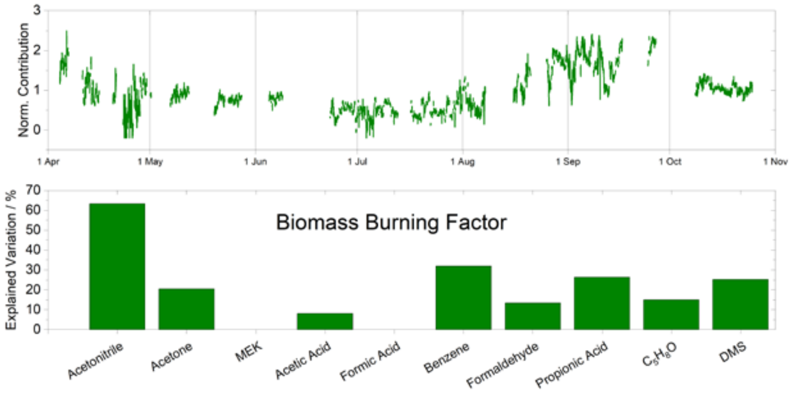

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Fig. ~~3~~4. (~~Top~~a) Time series of normalized contributions and **(~~Bottom~~b)** species profile for the Biomass Burning ~~factor~~Factor. Factor contributions are normalized to give a mean contribution of unity.

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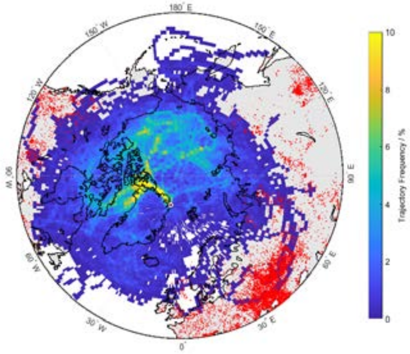
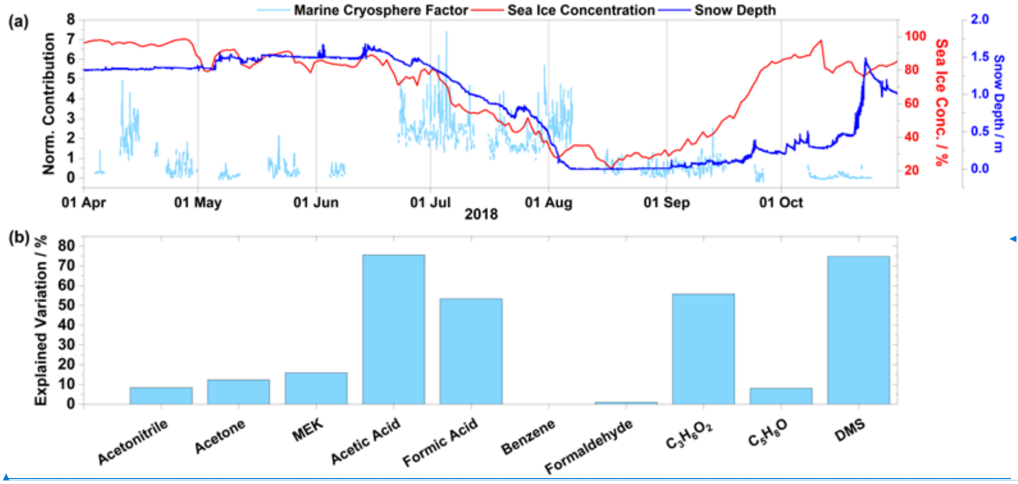


~~**Fig. 4.** HYSPLIT air mass back trajectory frequency maps arriving at 100 m altitude extending 336 hours backward in time. Active fire data from FIRMS are shown in red stars. The location of Villum is shown as a red and white circle. The period only includes the peak of the Biomass Burning factor (August 15–September 15, 2018).~~



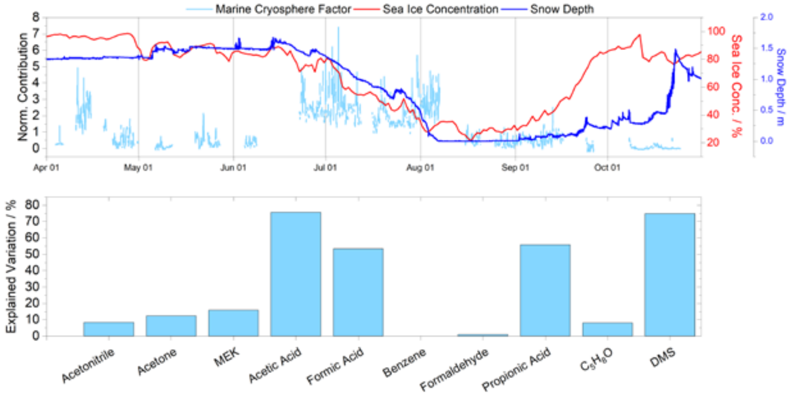


Fig. 5 (~~Top~~a) Time series of normalized contributions in light blue, left axis, and sea ice concentrations in red and snow depth in blue, right axes, and **(~~Bottom~~b)** species profile for the Marine Cryosphere ~~factor~~Factor. Factor contributions are normalized to give a mean contribution of unity.

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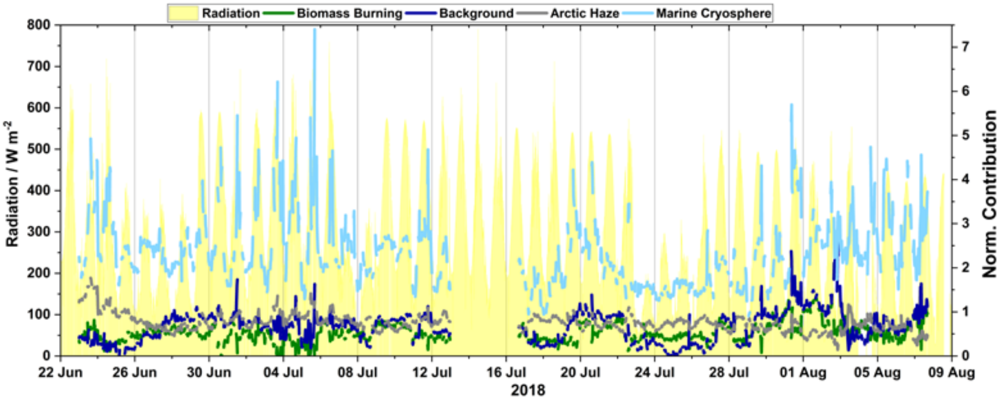

1155 **Fig. 6.** Time series of the four factors from 22 June–09 August displaying the diurnal profile together with radiation.

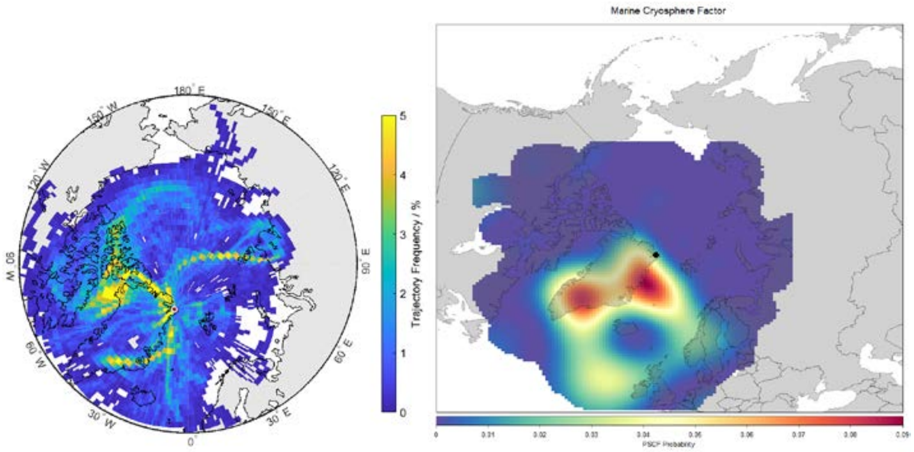

Fig. ~~6~~7**.** ~~Trajectory frequency map~~PSCF for the Marine Cryosphere Factor and air mass back trajectories arriving at 100 m altitude, extending backward ~~240~~120 hours in time. ~~Trajectory frequency calculation is described in Sect. 2.4. The color bar is capped at 5 % for visual clarity.~~ This plot and analysis method were produced in R and R Studio programs (R Foundation for Statistical Computing, Vienna, Austria, and R Studio Inc, MA, USA) and the OpenAir suite of analysis tools (Carslaw and Ropkins, 2012).

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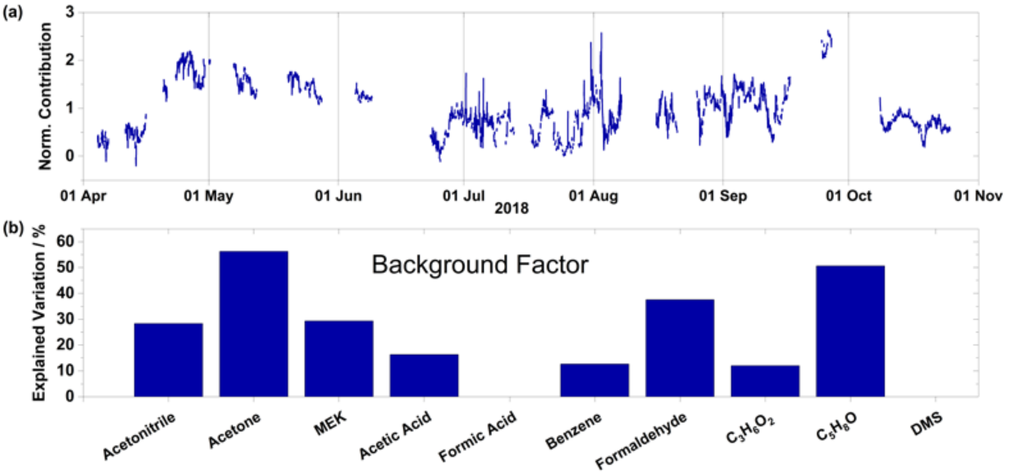

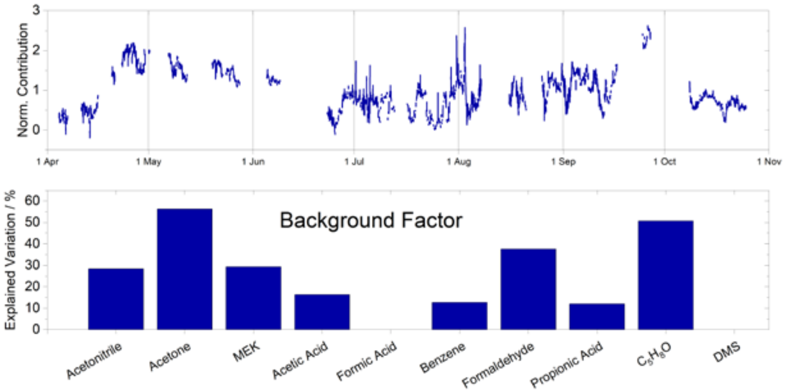

Fig. ~~7~~8. (~~Top~~a) Time series of normalized contributions and **(~~Bottom~~b)** species profile for the Background ~~factor~~Factor. Factor contributions are normalized to give a mean contribution of unity.

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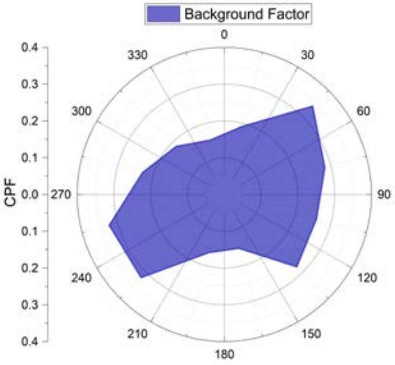

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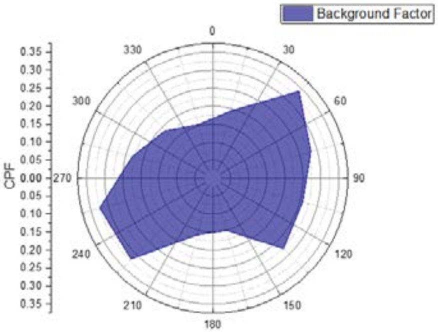
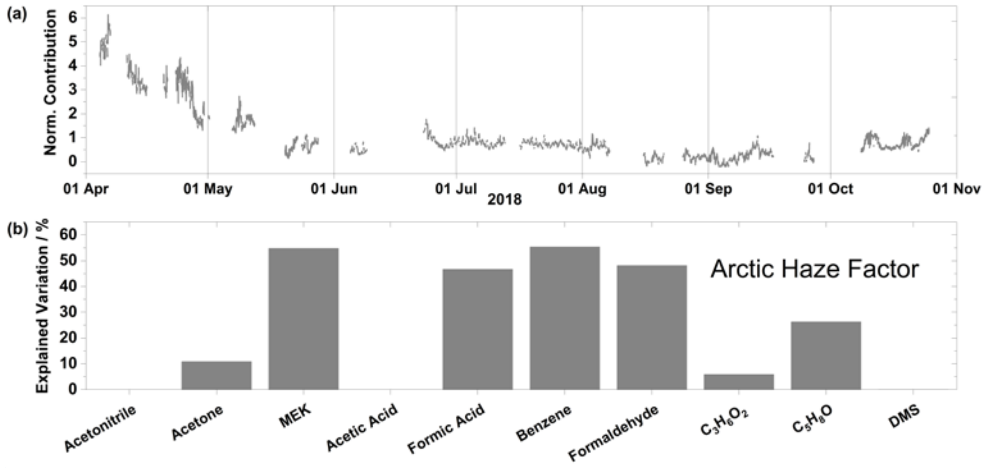


Fig. ~~8~~9. Conditional Probability Function for the Background Factor from the PMF analysis. CPF was calculated as described in Sect. 2.3.



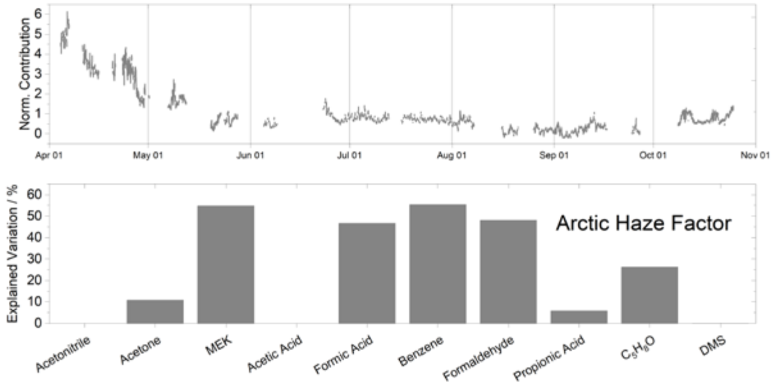


Fig. 10~~9~~. (~~Top~~a) Time series of normalized contributions and **(~~Bottom~~b)** species profile for the Arctic Haze ~~factor~~Factor. Factor contributions are normalized to give a mean contribution of unity.

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1. Mixing Ratio and Uncertainty Calculation

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Mixing ratios were calculated, in the absence of suitable reference materials, according to Equation S1, using the reaction kinetics quantification method.

$$R_{ppb} = \frac{RH^{+} \times 10^{9} \times U \times 2.8 \times 22400 \times 1013^{2} \times T^{2} \times Tr_{(H_3{}^{18}O^{+})}}{k \times 9.2^{2} \times H_3{}^{18}O^{+} \times 500 \times P^{2} \times 6.02 \times 10^{23} \times 273.15^{2} \times Tr_{(RH^{+})}} \tag{S1}$$

Where R_{ppb} is the mixing ratio of the analyte ion R, RH^{+} is the raw signal of the protonated analyte in cps, 10^{9} is the conversion to ppb, U is the voltage of the drift tube in volts, 2.8 is the reduced ion mobility (which has been experimentally determined) in cm^{2}/Vs, 22400 is the molar volume in moles per cm^{3}, 1013 is standard pressure in mbar, T is the temperature of the drift tube in K, $Tr_{(H318O+)}$ is the transmission of the primary ion isotope ($H_3{}^{18}O^{+}$), k is the rate reaction coefficient of the analyte ion with the hydronium ion, 9.2 is the length of the drift tube in cm, $H_3{}^{18}O^{+}$ is the raw signal of the isotope of the primary ion, 500 is the isotopic ratio correction factor, P is the pressure of the drift tube in mbar, 6.02×10^{23} is Avogadro's number in molecules per mole, 273.15 is standard temperature, and $Tr_{(RH+)}$ is the transmission of the protonated analyte ion. The isotope of the primary ion is used to avoid detector saturation. It must be noted that due to the backreaction of formaldehyde with water vapor in the drift tube, mixing ratios of formaldehyde are likely a lower limit (Holzinger et al., 2019; Hansel et al., 1997). However, due to the low absolute humidity levels in the Arctic, this reaction is negligible, furthermore, no correlation was observed between humidity (absolute or relative) and formaldehyde.

In the absence of suitable reference materials, an uncertainty budget was created based on the formula for kinetic calibration Eq. (S1). There are terms in Eq. (S1) that are assumed negligible including drift temperature, drift pressure, and ion transmission. These components are deemed negligible because they either are measured with high accuracy (temperature and pressure) or are lacking empirical error analysis (ion transmission). The greatest sources of uncertainty in this equation are the rate reaction coefficient and the counts of the primary ion and the analyte ion. According to Cappellin et al. (2010), the relative uncertainty of their rate reaction coefficients is stated at 15 %. The uncertainty from the raw ion cps was determined from the counting statistics by assuming a Poisson distribution (Hayward et al., 2002). The standard uncertainty for the ion counts is, therefore, the square root of the cps multiplied by the signal integration time (5 s~~ec~~). The analyte signal was blank corrected before uncertainty analysis. The expanded uncertainty is then calculated according to Eq. (S2), using a coverage factor of two.

$$U = 2 \times VMR \times \sqrt{0.15^{2} + \left(\frac{\sqrt{I_P}}{I_P}\right)^{2} + \left(\frac{\sqrt{I_{S-b}}}{I_{S-b}}\right)^{2}} \tag{S2}$$

Where U is the expanded uncertainty, VMR is the volume-mixing ratio, I_p is the raw counts of the primary ion, $I_{S\text{-}b}$ is the blank corrected counts of the analyte ion.

2. Quality Control Procedure

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Data were quality controlled by analysis of PNSD, ozone, wind direction and speed, and internal activity logs. Local pollution at Villum can arise from activity around the measurement site (e.g., passenger vehicles, all-terrain vehicles, snowmobiles, and heavy machinery) as well as from activities from Station Nord (e.g., waste incineration, vehicular activity, and aircraft landing, idling, and take off). Internal activity logs of visits to the measurement building were used to highlight periods when human activity could affect the measurements, periods where VOC levels were elevated over background levels for the duration of the visit to the station were removed. Measurements of PNSD and ozone were analyzed, in tandem, for sharp and sudden increases in the ultrafine mode (< 100 nm) aerosol particles and concurrent sharp and sudden decreases in ozone, increases in ultrafine mode particles are indications of vehicular emissions while decreases in ozone results from its titration with nitrogen oxides. These periods were further inspected for wind direction and speed, with winds coming from due north at low speeds indicative of local pollution from Station Nord. All periods where local pollution was suspected of influencing the measurements were visually inspected by a panel of three persons, a consensus was required before data were removed. Data were also quality controlled for abnormal levels of instrumental parameters (i.e., E/N ratio, drift tube temperature, pressure, and voltage), periods with large deviations from nominal values were removed. Certain compounds (DMS, formic acid, and acetic acid) exhibited a slow return to nominal values after a blank than before, this issue was especially evident in the summer, these periods were removed. All quality control was performed on VOCs at a 5 s time resolution, data was removed before averaging to 30-minute means.

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Table S1. Statistics for meteorological parameters (mean ± s.d.) for all seasons, spring (April ~~1~~ 4 – June 8), summer (June 9 – August 6), and autumn (August 7 – October 25~~31~~). During the campaign, there were several large gaps in the data, most noticeably one in July and one in August, as seen in Fig. 1. The seasons are therefore divided based on the continuous collection of data uninterrupted by large missing gaps. The seasons roughly correspond to the conventional definition of seasons.

	All Seasons	Spring	Summer	~~Fall~~Autumn
Wind Direction,~~/~~ °	207.5 ± 89.0	202.4 ± 91.8	189.3 ± 2.6	223.8 ± 81.2
Wind Speed,~~/~~ m s^{-1}	3.3 ± 2.6	3.1 ± 2.4	3.5 ± 2.4	3.4 ± 2.7
Temperature,~~/~~ °C	-6.5 ± 9.6	-13.8 ± 9.0	2.2 ± 4.1	-7.0 ± 7.9
RH,~~/~~ %	77.4 ± 12.6	74.6 ± 10.6	78.0 ± 15.6	79.1 ± 11.4
Radiation,~~/~~ W m^{-2}	174.9 ± 163.9	222.3 ± 146.3	295.9 ± 4.2	57.0 ± 97.4
Pressure,~~/~~ hPa	1010.6 ± 9.0	1014.8 ± 8.6	1007.5 ± 6.5	1009.6 ± 9.5
Snow Depth,~~/~~ m	0.9 ± 0.6	1.4 ± 0.1	1.1 ± 0.4	0.3 ± 0.4

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Table S2. Total hours of operation of the PTR-ToF-MS for each month of the campaign and for each compound. Periods removed through the QC procedure are not included.

	April	May	June	July	August	September	October
Formaldehyde	374	601	288	661	417	443	403
Acetonitrile	229	601	288	661	417	443	403
Formic Acid	349	601	288	641	417	443	403
Acetone	376	601	288	661	417	443	403
Acetic Acid	375	577	288	661	417	411	359
DMS	300	577	169	391	357	443	377
MEK	376	601	288	661	417	443	403
$C_3H_6O_2$	327	601	288	661	417	443	403
Benzene	376	601	288	661	417	443	403
C_5H_8O	376	601	288	661	417	443	403

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Table S3~~2~~: Pearson correlation coefficients[a] for chemical species, temperature and sun radiation measured during April at ~~VRS~~Villum. ~~All correlations, apart from the numbers typed in italics, have linear regression p-values below 0.01.~~

April 2018	Formaldehyde	Acetonitrile	Formic Acid	Acetone	Acetic Acid	~~Dimethyl Sulfide~~DMS	~~Methyl Ethyl Ketone~~MEK	Benzene	C-$_3$H$_6$O$_2$~~Propionic Acid~~	Temperature	Radiation	Ozo
Formaldehyde	1.00											
Acetonitrile	0.70	1.00										
Formic Acid	0.76	0.45	1.00									
Acetone	0.40	0.30	*-0.03*	1.00								
Acetic Acid	-0.63	-0.74	-0.45	-0.32	1.00							
~~Dimethyl Sulfide~~DMS	-0.47	-0.67	-0.16	-0.55	0.84	1.00						
~~Methyl Ethyl Ketone~~MEK	0.52	0.20	0.76	0.03	-0.27	-0.07	1.00					
Benzene	0.27	0.04	0.70	-0.43	*-0.07*	0.24	0.84	1.00				
C-$_3$H$_6$O$_2$~~Propionic Acid / Methyl Acetate~~	-0.52	-0.66	-0.25	-0.41	0.90	0.94	-0.15	0.11	1.00			
Temperature	-0.47	-0.34	-0.75	0.16	0.54	0.23	-0.74	-0.77	0.46	1.00		
Radiation	-0.26	-0.26	-0.38	0.28	0.20	*0.06*	-0.25	-0.34	0.21	0.34	1.00	
Ozone	-0.52	-0.48	-0.21	-0.83	0.56	0.64	-0.26	0.15	0.59	0.17	-0.12	1.00

[a] All correlations, apart from the numbers typed in italics, have linear regression p-values below 0.01.

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Table S~~3~~4: Pearson correlation coefficients[a] for chemical species, temperature and sun radiation measured during July at ~~VRS~~Villum. ~~All correlations, apart from the numbers typed in italics, have linear regression p-values below 0.01.~~

July 2018	Formaldehyde	Acetonitrile	Formic Acid	Acetone	Acetic Acid	~~Dimethyl Sulfide~~DMS	~~Methyl Ethyl Ketone~~MEK	Benzene	$C_3H_6O_2$~~Propionic Acid / Methyl Acetate~~	Temperature	Radiation	Ozon
Formaldehyde	1.00											
Acetonitrile	0.71	1.00										
Formic Acid	0.88	0.57	1.00									
Acetone	0.86	0.89	0.82	1.00								
Acetic Acid	0.85	0.58	0.95	0.85	1.00							
~~Dimethyl Sulfide~~DMS	0.36	*0.01*	0.50	0.23	0.42	1.00						
~~Methyl Ethyl Ketone~~MEK	0.85	0.55	0.93	0.81	0.97	0.41	1.00					
Benzene	0.57	0.50	0.50	0.61	0.59	0.26	0.60	1.00				
$C_3H_6O_2$~~Propionic Acid / Methyl Acetate~~	0.83	0.57	0.95	0.82	0.97	0.39	0.95	0.50	1.00			
Temperature	0.65	0.85	0.54	0.82	0.58	*0.08*	0.54	0.45	0.54	1.00		
Radiation	0.49	0.23	0.59	*0.40*	0.51	0.26	0.53	0.15	0.56	0.31	1.00	
Ozone	0.54	0.82	0.39	*0.69*	0.39	0.18	0.33	0.43	0.33	0.76	0.07	1.00

[a] All correlations, apart from the numbers typed in italics, have linear regression p-values below 0.01.

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Table S54: Pearson correlation coefficients [a] ~~coefficients~~ for chemical species, temperature and sun radiation measured during September at VillumRS. ~~All correlations, apart from the numbers typed in italics, have linear regression p-values below 0.01.~~

September 2018	Formaldehyde	Acetonitrile	Formic Acid	Acetone	Acetic Acid	DMS	MEK	Benzene	$C_3H_6O_2$	Temperature	Radiation	Ozon
Formaldehyde	1.00	-	-	-	-	-	-	-	-	-	-	-
Acetonitrile	0.61	1.00	-	-	-	-	-	-	-	-	-	-
Formic Acid	0.76	0.45	1.00	-	-	-	-	-	-	-	-	-
Acetone	0.72	0.96	0.57	1.00	-	-	-	-	-	-	-	-
Acetic Acid	*0.06*	0.29	*0.07*	0.28	1.00	-	-	-	-	-	-	-
DMS	-0.29	-0.76	-0.18	-0.68	-0.10	1.00	-	-	-	-	-	-
MEK	0.82	0.71	0.64	0.79	0.43	-0.35	1.00	-	-	-	-	-
Benzene	0.50	0.15	0.42	0.19	0.21	0.25	0.61	1.00	-	-	-	-
$C_3H_6O_2$	0.76	0.35	0.62	0.43	0.12	*-0.03*	0.69	0.64	1.00	-	-	-
Temperature	-0.81	-0.35	-0.77	-0.53	0.26	0.10	-0.58	-0.40	-0.68	1.00	-	-
Radiation	*-0.07*	*-0.04*	-0.09	-0.06	0.29	-0.07	*0.01*	-0.11	-0.10	0.33	1.00	-
Ozone	0.74	0.70	0.63	0.79	0.14	-0.26	0.72	0.31	0.56	-0.64	-0.23	1.00

~~September 2018~~	~~Formal-dehyde~~	~~Aceto-nitrile~~	~~Formic Acid~~	~~Acetone~~	~~Acetic Acid~~	~~Dimethyl Sulfide~~	~~Methyl Ethyl Ketone~~	~~Benzene~~	~~Propionic Acid/ Methyl Acetate~~	~~Tempe-~~		
~~Formaldehyde~~	~~1.00~~	-	-	-	-	-	-	-	-	-	-	-
~~Acetonitrile~~	~~0.61~~	~~1.00~~	-	-	-	-	-	-	-	-	-	-
~~Formic Acid~~	~~0.76~~	~~0.45~~	~~1.00~~	-	-	-	-	-	-	-	-	-
~~Acetone~~	~~0.72~~	~~0.96~~	~~0.57~~	~~1.00~~	-	-	-	-	-	-	-	-
~~Acetic Acid~~	~~*0.06*~~	~~0.29~~	~~*0.07*~~	~~0.28~~	~~1.00~~	-	-	-	-	-	-	-
~~Dimethyl Sulfide~~	~~-0.29~~	~~-0.76~~	~~-0.18~~	~~-0.68~~	~~-0.10~~	~~1.00~~	-	-	-	-	-	-
~~Methyl Ethyl Ketone~~	~~0.82~~	~~0.71~~	~~0.64~~	~~0.79~~	~~0.43~~	~~-0.35~~	~~1.00~~	-	-	-	-	-
~~Benzene~~	~~0.50~~	~~0.15~~	~~0.42~~	~~0.19~~	~~0.21~~	~~0.25~~	~~0.61~~	~~1.00~~	-	-	-	-
~~Propionic Acid / Methyl Acetate~~	~~0.76~~	~~0.35~~	~~0.62~~	~~0.43~~	~~0.12~~	~~*-0.03*~~	~~0.69~~	~~0.64~~	~~1.00~~	-	-	-
~~Temperature~~	~~-0.81~~	~~-0.35~~	~~-0.77~~	~~-0.53~~	~~0.26~~	~~0.10~~	~~-0.58~~	~~-0.40~~	~~-0.68~~	~~1.00~~	-	-
~~Radiation~~	~~*-0.07*~~	~~*-0.04*~~	~~-0.09~~	~~-0.06~~	~~0.29~~	~~-0.07~~	~~*0.01*~~	~~-0.11~~	~~-0.10~~	~~0.33~~	~~1.00~~	-
~~Ozone~~	~~0.74~~	~~0.70~~	~~0.63~~	~~0.79~~	~~0.14~~	~~-0.26~~	~~0.72~~	~~0.31~~	~~0.56~~	~~-0.64~~	~~-0.23~~	~~1.00~~

[a] All correlations, apart from the numbers typed in italics, have linear regression p-values below 0.01.

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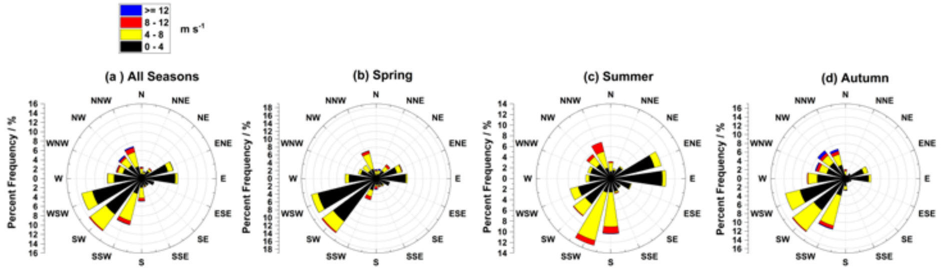


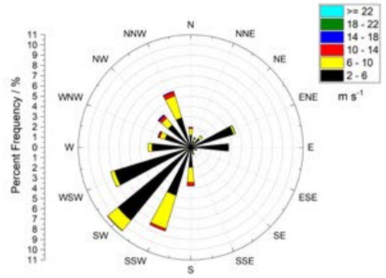
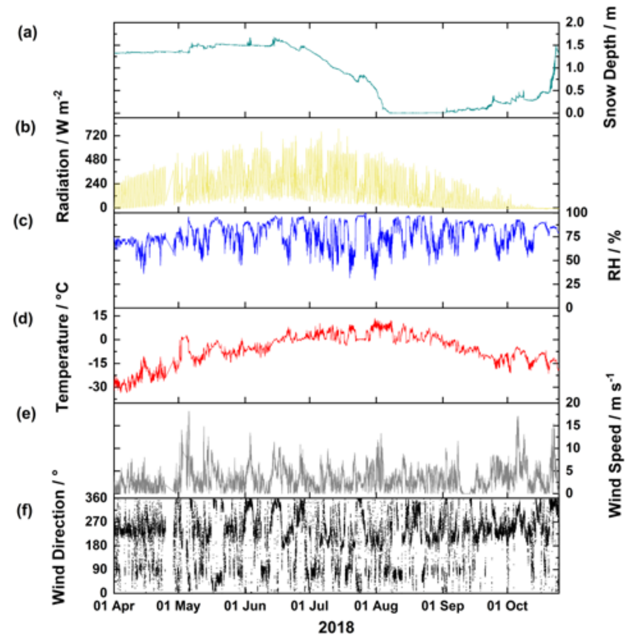


Fig. S1. Wind Rose for mean wind speed at ~~30~~ 5 min time resolution ~~over the sampling period~~for (a) all seasons, (b) spring, (c) summer, and (d) autumn. The y-axis represents the percent frequency of wind direction in percent and the colors indicate mean wind speed in m s^{-1}. The seasons follow the selection outlined in Table 1.



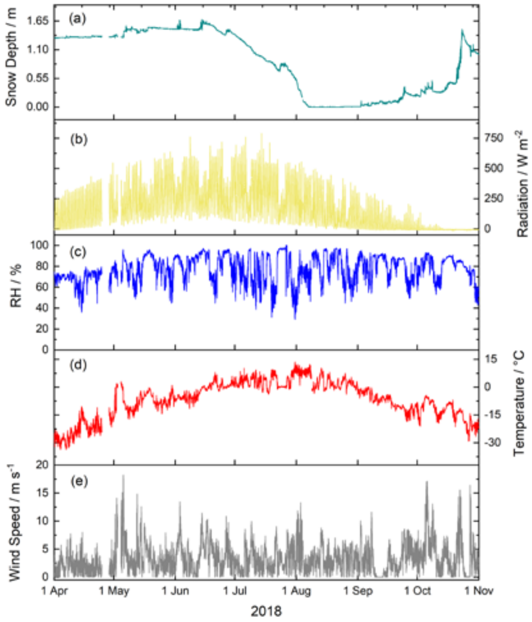


Fig. S2. Time series meteorological parameters **(a)** snow depth, **(b)** radiation, **(c)** relative humidity (RH), **(d)** temperature, ~~and~~ **(e)** wind speed, and **(f)** wind direction during the entire measurement period.

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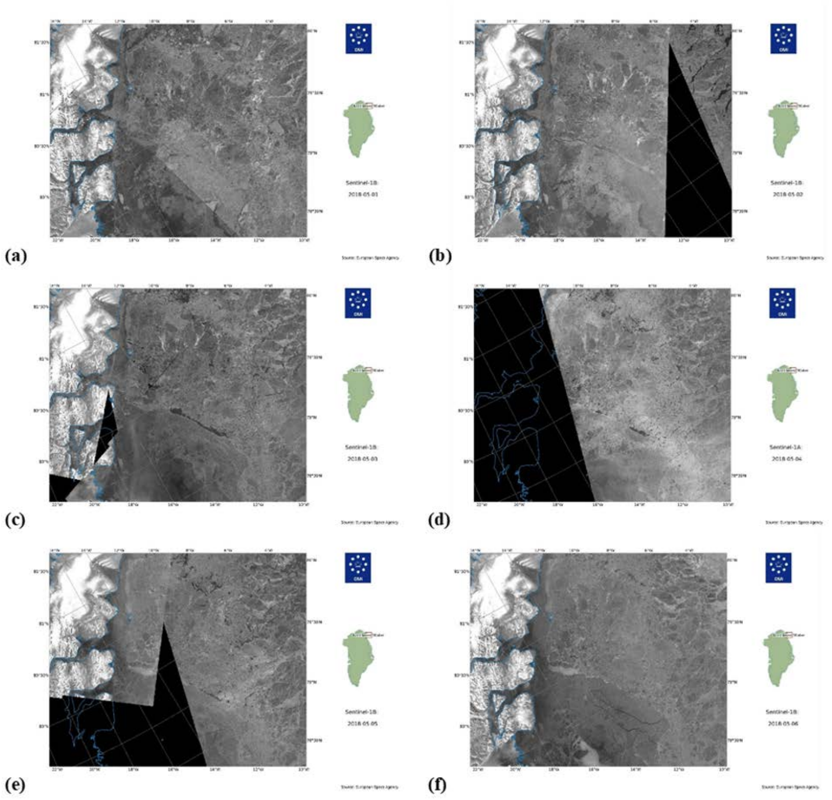
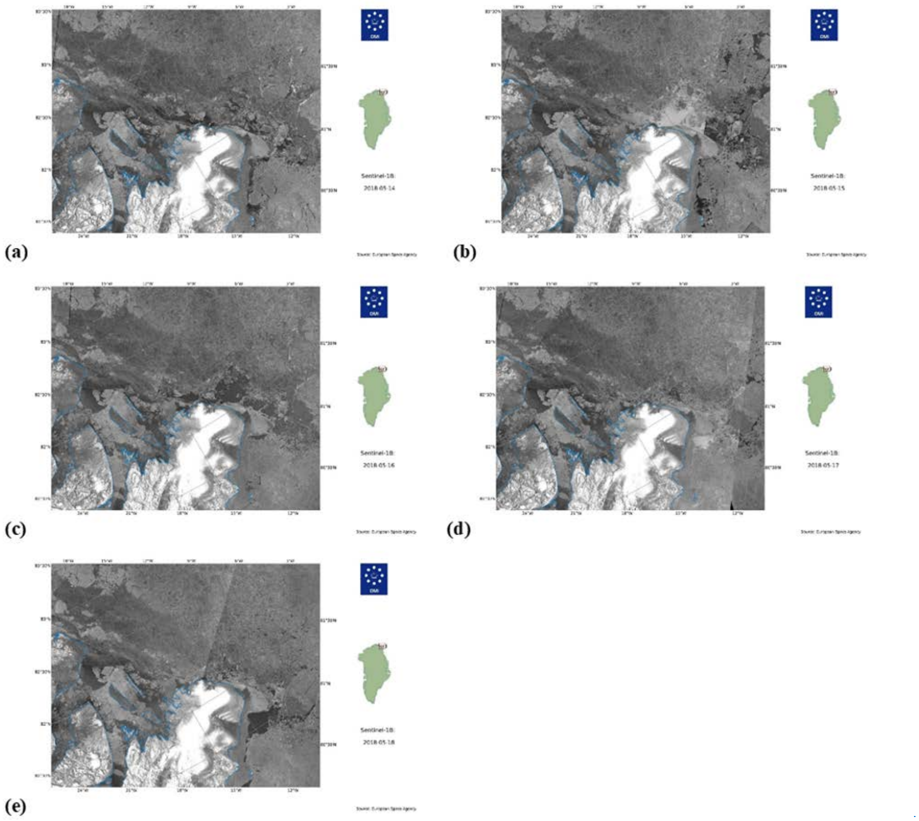


~~**Fig. S4.** Satellite images from Sentinel 1-B, delivered by the University of Dundee, Scotland and NASA's Goddard Space Flight Center; **(a)** May 1st **(b)** May 2nd **(c)** May 3rd **(d)** May 4th **(e)** May 5th **(f)** May 6th. The presence of open leads can be seen southwest of VRS at approx. 79° 30´ N and 12° W.~~



~~**Fig. S5.** Satellite images from Sentinel 1-B, delivered by the University of Dundee, Scotland and NASA's Goddard Space Flight Center; **(a)** May 14th **(b)** May 15th **(c)** May 16th **(d)** May 17th **(e)** May 18th. The presence of open leads can be seen northeast of VRS at approx. 81° 50´ N and 10° W as well as southwest of VRS at approx. 81° N and 12° W.~~

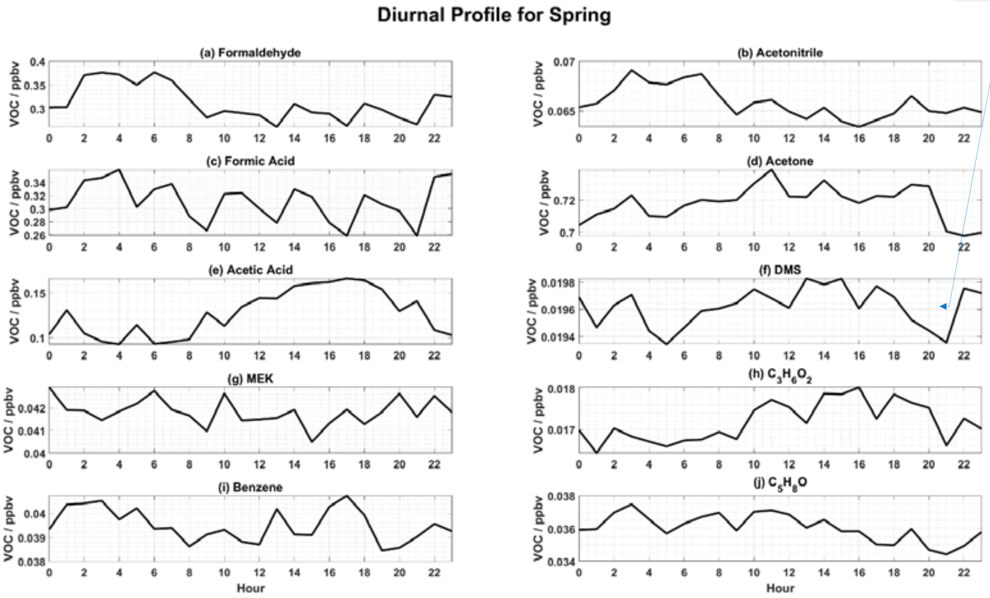


Fig. S3. Diurnal profile for the spring (April–May) of **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid, **(d)** acetone, **(e)** acetic acid, **(f)** DMS, **(g)** MEK, **(h)** $C_3H_6O_2$, **(i)** benzene, **(j)** C_5H_8O. Data were averaged to hourly medians.

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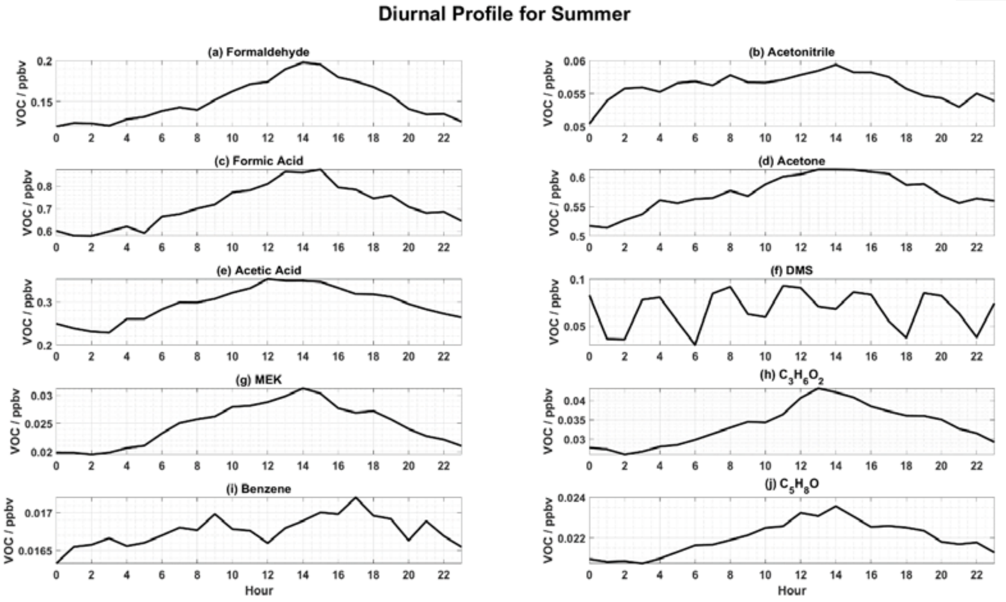

Fig. S4. Diurnal profile for the summer (June–August) of **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid, **(d)** acetone, **(e)** acetic acid, **(f)** DMS, **(g)** MEK, **(h)** $C_3H_6O_2$, **(i)** benzene, **(j)** C_5H_8O. Data were averaged to hourly medians.

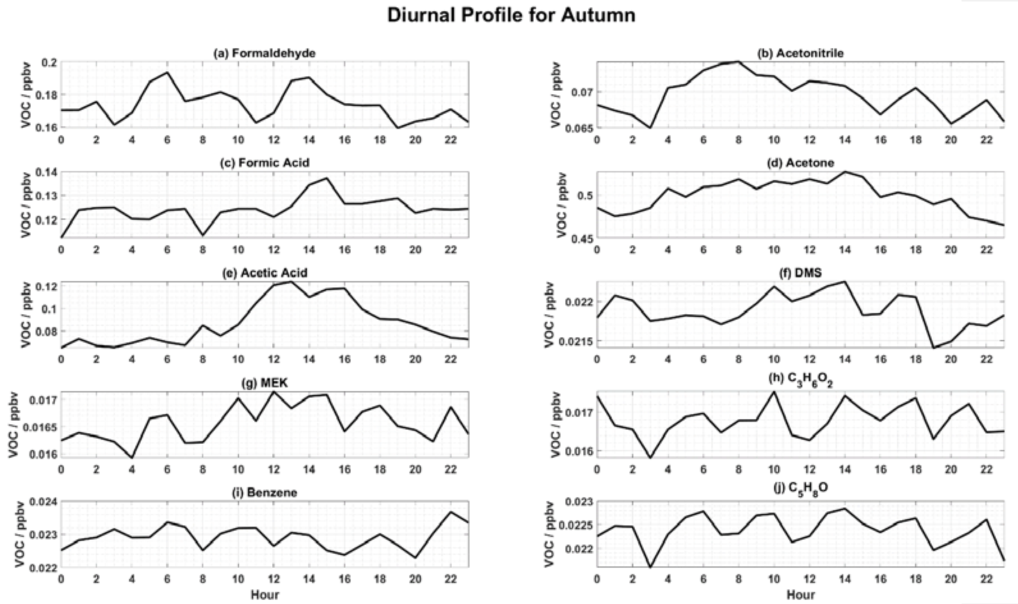

Fig. S5. Diurnal profile for the autumn (September–October) of **(a)** formaldehyde, **(b)** acetonitrile, **(c)** formic acid, **(d)** acetone, **(e)** acetic acid, **(f)** DMS, **(g)** MEK, **(h)** $C_3H_6O_2$, **(i)** benzene, **(j)** C_5H_8O. Data were averaged to hourly medians.

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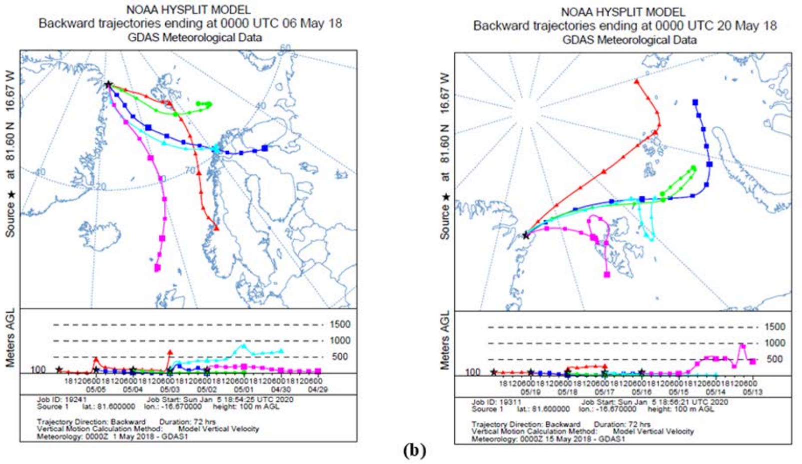


(a) **(b)**

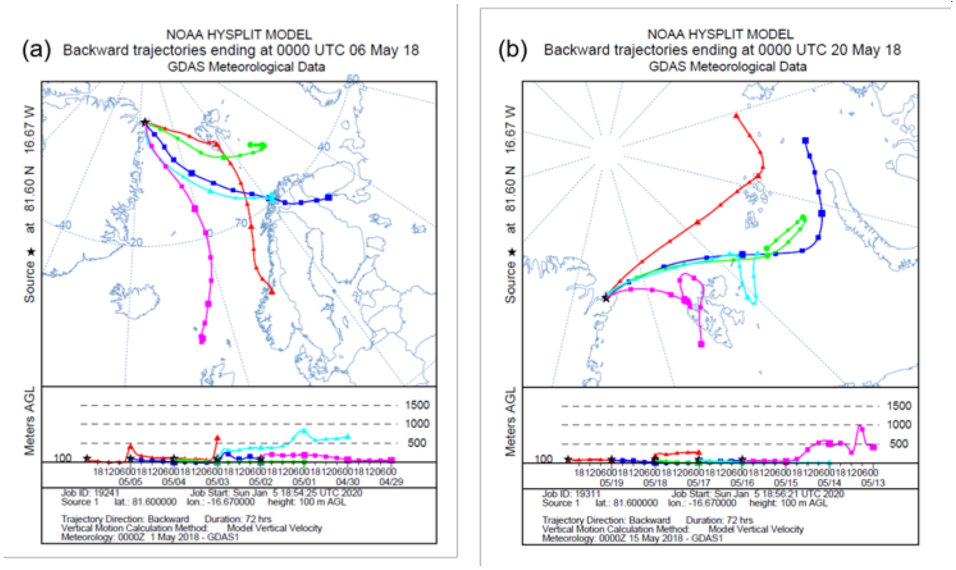


Fig. ~~S6~~S6. HYSPLIT back trajectory analysis for **(a)** May 2~~1~~nd~~st~~ – 6th **(b)** May 16th~~–~~–20th arriving at 100 m above ground level extending 72 hours backward in time. ~~A new trajectory was every 24 hours.~~ The colored trajectories represent a new trajectory started every 24 hours after the last day of each period until the first day, in descending order the trajectories are red (last day), blue (fourth day), green (third day), light blue (second day), and purple (first day).

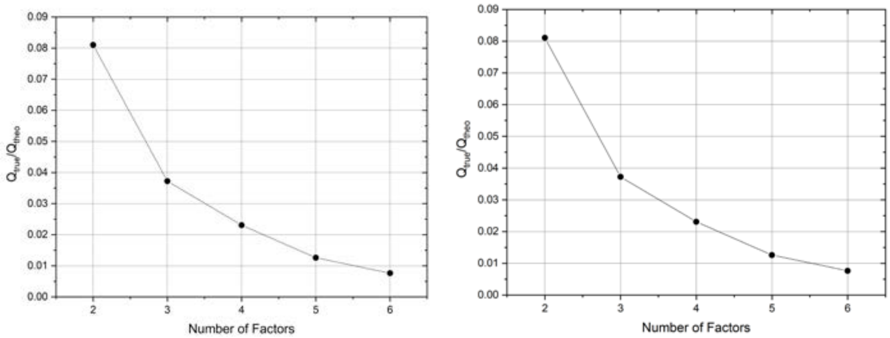
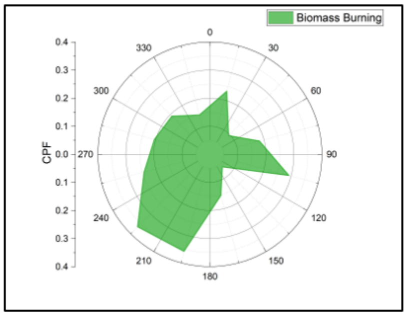
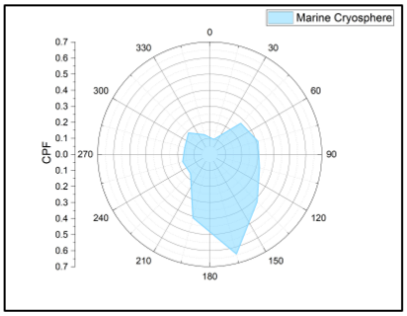


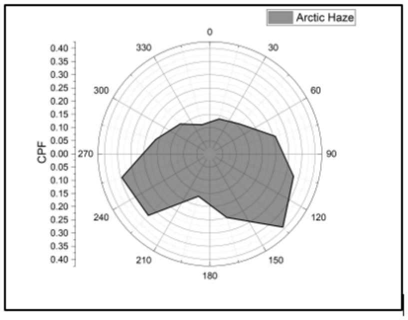
Fig. S7~~7~~. The ratio of Q_{true} to Q_{theo} versus the number of factors for the PMF analysis.


🟩 Biomass Burning
CPF
0.4
0.3
0.2
0.1
0.0
0.1
0.2
0.3
0.4
0
30
60
90
120
150
180
210
240
270
300
330

(a)


Marine Cryosphere
CPF
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
30
60
90
120
150
180
210
240
270
300
330

(b)


Arctic Haze
CPF
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0
30
60
90
120
150
180
210
240
270
300
330

(c)

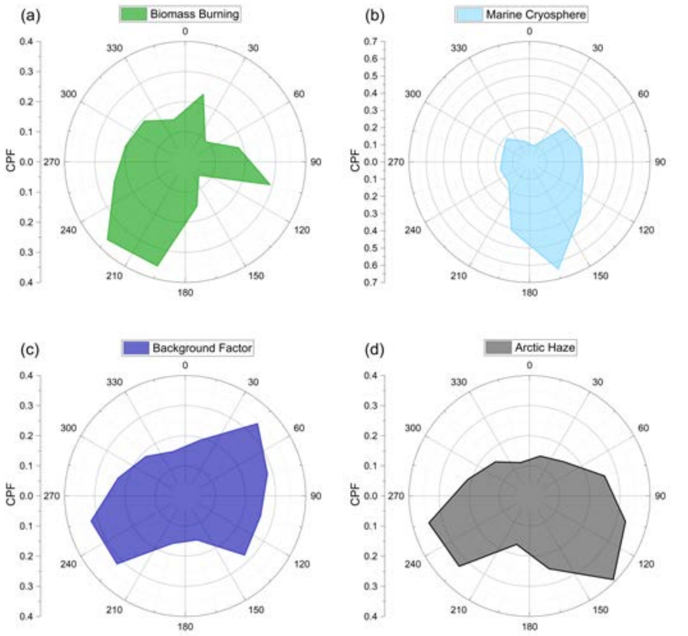


Fig. ~~S8~~S8. Conditional probability function roses for **(a)** Biomass Burning Factor, **(b)** Marine Cryosphere Factor, ~~and~~ **(c)**, Background Factor, and **(d)** Arctic Haze Factor.

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