Anonymous Referee #1

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The manuscript by Materic’ and colleagues deals with the deposition of organic matter/VOCs in alpine snow over a short period. They use PTR-MS, coupled with a new sample preparation method to directly analyse the dissolved organic compounds in snow. As someone who doesn’t work in the field of snow/ice, I must say that I did enjoy reading the manuscript. For the most part I followed it, and the results generally back up the authors’ conclusions. The paper contains a wealth of information which the authors use to make inferences about organic matter sources and weather variables.

The paper falls within the remit of The Cryosphere. Graphs are mostly well presented and easy to follow, as are tables. The purpose of the work is articulated well, the methods seem suitable. Some additional references are probably needed.

As a non-expert I cannot comment in any great detail on some parts of the paper, particularly the mass balance approach in section 3.1. I recommend publishing the paper after various, mostly minor, comments have been addressed.

1. L19. VOCs needs defining on first use

R1. We defined the term. (L19)

2. L45. On L19 you say that OM originates from anthropogenic sources, biomass burning, and biogenic sources. On L45 you discuss VOC deposition. Coming to this as a non-expert, are there reasons to believe that LMW OM is an important component of the emissions from anthropogenic sources, biomass burning, and biogenic sources. Perhaps the authors could add a few references and maybe a sentence or two for the general reader.

R2. The references in the line below (L48-49) apply here for general information of different OM. However, due to the word (and reference number) limit, we are not able to provide a more general introduction of OM sources and fractionation.

3. L54. I believe that the standard for TC submissions is to use SI brochure 8 (https://www.bipm.org/utils/common/pdf/si_brochure_8_en.pdf) which would suggest either a space or no space between the 3 and 1 in 3106 m, but certainly not a comma or period.

R3. We corrected as required “3106 m”. L55.

4. L75. For section 2.2 there is no detail of how many or how often samples were taken. Reading into the results and it seems one (?) sample was taken every three days, but this information needs including in section 2.2.

R4. One sample was taken every three days for this analysis. We clarified it in the section 2.2, as suggested. L76.

5. L81. Samples were melted. Were they melted (i.e. actively) or were they simply allowed to melt (i.e. at room temperature). Please clarify.

R5. Samples were melted at the room temperature. We clarified this in the text L82.


R6. We did not pre-rinsed. It seems that the contamination referred above does not affect PTR-MS results, as the system blanks sowed (L98-102). Also, we did not have a large volume of the samples to afford the sample lose, and we did not consider pre-rinsing with milliQ water for the dilution effect (on this small volumes).
7. L83. Sample were analysed in triplicate, but no detail is given about what happened with them. Were means taken for each ion for each set of triplicates? Additionally, whilst the authors provide a LoD, they provide no detail on the replicates. Have the authors done analysis showing variation between replicates? This seems important.

R7. The triplicates were averaged, and standard deviation is used for error bars, to express the variations between replicates (e.g. Fig 2). We added an explanation about averaging and LOD blanks in L86-88. As the Fig. 3 uses the boxplots, we clarified the meaning of the boxplot to make variation more obvious, L403.

8. L107. Ions m/z < 100 were excluded as the authors suggest these are mainly thermal byproducts. What evidence is there for this assumption?

R8. We noticed, increase level of ions m/z <100 towards the end of thermal desorption (TD). As our method loses higher volatility compounds during LPE and in the initial phase of TD (seen as very early peaks that we exclude as we integrate after TD ramp reached 50°C), we assume that these products, that show up much later, are indeed products of fragmentation due to the thermolysis.

9. L116, eq 1. What is “d”? Is it delta?

R9. We used Leibniz’s notation to express the derivative.

10. L131. 5 DPs for the $R^2$ value is too many to be of any meaningful use, surely. The same for Table A1. My preference would be 2DPs for sufficient information.

R10. For the consistency and clarity, we reduce all $R^2$ values to 4 decimal places. L135.

11. L156 and L159. The authors make a comparison between their VOC burden (833 ng m$^{-3}$) and that from Zhao et al (0.6 µg m$^{-3}$). Please amend one of these values so the units are the same, to help the reader immediately see the comparison.

R11. Changed to 600 ng m$^{-3}$. L163.

12. L177. The authors say they use Pearson correlation but then report $R^2$. Technically, Pearson correlation would be $R$. But I wonder if a Spearman correlation might be better than Pearson. Certainly Fig. 3A would seem to follow a Spearman (i.e. monotonic increase) better than a Pearson (i.e. linear increase). Was there any reason for using Pearson?

R11. Change to “linear regression model”, L181. For this simple correlation test, we did not consider using more advanced correlation models. (See also R3 of the Referee 2).

13. L185 – L192. The statements concerning pinonic acid and levoglucosan origins (forests and burning) need some references added.


14. L193 – L201. It may not be possible, but do the authors have any suggestions for group 3? i.e. can any of the compounds be identified, thus suggesting what sort of pollution event occurred?

R14. Not possible at the moment (see also R5 of the Referee 2).

15. L208. Amenability is a slightly unusual word choice. Maybe “susceptibility” might be better.

R15. Changed as suggested. L213.

16. L214 – L215. Please add a reference for “longer sVOC are in general less volatile”
R16. This is a general assumption in chemistry based on considering alkanes or fatty acids. Early works addressing this, e.g. (Bradley, 1954) and references within, would be outdated and thus not appropriate, considering the reference number limit of this journal.

17. L217 – L222. The authors look at changes that occurred on the 29th. Specifically, the observed increase in pinonic acid stalled. They also claim that levoglucosan was elevated, but as this was increasing anyway it seems difficult to attribute it to the same cause? Anyway, a halt in the rise of pinonic acid would suggest (according to the earlier hypothesis involving conifer forests) that the wind has switched direction and is coming from an area less dominated by forests. Did the authors consider this? The rise in levoglucosan might suggest the wind comes from an area with more biomass burning. Again, was this considered? Fig 1 also suggests quite a pronounced humidity change on this date. What are the implications of this?

R17. We considered the “rise in levoglucosan might suggest the wind comes from an area with more biomass burning.” We further elaborated this in L227.

Humidity might be related to the change in the height of the boundary layer, but we chose not to address this at the time. More data is needed for further conclusions regarding this.

18. L236. Reading on I see the authors discuss biomass burning in relation to my above comment, but it still needs elaborating on.

R18. See the comment R17.

19. L241. The authors suggest there is lower total OM on the 29th (fig 2A). Considering the error bars, I would say there is no difference in total OM between the 26th and the 29th.

R19. To be more accurate, and to agree with the discussion afterwards, we corrected it to “…we also observed lower average total OM concentration…”. L247.

20. L262. Biomass burning is mentioned previously, but here, for the first time in the paper we have mention that the source of this is residential fires. This should be mentioned earlier in the paper.

R20. It has been introduced in L194 when first time used “biomass burning”.

21. “Fig 3. The labels could be increased in size, especially on the y axes, as they are difficult to read.”

Also, the four panels of Fig 3 and Table A1 should follow the same order. That is, Fig 3 shows pinonic (A), levoglucosan (B), decreasing trend (C), then increasing trend (D). However, in Table A1 the order is pinonic, levoglucosan, increas- ing, decreasing. Maybe easiest to swap columns 3 and 4 around in table A1 so the orders are the same.

Also, for the legend of Fig 3, it would help the reader to note that panel C is increasing (then decreasing), and panel D is increasing (then saturating). Also, what do the weather symbols mean on panel A?

R21. Fig 3 labels increased in size.

Columns in the table replaced as suggested.

The lines added in the Fig 3 a-d should be sufficient to describe the trend: “The lines illustrate the change in the concentration over the time that is typical for each group” L410. We further explained the weather symbols in the figure caption (L411-413).

22. Table A1. The authors say “Note that different thresholds of R values are used to isolate the groups.” This needs expanding on. Looking at Fig 3, ions that fit into panels A, B and C must all correlate with ions from other panels (they all increase to some extent). I.e. it is possible for an ion in the pinonic acid group to probably correlate with an ion in the D/increasing group. I assume that the authors are trying to say is that they used R2 cutoffs to decide which ions went into each group. Perhaps this could be clarified.
R22. We further clarified the table caption as suggested - L415. R² cutoffs also added for clarity.

23. Acknowledgements. There is a typo: “tis”

R23. We corrected this.

Anonymous Referee #2

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The manuscript “Brief communication: Analysis of organic matter in surface snow by PTR-MS—implications for dry deposition dynamics in the Alps” by Materic et al., describes organic matter composition in Alpine snow samples during 12 days in spring 2017. A simple mass balance model is discussed and used to determine atmospheric deposition of VOCs on snow. A grouping method for the PTR-MS mass ions based on Pearson correlations is then used in order to highlight specific emission sources or atmospheric events that influenced the sampling site. I find the manuscript interesting, novel, and nice at reading. Specifically, it is promising the novel approach of using a state-of-the-art technique as PTR-MS, commonly used in atmospheric chemistry to monitor air samples, in the field of cryosphere. I find the manuscript suitable to the journal and I recommend its publication after some minor comments have been addressed.

1. “L. 85: As the approach of analysis used by the authors is quite novel it would be nice to have more details about the TD method and the PTR-MS conditions of analysis.”

R1: Unfortunately, space is limited in this brief communication format so include more on the method. However, our method paper (reference provided in the text) is published as an open-source so the information on the method is easily accessible. PTR-MS conditions are additionally explained in the text L88-89.

2. “L. 88: How much is the percentage of recovery with the TD method for 20-500 amu? Why the maximum temperature used is 250 °C?”

R2. The exact percentage of recovery for this samples are unfortunately not available as we did not measure dissolved organic matter concentrations. From our previous works, we had the mean recovery of 0.6% desorbing at maximum 240 °C (5-minute protocol) (Materic 2017), and later 5.5% at 250 °C (8-minute protocol) (Peacock 2018). We followed our experience and used 250 °C and 8-minute protocol, so we expect ~5% recovery.

3. L. 177: Which threshold of the Pearson correlation was used to group the mass ions? Why the authors have not considered to try a more robust approach for sources apportionment as for example, the positive matrix factorization analysis?

R3. In this pilot, for the ion correlation we used the linear regression for its simplicity (thresholds: group 1 and 2 R²>0.98 saturating > 0.995, decreasing R²>0.70. PMF). PMF is however planned for the experiments which involve more frequent sampling rate.

4. L. 182: These numbers seem higher compared to atmospheric concentrations of a remote site. Could you include a short discussion with comparisons with reported values in literature of concentrations found in snow samples for similar compounds?

R4. Our concentration seems realistic compared to the literature values for the same location (Sonnblick Observatory, AU), although different methods have been used. E.g. in (Gröllert et al., 1997), they measured aliphatic hydrocarbons at 14 ng/mL (µg/L reported), aliphatic alcohols 18 ng/mL and fatty acids 43 ng/mL. We added the discussion in L188-189.
5. “L. 210: Was any compound associated to “group 4” identified? In general, was also any other method applied simultaneously to PTR-MS analysis to cross-validate some information? “

R5. We did not perform GC-MS or similar for cross-validation at this stage. So, we are not certain for the group 4 ion identification.

6. Figure 1: on 29/03/2017

R6. Corrected to the same format L401.

7. Figure 3: a, b, d show a general increase. Is this due to any specific atmospheric event or driver?

R7. As the snow is exposed to the air (which has certain levels of OM), the dry deposition it is expected to increase toward the equilibrium (see L115 and the following lines).

8. Table A1: This table should be moved from the appendix to the main body of the manuscript. Here a few adjustments are needed: the text refers to Pearson coefficients but the table shows the R2. The labels of the table do not correspond to what the grouping described in the text. It is not clear which ion correlate with which. Would it be possible to the authors to re draw the table to see the correlation of each pairs of ions? Is there any of this ion identified with a compound or previously reported in literature? If yes, please mention it.

R8. Instead of “Pearson…” we used “linear regression model”. The caption of the table improved. Table columns adjusted. Correlation of each pair would be complicated to present in one table, instead, we gave correlations against a “typical” ion of the group, highlighted bold. Using the limited literature sources for TD-PTR-MS, no further identification of the ions is possible at this stage (see also R5). The limited number of figures and tables in the brief communication format prevents us to move the table to the main text.

9. How were the fragments/clusters excluded from the correlation analysis? Could you shortly discuss the possibility of having fragments or water clusters included in the analysis?

R9. We reduced the effect of fragments by excluding low molecular mass compounds (comment R8 referee 1.). Water clusters are not addressed here as we measure at reasonably high E/N (122 Td). More detailed discussion on the fragments/clusters impact on the analysis is planned for a different experiment where we measured using different E/N, in which case this could be properly addressed.
Brief communication: Analysis of organic matter in surface snow by PTR-MS – implications for dry deposition dynamics in the Alps

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Abstract. The exchange of organic matter (OM) between the atmosphere and snow is poorly understood due to the complex nature of OM and the convoluted processes of deposition, re-volatilisation, chemical, and biological processing. OM that is finally retained in glaciers potentially holds a valuable historical record of past atmospheric conditions; however, our understanding of the processes involved is insufficient to translate the measurements into an interpretation of the past atmosphere. This study examines the dynamic processes of post-precipitation OM change at the alpine snow surface with the goal to interpret the processes involved in surface snow OM.

1 Introduction

Organic matter (OM) in the cryosphere originates from different sources (e.g. oxidation products of anthropogenic, biogenic, and biomass burning volatile organic compounds - VOCs), is transported from short and long distances and is deposited via dry or wet deposition (Antony et al., 2014). From the moment of the emission, OM undergoes atmospheric chemistry processes, which profoundly alter the chemical composition of OM, resulting in numerous chemical species that are finally deposited on the snow/ice surface (Legrand et al., 2013; Müller-Tautges et al., 2016). Fingerprints of OM stored in the snow and ice therefore potentially hold a rich historical record of atmospheric chemistry processes and the transport pathways in the atmosphere (Fu et al., 2016; Giorio et al., 2018; Grannas et al., 2006; Pokhrel et al., 2016). The vast diversity of OM, which is found in snow and ice samples, is impossible to characterise by one single method. The most used methods so far in snow/ice OM research are based on gas chromatography (GC) and liquid chromatography mass spectrometry (LC-MS) (Giorio et al., 2018; Gröllert et al., 1997). Novel high-resolution mass-spectrometry-based analytical methods, such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), Orbitrap mass spectrometry, and Thermal Desorption – Proton Transfer Reaction – Mass Spectrometry (TD-PTR-MS), have recently been developed and can be used to characterise OM in the cryosphere with high mass resolution (Hawkes et al., 2016; Kujawinski et al., 2002; Marsh et al., 2013; Materić et al., 2017).
Therefore, numerous new proxies are now potentially available to interpret the rich composition of OM in the cryosphere. Reconstructing past atmospheric conditions from measurements of OM in the cryosphere is analytically challenging because of (1) low concentrations of target organics in the sample, and (2) chemical changes that (might) happen after OM deposition. A recently developed method using Thermal Desorption – Proton Transfer Reaction – Mass Spectrometry (TD-PTR-MS) has partly solved the first issue enabling the detection of low molecular weight OM ranging from 28 to 500 amu (Materić et al., 2017). However, chemical changes (e.g. photochemical, biological etc.) and re-emission from the snow/ice surface still remain challenging to quantify, especially in the context of the diversity of OM species, both high and low molecular weight OM.

The low molecular weight fraction represents an important part of OM in the cryosphere and the group includes volatile and semi-volatile organic compounds (VOC, sVOC) that deposit directly from the gas phase or as part of secondary organic aerosols (SOA). Low molecular weight OM has been extensively studied in atmospheric context by real-time or off-line PTR-MS techniques (Gkatzelis et al., 2018; Holzinger et al., 2010a, 2013; Materić et al., 2015; Timkovsky et al., 2015), however, not so in the context of deposited (e.g. dissolved) OM in the cryosphere. In this work, we applied a novel TD-PTR-MS method to measure concentrations of OM present in Alpine snow. The first application of this new technique is investigation of snow-atmosphere interaction of OM during a dry weather period.

2 Material and methods

2.1 Sampling site

The snow samples were taken at 3106 m altitude at Mt. Hoher Sonnblick, Austria, close to the research station Sonnblick Observatory. The sample site was next to the southern precipitation-measuring platform, which is about 50 m southeast of the observatory. The sampling location was carefully chosen to be least affected by potential contamination coming from the observatory. Average temperature of the site is about 1.1°C in summer and -12.2°C in winter considering the meteorological data being gathered since 1886.

The sample period spans the days from March 20th to April 1st of 2017. During this time period the Sonnblick Observatory experienced an average day length of 12.5 hours, and an average temperature of -4°C, 78% relative humidity, an average wind speed of 7.3 m s\(^{-1}\) and pressure of 696 hPa. There was no significant precipitation observed but these days were mostly foggy in the morning with the exception of March 27th and 28th 2017, which were nearly clear-sky days, followed by less cloudy days till April 1st 2017. The measured air temperatures (2 m above the surface) on the site were below zero for all the time, with exception of 3 brief instances where the temperature was recorded 0.1°C for 10 minutes (Fig. 1a). However, hourly temperature averages for these events were also < 0°C. If we use a Positive Degree Day model (PDD) to assess the melting possibility of those single 10 minutes periods, we calculated the depth of the melt water 1.4-5.5 µm (using the snow melt factor 2-8 mm °C\(^{-1}\) day\(^{-1}\)) (Singh et al., 2000). Thus, we conclude that no significant melting and runoff happened for the entire sampling period.
More information on the meteorological conditions can be found in Fig. 1 and Fig. A1.

2.2 Sampling

Snow samples were taken every third day from the surface snow (<2 cm) scooping the snow directly into clean 50 mL polypropylene vials. We also took field blanks (ultrapure water) to assure that our blanks were exposed to the same impurities as the snow samples. The samples were stored in a freezer at -20°C until the end of the sampling campaign and then shipped on dry ice to the analysis lab, where they were kept frozen until the analysis.

2.3 Analysis

Prior to the analysis the samples (and blanks) were melted at the room temperature and filtered through a 0.2 μm PTFE filter. We loaded 1 mL of each sample into clean 10 mL glass vials that had been prebaked at 250°C overnight. The samples together with the field blanks, were dehydrated using a low-pressure evaporation/sublimation system and analysed by TD-PTR-MS (PTR-TOF 8000, IONICON Analytik), following the method described before (Materić et al., 2017). The samples (triplicates) were run randomly and the blanks (four replicates) were run in-between covering the entire period of the experiment. PTR conditions were drift-tube pressure 2.95 mbar, drift-tube temperature 120°C, drift-tube voltage 603 V, yielding E/N 122 Td. The thermal desorption procedure was optimized for snow-sample analysis and has the following temperature sequence: (1) 1.5 min incubation at 35 °C, (2) ramp to 250 °C at a rate of 40 °C min⁻¹, (3) 5 minutes at 250 °C, and (4) cooling down to <35 °C. The method is fast (<15 min per run), sensitive (e.g. LoD <0.17 ng mL⁻¹ for pinonic acid, LoD<0.26 ng mL⁻¹ for levoglucosan), requires a small sample size (<2 mL of water), and it provides reasonably high mass resolution data (>4500, FWHM).

For the data analysis, we used the custom made software package PTRwid for peak integration and identification, and R scripts for statistical analyses (linear regression, fitting etc.) (Holzinger, 2015). We used 3σ of the field blanks for estimating the limit of the detection (LoD), so only ions that are above this value were taken into account for the scientific interpretation (Armbruster and Pry, 2008). We evaluated the impurities in the field blanks by comparing them with the system blanks (clean vials) and discovered that the average impurity level of a field blank was reasonably low (7.0 ng mL⁻¹), which mostly (60 %) originated from the ion m/z 81.035 (C₅H₄OH⁺). The impurities here might originate from the polypropylene vials we used, however, the levels are much lower compared to the methods used for measuring total and dissolved OM (Giorio et al., 2018). The impurities were taken into account by means of field blank subtraction and LoD filtering (Materić et al., 2017).

From the mass spectra, identified peaks were integrated over 8 minutes starting when the temperature in the TD system reached 50°C. Extracted peaks were quantified by PTRwid and the concentration was expressed in ng mL⁻¹ of sample. We calculated the molar concentration of C, H, O and N for each sample, from which atomic ratios (O/C, H/C, N/C), mean carbon number (nC), and mean carbon oxidation state (OSC) are calculated as described earlier (Holzinger et al., 2013; Materić et al., 2017).

For the elemental composition calculation, we excluded ions m/z <100 as these are dominated by
thermal dissociation products of non-volatile high molecular weight compounds. Taking into account these fragments of bigger molecules would substantially alter elemental composition and atomic ratios.

3 Results and Discussion

3.1 Total ion concentration and simple mass balance model

During our sampling period, the total concentration of organics increases in general over the time that the snow was exposed to the atmosphere (Fig. 2a). The concentration of organics in the snow surface reflects a dynamic balance between two opposing processes that work independently: deposition as source and loss. If we consider just dry deposition (it was a period without precipitation), the retained (actual) concentration of the organics in the snow can be described as:

\[
\frac{dm}{dt} = D - L,
\]

where \( m \) is the concentration of organics remaining in the snow, \( D \) is the total dry deposition rate and \( L \) is the overall loss rate due to re-volatilisation, photochemical reactions, biological processes etc. As our samples generally show an increase in the ion concentrations (Fig. 2 and 3), the loss rate by re-volatilisation, photochemical reaction and biological decay is lower than the total deposition rate (\( D > L \)). A negative mass balance, i.e. \( D < L \), can happen, for example, in periods of extensive photochemical reactions together with snow exposure to an air mass with a low concentration of OM.

Our total concentration data (as well as many individual ion groups, see below) indicate a relaxation towards a source-sink equilibrium. Mathematically, the simplest model that has these characteristics is a system with quasi-constant deposition rate \( D \) (i.e. changes in deposition are much slower than changes in the loss rate) and a first order loss rate (\( L = km \) in equation 1), which can be integrated to yield

\[
m = m_0 e^{-kt} + \frac{D}{k} \left(1 - e^{-kt}\right),
\]

where \( m_0 \) is the initial concentration of \( m \), \( k \) is the first order loss rate coefficient and \( t \) is time. In our experiment, we measured \( m \) with a time step \( t \) of three days and consider \( m_0 \) as our measurement of the fresh snow in the beginning of the analysis period. Eq. 2 can then be fit to the data and the best fit for the total concentration of semi-volatile organic traces (\( R^2 > 0.9899 \) and \( \text{rRMSE} < 3.5\% \)) was found for \( k = 0.31 \text{ day}^{-1} \) and \( D = 206 \text{ ng mL}^{-1} \text{ day}^{-1} \). When the fit is applied to the mass of carbon in the detected organics the best fit values for the two parameters are \( k = 0.30 \text{ day}^{-1} \) and \( D = 114 \text{ ng mL}^{-1} \text{ C day}^{-1} \) respectively. Considering reported average organic aerosol (OA) concentration we assume the winter air concentration (\( C \)) to be at most 2 \( \mu \text{g C m}^{-3} \) (Guillaume et al., 2008; Holzinger et al., 2010b; Strader et al., 1999). Further taking an average sampling depth of 2 cm and a snow density of 250 mg mL\(^{-1}\) we calculated a deposition velocity of 0.33 cm s\(^{-1}\) according to equation (3):

\[
v = \frac{D}{C \times A}
\]
where \( D \) is the measured deposition rate, \( C \) is concentration (2 \( \mu \)g C m\(^{-3}\)) and \( A \) is the area that was typically sampled (combining sampling depth and snow density relates 1 mL of sample to an area of 2 cm\(^2\)). Assuming slightly higher (3 \( \mu \)g C m\(^{-3}\)) or lower (1 \( \mu \)g C m\(^{-3}\)) organic aerosol concentration in air, and sampling variation between 1.5–2 cm depth we calculated positive error of factor of 2 and negative error of factor of 2\(^{-1}\). Thus, deposition velocity for organic aerosols of 0.17-0.66 cm s\(^{-1}\) would be required to be consistent with the observations. However, the deposition velocities for organic aerosol were previously estimated to be 0.034 ± 0.014 and 0.021 ± 0.005 cm s\(^{-1}\) for particles in 0.15–30 and 0.5–1.0 \( \mu \)m size ranges (Duan et al., 1988; Gallagher et al., 2002). The required deposition velocities are approximately an order of magnitude higher than the previously reported estimates even if we use the upper limit of expected organic aerosol concentration (2 \( \mu \)g C m\(^{-3}\)). Therefore, we conclude that the dominating contribution to OM in the snow is from gas phase sVOCs. As direct measurements of bulk sVOCs do not exist, we estimated the required average loads of sVOCs in the air passing the sampling location to explain the observations. Using the deposition rate calculated from our measurements (Eq. 2), the concentration-weighted average molecular mass of measured compounds, and deposition velocities of 1 cm s\(^{-1}\) (assuming that sVOC deposition velocities are similar to the one of formic acid) (Nguyen et al., 2015), we calculated an average gas phase sVOC burden of 883 ng m\(^{-3}\) of air which is equivalent to 247 ppt. Assuming slightly higher or lower deposition velocities (± 0.2 cm s\(^{-1}\)) yield errors of +221 and -148 ng m\(^{-3}\), or +62 and -41 ppt. Our calculated value of average sVOC concentration agrees with previous estimates of 600 ng m\(^{-3}\) (Zhao et al., 2014). Thus, our data suggest that dynamic processes of DOM on the surface snow are dominated by deposition and re-volatilisation of gas phase sVOCs. This has important implications for our understanding of the snow surface processes. Our analysis suggests that air masses with different sVOC composition can leave different OM fingerprints in the snow (discussed in the sections below).

The \( D/k \) ratio quantifies the equilibrium point (asymptote) for the model described in Eq. (2). This represents a point at which the equilibrium is established between deposition and losses. The derived time constant for loss of about 3 days implies that 90% equilibrium is established for the total ion concentration in only 6 days. This value, however, represents an average equilibrium time for total measured DOM, and it is reasonable to assume that this equilibration timescale differs between different compounds. In particular, it is estimated to be established much faster for the gas-phase sVOCs compared to SOA.

Similar mass balance calculations will be carried out in the following section for individual ion groups.

### 3.2 Grouping of ions with similar time evolution

In the data analysis of TD-PTR-MS spectra, we found 270 organic ions above the detection limit present in the samples. Compounds that have the same origin (similar sources or atmospheric chemistry processes) should feature similar time evolution, if the lifetime is not so short that such a common time evolution is lost. Based on the pattern of concentration change over time (using linear regression model) we identified four groups of ions with similar time evolution (Fig. 3, Table A1). In the group 1, 2, 3 and 4 we assigned 25, 33, 9 and 21 ions respectively (88 ions in total 33%), and 175 ions did not fall in any of these groups. Ions which we did not assign to any group either showed different time evolution or
had concentrations close to the detection limit causing poor correlation. In average, the total concentration levels of the ions within the four groups were 30, 56, 16, 57 ng mL$^{-1}$ respectively, and 315 ng mL$^{-1}$ for ions which did not fall in any of the described groups. Specific information can be found in the supplementary data. These levels of OM retrieved by PTR-MS agree with previous measurements at the site although different methods have been used (Gröllert et al., 1997).

In the first two groups (Fig. 3a and b), among the numerous ions we identified masses that we tentatively attribute to pinonic acid (m/z 115.07 fragment) and levoglucosan (e.g. m/z 85.03 and 97.03 fragments) (Salvador et al., 2016). Pinonic acid is an oxidation product of monoterpenes and the main source is expected to be emission from surrounding alpine conifer forests, thus group 1 ions indicate air masses that were originally rich in biogenic VOC, which have been processed during transport. Levoglucosan is a clear indicator of biomass burning and the most likely source during this period is domestic wood combustion. Therefore, we associate group 2 ions to the anthropogenic wood combustion sources and their products in the complex atmospheric processing.

The compounds that fall in group 3 show, after an initial increase in the concentration on 23/03/2017, a decreasing trend (Fig 3c, see also Table A1). The change in the concentration of the compounds constituting this group may point to a one-time significant pollution event which happened between 20$^{th}$ and 23$^{rd}$ of March. The total concentration of ions in this group was measured to be 34 ng mL$^{-1}$ (8.2% of the total organics) on 23/03/2017. This deposition event could have come from a single source, however higher time resolution measurements are needed to further characterize the potential source. As total concentration of ions in this group drops in 6 days below 20 ng mL$^{-1}$ (3.1% of the total organics), this group is also an example how contaminated snow equilibrates with the cleaner atmosphere on similar timescales as we derived from the simple box model.

As for total concentration, most of the ions and ion groups show an increase in the ion concentrations throughout the sampling period. Group 4 (Fig. 3d, Table A1) represents the compound group for which the concentration seems steadily increasing towards an equilibrium. This indicates that the simple mass balance model may be applicable, i.e., the assumption of a (close to) constant deposition and first order loss rate. Therefore we applied the simple mass balance model (see 3.1.) also to the individual ions in group 4 to investigate whether individual organic compounds have different $k$ values. This is expected due to the different chemical and physical properties (such as volatility, susceptibility to photolysis etc.) as well as different nutrition adequacy for potential biodegradation. For the sum of organic ions in the group 4 (Fig. 3d, Table A1), $k = 0.20$ day$^{-1}$. Generally, the lower $k$ value of this group compared to the total sVOC could be related to the fact that most of the ions here are heavier (thus, less volatile). However, within this group $k$ values of individual ions were found to be independent of the molecular weight, and also independent of the composition, i.e. O/C, H/C, OSC and nC ($R^2 < 0.12$). As the volatility of sVOC is expected to depend on molecular weight and functional groups (longer sVOC are in general less volatile, unless additional functional groups are involved), this suggests that volatility might not play the only role in the loss processes of this group.

A deviation in the general concentration trend of individual ions (from the expected growth, section 3.1) was observed on 29/03/2017, particularly in the groups 1 and 2 represented by pinonic acid and levoglucosan (Fig. 3a and b). Elevated levoglucosan and lower pinonic acid levels observed at 29$^{th}$ are temporally related to a change in wind direction. On the 29$^{th}$, the air masses originate from the North-East direction, rather than North-West direction, seen for other samples (Fig 1c), so this event is
attributed to the meteorological situation, and possibly more pronounced source of biomass burning following the transport regime at the time.

Presence of such distinctive patterns of concentration change over time, ion grouping, and their relation with the meteorological data indicate that meteorology and deposition of sVOCs after fresh precipitation strongly affect the organic composition in snow, which questions the most straightforward approach of interpreting of OM signals in terms of organic aerosol in the air.

### 3.2 Elemental composition

We further investigate the processing of OM in snow during the study period by calculating cumulative metrics of the OM composition from the PTR-MS data, namely the elemental ratios O/C and H/C, the number of carbon atoms per compound, nC, and the oxidative state OSC of the organic carbon, in order to further characterize the processes behind the observed changes. The fresh snow sample (20/04/2017) has the lowest total concentration of all measured organics, low OSC, the lowest O/C and N/C value, and high H/C and nC value (Fig. 2), which all indicate ‘fresh’ OM in the air (Kroll et al., 2011), which was captured in the snow.

An interesting signature in the metrics is observed on 29/03/2017 when the prevailing air flow regime was interrupted (wind direction change, Fig. 1c). This sample showed the highest value of nC, the lowest OSC, as well as elevated H/C and low O/C ratios (Fig. 2). This all indicates photochemically younger (fresher) emissions of VOC and semi-volatiles, originating from air-masses rich in biomass burning aerosols (Fig. 3b), which is in agreement with previous results linking low OSC and high nC to biomass burning aerosols (Kroll et al., 2011). However, on the 29th we also observed lower average total OM concentration in the sample compared to the previous period which clearly indicates a net loss of OM. Potential processes that could explain such loss of OM involve photolysis induced re-volatilisation, OM runoff (e.g. snow melting), or oxidation. The photolysis induced volatilization should be higher for this sample as the previous days (27th and 28th) had the highest global radiation values (33% higher the average for the sampling period) and the longest sunshine duration (>12 hours) (Fig 1b and Fig. A1). On the other hand, no significant temperature increase has been measured to support increased melting and OM runoff. Loss by oxidation (referring to “dark” oxidation that is uncoupled from photooxidation) is also unlikely as main process since the O/C ratio did not increase for 29th of March (Fig. 3c). Thus, the most likely cause of the lower total OM concentration observed on march 29 is re-volatilization, possibly enhanced by photolysis, which would indicate that the air contained a lower burden of SVOCs. In addition, new OM material with different characteristics was deposited before that sample was collected. Combining all metrics (Fig. 2) and meteorological data available (Fig. 1), we can conclude that the air passing the site prior to 29/03/2017 was cleaner and photochemically younger, and contained higher MW compounds that might have originated from anthropogenic emissions such as biomass burning (high levels of levoglucosan, Fig. 3).
4 Conclusion

In this work, we analysed the concentrations of low molecular weight organic matter (20 – 500 amu) in Alpine snow samples during a 12-day no-precipitation period, 20.03-01.04.2017. We noticed four distinctive groups of ions with similar concentration trend over that time ($R^2 > 0.9$), suggesting common sources, chemistry processes, or transport pathways. The largest two groups of ions came from (a) surrounding forests (e.g. pinonic acid – associated with monoterpane oxidation) and (b) residential fires (levoglucosan – common biomass burning marker). The snow sample taken on 29th of March showed a change in the general concentration trend, consistent with a shift in wind direction, indicating different air mass origin. This is also in agreement with a change in atomic ratio metrics (O/C, H/C, OSC and nC), which also indicated that re-volatilization is the most important pathway of OM loss here, suggesting that the advected air was cleaner during this period. Dry deposition can be approximated by a mass balance model with a roughly constant deposition rate of $D = 206 \text{ ng mL}^{-1} \text{ day}^{-1}$ and a first order loss rate constant $k = 0.31 \text{ day}^{-1}$. Calculated deposition velocities were inconsistent with the idea that organic aerosols contribute the bulk of deposited OM, instead we suggest a dominant contribution of gas-phase sVOC over the OA in the total bulk organic matter. This all indicates that, at least for this site and location, snow-atmosphere DOM exchange processes are mostly driven by gas-phase sVOCs, for which equilibration with air is fast. This has implications for the reconstruction of recent atmospheric conditions by analysis of organics in the snow.

Data availability

Data are available via:
http://www.projects.science.uu.nl/atmosphereclimate/Data/Suplement_data_PTR-SNOW.xlsx

Author contribution

DM and RH designed the experiments and DM carried them out. LE provided the samples and meteorological data. DM prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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References


Figure 1: Meteorological data measured at Sonnblick station during the sampling: (a) temperature, (b) global radiation (c) wind direction, (d) relative humidity. Vertical lines represent the sampling time. Note the wind direction change in the period preceding the sampling at 2017-03-29.
Figure 2: Total concentration of organic ions and cumulative metrics of atomic ratio distribution. (a) Total concentration in ng mL\(^{-1}\), the line represents the fit from the simple deposition model explained in the text (Eq. 1); (b) H/C ratio, (c) O/C ratio, (d) N/C ratio, (e) oxidative state of carbon, (f) mean numbers of carbon. The error bars represent the standard deviation of three replicates.
Figure 3: Boxplots of concentration for ions representing four distinctive groups (tick line of a box represent the median, upper and lower lines maximum and minimum values): (a) ion m/z 115.070 - pinonic acid, (b) ion m/z 85.029 - levoglucosan, (c) ions m/z 99.008 and (d) ion m/z 159.065. The lines illustrate the change in the concentration over the time that is typical for each group. The first sample is taken just after the precipitation (snow symbol), followed by a non-precipitation period for the rest of the experiment (other weather symbols).
Figure A1: Light conditions and precipitation during the sampling period. (a) Global radiation [W m\(^{-2}\)] integrated for each day, (b) total daily sunshine duration in hours, (c) precipitation for the sampling period.
Table A1: Groups of ions as identified using linear regression model. Note that different thresholds/cutoffs of $R^2$ values are used to assign different ions to the groups (cutoffs: $R^2 > 0.98$, 0.98, 0.995, and 0.70, respectively)

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