

Responses to reviewers' comments for manuscript

Seasonal characteristics of organic aerosol chemical composition and volatility in Stuttgart, Germany

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We thank all the reviewers for their evaluation of the manuscript, and for their constructive feedback. Replies to the individual comments are directly added below them in italics. Please note that only references that are part of the replies to the comments are listed in the bibliography at the end of this document. References in copied text excerpts from the manuscript are not included in the bibliography. Page and line numbers refer to the original manuscript text.

Reviewer #1 (*responses in italics*)

This manuscript presents seasonal differences in organic aerosol loading, chemical

composition and volatility in Stuttgart, Germany using AMS and FIGAERO-CIMS measurements. They found that organic aerosols in the winter show lower volatilities and higher O:C compared to organic aerosols in the summer. Their dataset also provides information on sources of organic aerosols in the two seasons using identified species. Before this work is published in ACP, the authors need to provide careful clarification and further discussion of several important aspects in this manuscript. Please find the comments below.

General comments:

1. Were the filters that were collected in different seasons analyzed at different times of the year? If so, T_{max} calibration using compounds with known vapor pressures may be required to constrain the instrument variability. It is possible that T_{max} shifted for the same compounds due to differences in FIGAERO configuration and setup.

The filters, which were collected in different seasons, were analyzed at different times of the year. However, the instrument configuration and setup were kept exactly the same during these two measurements, and temperature is kept constant in our laboratory throughout the year. We therefore do not expect significant shifts in T_{max} due to experimental setup. However, as shown recently (Huang et al., 2018; Wang and Ruiz, 2018), CIMS thermograms and corresponding T_{max} can be influenced by different mass loadings on the filter. This was taken care of in our study by controlling the mass deposited on the filters by differing deposition times based on ambient concentrations of organic $PM_{2.5}$ measured concurrently by an AMS (compare lines 151-153 of the manuscript and specific comment 2 by reviewer 1 and minor comment 1 by reviewer 2).

2. If I understand correctly, the filters were set up in the temperature-controlled room as well. Is it possible that in the winter campaign, when particles were sampled from the cold ambient air onto the filters held in the 298 K room, compounds with higher vapor pressures (probably SVOCs) already evaporated? If so, this will lead to underestimation of the SVOC contribution in the winter.

For summer, the average ambient temperature during the deposition time (between 10:00 and 16:00) was 23.6 ± 1.7 °C, which is similar to the container temperature (25 °C). We therefore expect little effect of gaseous compounds condensing on or evaporating from the particles/filter during the summer period. For winter, the average ambient temperature during the deposition time (between 10:00 and 16:00) was lower

(2.3 ± 1.5 °C) than the container temperature (25 °C). We calculated a maximum temperature of ~ 19 °C for the air sample to reach potentially during deposition (Fitzer and Fritz, 1989). It is therefore possible that we will lose some highly volatile organic compounds during deposition in winter. For an attempt at characterizing these potential losses, we compared the CIMS mass spectra of chamber α -pinene SOA particles at room temperature (25 °C) and 5 °C (for both cases, the particle formation temperature and precursor concentrations were the same, and the CIMS was kept at room temperature; more information about the experimental setup can be found in Wagner et al. (2017) and Huang et al. (2018)). We find the mass spectra from these two experiments do not change significantly (Figure R1). In addition, thermograms (e.g. Figure 4) show the majority of organic compounds to start evaporating at desorption temperatures higher than 30 °C, with maximum desorption temperatures of >45 °C, even for SOA particles formed at -50 °C (Huang et al., 2018). We therefore assume that evaporation of highly volatile organic compounds during deposition in winter has a negligible influence on the main results of this study.

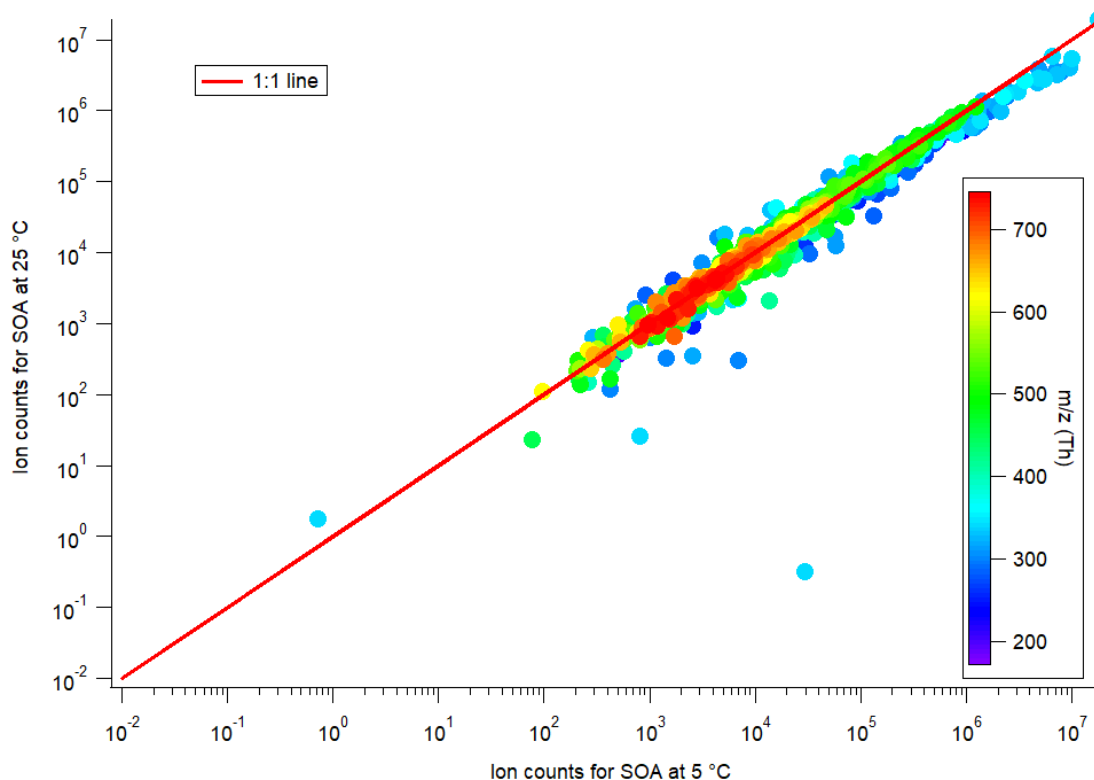


Figure R1. Scatter plot of particle phase signal for individual organic compounds of α -pinene SOA at 25 °C and 5 °C.

Specific comments:

1. I suggest using O:C without the word “ratio” because the “:” means “ratio”. The authors can just say “the oxygen to carbon ratio (O:C)” and subsequently just use O:C.

Changed as suggested throughout the manuscript.

2. How similar are mass loadings for different filters? I suggest providing the mean and the standard deviation.

The organic mass deposited on the filter (summer: $3.5 \pm 1.4 \mu\text{g}$; winter: $4.0 \pm 1.0 \mu\text{g}$) was determined based on concurrent AMS measurements. This information was added to lines 152-153 of the manuscript: “[...] in order to achieve similar organic mass loadings on the filter (summer: $3.5 \pm 1.4 \mu\text{g}$; winter: $4.0 \pm 1.0 \mu\text{g}$ based on concurrent AMS measurements during the deposition period) and to avoid mass loading effects [...]”.

3. In line 187-191. How statistically different are the values in the Summer vs those in the Winter? It looks like they all fall within the uncertainty range.

We agree with the reviewer that the differences between these values fall within the uncertainty range. Therefore, the sentences in lines 187-193 were rephrased as following: “Contributions of fragments containing only C and H atoms(CH), or also one oxygen atom (CHO_1), or more than one oxygen atoms ($\text{CHO}_{\text{gt}1}$), to total OA measured by AMS are similar for both seasons (CH: $29.4 \pm 3.9 \%$ for summer and $27.9 \pm 4.6 \%$ for winter; CHO_1 : $15.7 \pm 1.6 \%$ for summer and $15.3 \pm 1.9 \%$ for winter; $\text{CHO}_{\text{gt}1}$: $14.0 \pm 2.6 \%$ for summer and $15.8 \pm 2.8 \%$ for winter). Higher elemental oxygen-to-carbon ratios (O:C) measured by AMS were observed in winter (0.61 ± 0.12) than in summer (0.55 ± 0.10), implying that OA is more oxygenated in winter.”

4. In line 203, I suggest showing the time series plot of the OA concentration measured by the AMS versus the CHO_X measured by the FIGAERO CIMS.

As we mention in lines 166-168 and line 203 of the manuscript, we do not derive any atmospheric mass concentrations from these filter measurements, since the actual deposited area of aerosol particles on the filter was larger than the area of the desorption flow, and the deposition was not evenly distributed across the filter. Therefore, the absolute CHO_X mass concentrations are uncertain. We have, however,

calculated the correlation coefficients between the OA concentrations measured by AMS and the CHO_X measured by FIGAERO-CIMS (the latter in $\mu\text{g m}^{-3}$, assuming a sensitivity of 22 cps ppt⁻¹, Lopez-Hilfiker et al., 2016; Huang et al., 2018), and they were added to lines 203-205 of the manuscript: “[...] the time series of the sum of the deposited mass of all detected CHO_X compounds follows the trend of the OA concentrations measured by AMS quite well (Pearson’s R: 0.95 for summer and 0.96 for winter).”

5. In line 258, although filters were deposited during daytime, the CHON compounds can come from NO₃ oxidation from previous nights.

The sentence in lines 257-258 of the manuscript was rephrased as following: “The filters in Stuttgart were deposited during daytime, therefore the chemistry involved in the formation of these CHON compounds is likely dominated by the reaction of organic peroxy radicals (RO₂) with NO_x; contributions of oxidation products formed via nighttime NO₃ radical chemistry cannot be ruled out.”

6. In line 273, I suggest presenting the volatility calculation here instead of just citing the reference.

Volatility calculation formula added as suggested.

7. In Figure 3, is there a reason why compounds with $\log C^* > -1.5$ are all labeled as SVOC? I suggest changing to the commonly-used volatility classes (SVOC: $-0.5 < \log_{10} C^* < 2.5$; IVOC: $2.5 < \log_{10} C^* < 6.5$).

Based on reviewer 1’s and reviewer 2’s suggestion, we have added the IVOC category to Figure 3, and rephrased the corresponding text of the manuscript as following:

Lines 275-277: “Organic compounds with C_{sat} lower than $10^{-4.5} \mu\text{g m}^{-3}$, between $10^{-4.5} - 10^{-0.5} \mu\text{g m}^{-3}$, between $10^{-0.5} - 10^{2.5} \mu\text{g m}^{-3}$, and between $10^{2.5} - 10^{6.5} \mu\text{g m}^{-3}$ are termed extremely low volatile organic compounds (ELVOC), low volatile organic compounds (LVOC), semi-volatile organic compounds (SVOC), and intermediate volatile organic compounds (IVOC), respectively (Donahue et al., 2009).”

Lines 285-288: “In winter we observe much lower contributions of IVOC with C_{sat} between $10^5 - 10^6 \mu\text{g m}^{-3}$ in the particle phase. However, we may also have contributions from thermal decomposition products of oligomers to these low-molecular weight

compounds [...]”.

8. The paragraph starting in Line 141 is too long. I suggest breaking it into two or three shorter paragraphs.

This paragraph was changed into two shorter paragraphs as suggested.

Reviewer #2 (responses in italics)

Huang et al. present a study investigating ambient organic aerosol in a German city with high air pollution for European standards. The combined information from two mass spectroscopy methods, AMS and FIGAERO-CIMS, gives insights into organic aerosol mass loadings, molecular composition, and apparent particle volatility. The study is well designed and enhances the current understanding of seasonal variability in the investigated organic aerosol properties. However, a few issues need to be addressed and discussed in the manuscript.

1.) The description of the filter collection suggests that the filters were collected inside the measurement container at ~298K. This would be ~25 °C warmer than the average ambient temperature in winter leading to a substantial evaporation of semi volatile compounds during sample collection even with the shortest collection times. The opposite could happen on hot summer days when the outside temperature is higher than in the container. Gas phase compounds would condense on the particles and filter increasing the observed volatile fraction. This needs to be discussed.

Please see response to the general comment 2 of reviewer 1.

2.) It should be clearly stated in the text that the C* values from the elemental composition parameterization are calculated at a reference temperature. The “acting” C* values at the ambient temperature in summer and winter are different and with this the classification of compounds into EL/L/S/IVOC. It is possible to calculate the shift in C* values due to the different temperatures similar to Stolzenburg et al. 2018 and present them at least in the SI material.

We thank the reviewer for this suggestion. We have recalculated the VBS distributions

in Figure 3 and Figure S9 by taking the difference in ambient temperature between summer and winter into consideration. As a result, the VBS distribution for winter is shifted to lower volatility bins, making one of our main conclusions (winter OA particles are less volatile) even more clear. We have added/rephrased the corresponding text of the manuscript as following:

Lines 272-274: “[...] parameterized for each CHO and CHON compound using the approach by Li et al. (2016):

$$\log_{10} C_{sat}(298 \text{ K}) = (n_C^0 - n_C)b_C - n_O b_O - 2 \frac{n_C n_O}{n_C + n_O} b_{CO} - n_N b_N \quad (1)$$

and then corrected for the summer (24 °C) and winter (2 °C) periods (Stolzenburg et al., 2018; Donahue et al., 2011; Epstein et al., 2010):

$$\log_{10} C_{sat}(T) = \log_{10} C_{sat}(298 \text{ K}) + \frac{\Delta H_{vap}}{R \ln(10)} \left(\frac{1}{298} - \frac{1}{T} \right) \quad (2)$$

$$\Delta H_{vap}(\text{kJ mol}^{-1}) = -5.7 \cdot \log_{10} C_{sat}(298 \text{ K}) + 129 \quad (3)$$

[...].”

Lines 292-294: “[...] higher mass contributions in winter (LVOC: 37.0 ± 2.2 %; ELVOC: 15.9 ± 3.5 %) than in summer (LVOC: 22.6 ± 2.5 %; ELVOC: 4.8 ± 1.2 %; see Fig. 3b–c). The average mass-weighted $\log_{10} C_{sat}$ value is $0.97 \pm 0.28 \mu\text{g m}^{-3}$ for summer and $-1.2 \pm 0.48 \mu\text{g m}^{-3}$ for winter.”

3.) Generally, a little bit more information about the C* parameterization should be added. Especially a note that this assumes that each detected elemental composition is indeed only one isomer with one C* value and that no thermal decomposition occurred. The ion thermograms shown in Figure S10 indicate that this assumption is not universally valid, and you do discuss this later in the text. But in my opinion, this needs to be pointed out already when introducing the parameterization as it impacts the interpretation of the calculated C* values.

The C_{sat} parameterization was developed for bulk aerosol molecular composition based on volatility properties of functional groups (Donahue et al., 2011). When applied to individual molecules, with the only input being the molecular composition, isomers cannot be differentiated, as pointed out by the reviewer. It is also correct that the C_{sat} parameterization cannot tell if a compound in the particle phase is a thermal

fragmentation product. We can only get this information when we look at e.g. the thermograms. To clarify these points, the following information was added to lines 273-274 of the manuscript: “We stress here that isomers cannot be differentiated with the C_{sat} parameterization (Donahue et al., 2011) and that thermal fragmentation of organic compounds (Lopez-Hilfiker et al., 2015; Huang et al., 2018) during particle desorption with the FIGAERO can bias the C_{sat} results towards higher volatilities. This will be discussed later. The CHO and CHON compounds were then grouped [...]”.

4.) The specific borders for the volatility categories vary between publications. But more recent ones (Donahue et al 2009) defines SVOC as -0.5 to $2.5 \log_{10}C^*$ and IVOC from 2.5 to $6.5 \log_{10}C^*$. Is there a reason for your different choice of categories?

Based on reviewer 1's and reviewer 2's suggestion, we have added the IVOC category to Figure 3, and rephrased the corresponding text of the manuscript. The changes in the manuscript can be found in the response to specific comment 7 by reviewer 1.

5.) The dominant wind direction changes with the seasons from east to south-west coming over the inner city of Stuttgart including busy roads and the main train station with a big construction site. However, when discussing the seasonal changes in OOA sources this is not mentioned at all. Are the emissions so well mixed in that region that no influence on the SOA is expected?

We thank the reviewer for this input. We double-checked the mass contribution of the toluene oxidation product $C_7H_8O_5$, a marker compound for traffic emissions, as a function of wind direction for both seasons. Higher contributions are observed when the main wind direction is from the inner city of Stuttgart. The sentence in lines 238-239 of the manuscript was rephrased as following: “[...] with higher contributions in summer (when the main wind direction was from the inner city of Stuttgart, see Fig. S3) than in winter, indicating anthropogenic influences related to traffic or industrial activities (EPA, 1994).”

Minor comments:

+ What were the mass loadings on the collected filters? Also, summer and winter samples had ~20% different amounts of BC which is “invisible” to FIGAERO. Was the collected aerosol mass corrected for that?

Compare response to specific comment 2 by reviewer 1. The organic mass deposited on the filter (summer: $3.5 \pm 1.4 \mu\text{g}$; winter: $4.0 \pm 1.0 \mu\text{g}$) was determined based on concurrent AMS measurements.

+ In Figure S10, distinct changes in the ion thermograms are visible. However, due to the multitude of lines and the limited number of colours it is impossible to identify if e.g. any of the 3 dominant green lines in panel (a) are the same ion as the bimodal green line in panel (b). Adding the ion compositions as labels to a few ion thermograms may make reading this figure easier and may reveal some interesting details.

We thank the reviewer for this suggestion. We have added labels to the lines of a few dominant ion compositions to make this figure clearer.

+ 1808 out of 2138 ions were of type CHO_x. What were the other ones?

The other ions are the reagent ion (I⁻), inorganic compounds clustered with I⁻, organic compounds and inorganic compounds not clustered with I⁻, etc. Organic compounds not clustered with I⁻ (289 compounds) were excluded in this analysis, as their ionization mechanism is highly uncertain. Assuming the same sensitivity as for the organic compounds detected as I⁻-clusters, they only account for <0.03 % of the total particulate CHO_x mass.

Technical comments:

page 2 line 63 “suggested” should be “suggesting”

We replaced “suggested” by “suggest”.

page 4 line 127 “298 K” authors use Kelvin here and everywhere else temperature is given in Celsius. Should be changed to Celsius.

Done.

page 4 line 148 “filters were deposited” Particles are deposited on the filters, but the filters are not deposited in the filter holders.

Sentence rephrased as following: “Aerosol particles were deposited during daytime (between 10:00 and 16:00) on polyolytetrafluoroethylene (PTFE) filters (Zefluor PTFE

membrane, 2 μm pore size, 25 mm diameter, Pall Corp.) which were prebaked at 200 °C in an oven overnight and stored in clean filter slides, using a stainless steel filter holder [...].”

page 5 line 175 “ m^{-3} ” is broken over lines

Corrected.

page 5 line 189 “%” is broken in next line

Corrected.

page 10 line 360 “Potential possible reason” use either potential or possible.

We replaced “Potential possible reason” by “Potential reason”.

References:

- Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos Chem Phys*, 11, 3303–3318, <https://doi.org/10.5194/acp-11-3303-2011>, 2011.
- Fitzer, E., and Fritz, W.: *Technische Chemie*, Third ed., Springer, Berlin, 140 pp., 1989.
- Huang, W., Saathoff, H., Pajunoja, A., Shen, X. L., Naumann, K.-H., Wagner, R., Virtanen, A., Leisner, T., and Mohr, C.: α -Pinene secondary organic aerosol at low temperature: chemical composition and implications for particle viscosity, *Atmos Chem Phys*, 18, 2883–2898, <https://doi.org/10.5194/acp-18-2883-2018>, 2018.
- Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurtén, T., and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmos Meas Tech*, 9, 1505–1512, <https://doi.org/10.5194/amt-9-1505-2016>, 2016.
- Wagner, R., Höhler, K., Huang, W., Kiselev, A., Möhler, O., Mohr, C., Pajunoja, A., Saathoff, H., Schiebel, T., Shen, X. L., and Virtanen, A.: Heterogeneous ice nucleation of α -pinene SOA particles before and after ice cloud processing, *J Geophys Res-Atmos*, 122, 4924–4943, <https://doi.org/10.1002/2016JD026401>, 2017.
- Wang, D. S., and Ruiz, L. H.: Chlorine-initiated oxidation of *n*-alkanes under high-NO_x conditions: insights into secondary organic aerosol composition and volatility using

a FIGAERO-CIMS, *Atmos Chem Phys*, 18, 15535–15553,
<https://doi.org/10.5194/acp-18-15535-2018>, 2018.

Seasonal characteristics of organic aerosol chemical composition and volatility in Stuttgart, Germany

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Abstract. Chemical composition and volatility of organic aerosol (OA) particles were investigated during July–
15 August 2017 and February–March 2018 in the city of Stuttgart, one of the most polluted cities in Germany. Total non-refractory particle mass was measured with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; hereafter AMS). Aerosol particles were collected on filters and analyzed in the laboratory with a filter inlet for gases and aerosols coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (FIGAERO-HR-ToF-CIMS; hereafter CIMS), yielding the molecular composition of oxygenated OA (OOA)
20 compounds. While the average organic mass loadings are lower in the summer period ($5.1 \pm 3.2 \mu\text{g m}^{-3}$) than in the winter period ($8.4 \pm 5.6 \mu\text{g m}^{-3}$), we find relatively larger mass contributions of organics measured by AMS in summer ($68.8 \pm 13.4 \%$) compared to winter ($34.8 \pm 9.5 \%$). CIMS mass spectra show OOA compounds in summer have O:C ~~ratios~~ of 0.82 ± 0.02 and are more influenced by biogenic emissions, while OOA compounds in winter have O:C ~~ratios~~ of 0.89 ± 0.06 and are more influenced by biomass burning emissions. Volatility parametrization
25 analysis shows that OOA in winter is less volatile with higher contributions of low volatile organic compounds (LVOC) and extremely low volatile organic compounds (ELVOC). We partially explain this by the higher contributions of compounds with shorter carbon chain lengths and higher number of oxygen atoms, i.e. higher O:C ~~ratios~~ in winter. Organic compounds desorbing from the particles deposited on the filter samples also exhibit a shift of signal to higher desorption temperatures (i.e. lower apparent volatility) in winter. This is consistent with
30 the relatively higher O:C ~~ratios~~ in winter, but may also be related to higher particle viscosity due to the higher contributions of larger molecular-weight LVOC and ELVOC, interactions between different species and/or particles (particle matrix), and/or thermal decomposition of larger molecules. The results suggest that whereas lower temperature in winter may lead to increased partitioning of semi-volatile organic compounds (SVOC) into the particle phase, this does not result in a higher overall volatility of OOA in winter, and that the difference in

35 sources and/or chemistry between the seasons plays a more important role. Our study provides insights into the seasonal variation of molecular composition and volatility of ambient OA particles, and into their potential sources.

1 Introduction

Air pollution has significant impacts on human health (D'Amato et al., 2014), visibility (Majewski et al., 2014), and also interacts with climate change (Seinfeld and Pandis, 2016). Due to rapid urbanization, industrialization,
40 and growing human population, air quality in urban environments has become a severe issue in more and more cities all over the world, particularly in densely populated megacities (Guttikunda et al., 2014; Chan and Yao, 2008; Mayer, 1999; Marlier et al., 2016). Air quality in urban environments is influenced by emissions, e.g. from sources such as industrial processes, automobile traffic, and domestic heating, and also by meteorological conditions (e.g. solar radiation, wind, temperature, precipitation), atmospheric dispersion, chemical
45 transformation, location, and topography (D'Amato et al., 2014; Baumbach and Vogt, 2003; Kinney, 2018). Moreover, air pollution is not limited within the boundaries of urban areas, but can be transported over long distances and contribute to background pollution on the regional to global scale (Baklanov et al., 2016).

The most abundant air pollutants are nitrogen dioxide (NO₂), ozone (O₃), sulfur dioxide (SO₂), and particulate matter (PM; D'Amato et al., 2014). Despite its abundance and important impacts on climate and health, PM
50 sources, physicochemical transformation, and fate in the atmosphere still remain to be fully understood in urban areas. This is especially true for the organic fraction (Hallquist et al., 2009; Fuzzi et al., 2015). Organic aerosol (OA) often makes up a significant fraction of submicron particulate mass in urban areas (Hallquist et al., 2009; Jimenez et al., 2009). OA can be directly emitted into the atmosphere from sources such as fossil fuel combustion and biomass burning (primary organic aerosol, POA), or be formed in the atmosphere from the oxidation of gas-
55 phase precursors (secondary organic aerosol, SOA). POA is dominated by vehicular emissions in urban environments (Bhattu, 2018). SOA, which dominates the global budget of OA (Shrivastava et al., 2015), can be of biogenic and/or anthropogenic origin with biogenic sources dominating on a global scale (Heald et al., 2008). SOA also generally makes up the biggest mass fraction of OA in urban areas, as observed e.g. in Mexico City (Volkamer et al., 2006; Kleinman et al., 2008), some heavily urbanized areas in the U.S. (de Gouw et al., 2005; Zhang et al.,
60 2005), and during the severe haze pollution events in the big cities in China (Huang et al., 2014). In European cities, most of the OA mass observed consists of oxygenated compounds (oxygenated organic aerosol, OOA), and most OOA is of secondary origin and thus SOA (Lanz et al., 2007; Jimenez et al., 2009; Zhang et al., 2007; El Haddad et al., 2013). Robinson et al. (2007) suggested that semi-volatile and intermediate VOC may play a dominant role in SOA formation in urban locations. In order to design effective mitigation strategies for urban air
65 pollution, it is therefore of great importance to identify the sources of OA, and especially SOA, in urban areas.

Source apportionment of OA has been advanced by the application of positive matrix factorization (PMF) to aerosol mass spectrometer (AMS) or aerosol chemical speciation monitor (ACSM) data (Canonaco et al., 2015; Crippa et al., 2014; Ulbrich et al., 2009). However, the distinction of OOA sources (biogenic or anthropogenic) by AMS- or ACSM-PMF remains difficult due to excessive fragmentation and thus loss of molecular information in
70 the AMS or ACSM. The recent advent of new methods provides more insights into the molecular composition of OA, such as linear trap quadrupole (LTQ) Orbitrap mass spectrometry (Daellenbach et al., 2019), filter inlet for gases and aerosols coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (FIGAERO-HR-ToF-CIMS; Huang et al., 2019), and the newly developed extractive electrospray ionization time-of-flight

75 mass spectrometer (EESI-ToF; Qi et al., 2019). Whereas AMS-/ACSM-PMF is not directly able to reveal OOA
sources, it separates OOA into factors with different degrees of oxygenation and thus presumed volatility, such as
semi-volatile oxygenated organic aerosol (SV-OOA) and low-volatile oxygenated organic aerosol (LV-OOA;
Ulbrich et al., 2009; Jimenez et al., 2009; Lanz et al., 2007). Abovementioned state-of-the-art instruments (e.g.
Orbitrap, FIGAERO-HR-ToF-CIMS, EESI-ToF) enable the link between the molecular composition of OA and
80 its physicochemical properties by use of molecular information in volatility parameterizations to calculate effective
saturation mass concentrations (C_{sat}) of different compounds (Li et al., 2016; Donahue et al., 2011). This can be
used to define e.g. volatility basis sets (VBS), a framework that has been proposed and widely used for grouping
the organic compounds into volatility classes (or bins) based on their C_{sat} values (Donahue et al., 2006; 2011; 2012;
Cappa and Jimenez, 2010).

Volatility determines whether an organic compound partitions into the particle phase and contributes to OA
85 particulate mass. It is thus an important physicochemical property of OA that influences the lifetime of OA and
with that air quality. As a consequence of the connection between a compound's molecular composition and
structure with its volatility, different types of OA fall into different categories of volatility. For e.g. OA measured
in Mexico City, biomass burning OA (BBOA) was found to be the most volatile, followed by hydrocarbon-like
OA (HOA), SV-OOA, and LV-OOA (Cappa and Jimenez, 2010). Isoprene epoxydiol (IEPOX) derived SOA was
90 observed to have the highest volatility of the OA measured in the southeastern U.S. (Lopez-Hilfiker et al., 2016).
As ambient particles generally consist of a matrix of thousands of different compounds, OA apparent volatility can
also be influenced by particle-phase diffusion limitations, e.g. due to amorphous phase state and/or the presence
of a high mass fraction of oligomers (Vaden et al., 2011; Roldin et al., 2014; Cappa and Wilson, 2011; Yli-Juuti
et al., 2017; Huang et al., 2018). Overall, the relationship between OA molecular composition and its volatility,
95 and how this relationship is influenced by environmental conditions and particle physicochemical properties, are
not well characterized, particularly for field data.

Here we present detailed chemical composition measurements of OA from July–August 2017 and February–
March 2018 in the city of Stuttgart, Germany. We investigate the molecular composition and volatility of OA
particles, and discuss their seasonal variations as well as their potential sources. Stuttgart, a city located in
100 southwest Germany with a population of more than 600000 in a metropolitan area of 2.6 million inhabitants, is an
important industrial center in Germany. It is situated in the steep valley of the Neckar river, in a “bowl” surrounded
by a variety of hills, small mountains, and valleys. The complex topography can prevent the dispersion of air
pollutants, and the location is characterized by low wind speeds and weak air circulation (Schwartz et al., 1991;
Hebbert and Webb, 2012). Air quality has been a long-standing concern in Stuttgart, as it is one of the most polluted
105 cities in Germany (Schwartz et al., 1991; Süddeutsche Zeitung, 2016; Office for Environmental Protection, 2016);
however only few detailed studies are available. For the year 2017, the state environmental protection agency,
LUBW (Landesanstalt für Umwelt Baden-Württemberg), attributes 58 % of the annual mean PM_{10} at their
monitoring station “Am Neckartor” in downtown Stuttgart to road traffic (45 % abrasion, 7 % exhaust, 6 %
secondary formation), 8 % to small and middle size combustion sources, and 27 % to regional background (LUBW,
110 2019). Mayer (1999) showed the temporal variability of urban air pollutants (NO , NO_2 , O_3 , and O_x (sum of NO_2
and O_3)) caused by motor traffic in Stuttgart based on more than 10 years of observations, with higher NO
concentrations in winter and higher O_x concentrations in summer. Bari et al. (2011) characterized air pollutants
such as polycyclic aromatic hydrocarbons (PAHs) and other wood smoke tracer compounds (levoglucosan,
methoxyphenols) from wood-burning in the residential areas of Dettenhausen (about 30 km south of Stuttgart) and

115 attributed 57% of the ambient PM₁₀ pollution to hardwood combustion during wintertime. Our study therefore adds an important piece of information on air quality in Stuttgart by investigating the chemical composition, physicochemical properties, and potential sources of the OA particles in this city.

2 Methodology

2.1 Measurement site

120 We performed particle and trace gas measurements from July 5th to August 17th, 2017 and from February 5th to March 5th, 2018 in the city of Stuttgart, Germany (48°47'55.1"N, 9°12'13.5"E). The measurement site was located near the park "Unterer Schlossgarten" of Stuttgart and can be classified as an urban background site. The only nearby source is a parcel distribution center with delivery trucks passing by with low frequency during daytime. It was set up on a bridge over a train track about 2.2 km northeast of the Stuttgart main station with frequent train traffic (electric). The air quality monitoring station of LUBW, "Am Neckartor", is 1.5 km southwest and one of the busiest roads in Stuttgart, B14 (LUBW, 2019), is about 360 m southwest of the measurement location.

125 All instruments were set up in a temperature-controlled measurement container kept at ~~~298 K~~25 °C. The container has been described elsewhere (Huang et al., 2019; Shen et al., 2018). All sampling inlets were located 3.7 m above ground level and 1.5 m above the container roof. An overview of instruments and parameters measured is given in Table S1 in the Supplement.

2.2 Meteorological, particle and trace gas measurements

Temperature, relative humidity, wind direction, wind speed, global radiation, pressure, and precipitation data were measured by a meteorological sensor (WS700, Lufft GmbH; see Table S1). The main wind directions during the campaign were southwest during the summer and northeast during the winter. Trace gases (O₃, CO₂, NO₂, SO₂) were measured with the corresponding sensors (Table S1). Particle number concentrations were recorded with two condensation particle counters (a CPC3022, measuring particles with mobility diameters larger than 7 nm, and a CPC3776, measuring particles with mobility diameters larger than 2.5 nm, both TSI Inc.). Particle size distributions were measured with a nanoscan scanning mobility particle sizer (NanoScan SMPS3910, measuring particles with mobility diameters between 10 nm and 420 nm, TSI Inc.). Black carbon (BC) concentrations were measured with an Aethalometer (AE51, Aethlabs Inc.).

140 A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., hereafter AMS) equipped with an aerodynamic high-pressure lens (Williams et al., 2013) was deployed to continuously measure total non-refractory particle mass as a function of size (up to 2.5 μm particle aerodynamic diameter d_{va}) at a time resolution of 0.5 min. The AMS inlet was connected to a PM_{2.5} head (flow rate 1 m³ h⁻¹, Comde-Derenda GmbH) and a stainless steel tube of 3.45 m length (flow rate 0.1 L min⁻¹, residence time 0.9 s). AMS data were analyzed with the AMS data analysis software packages SQUIRREL (version 1.60C) and PIKA (version 1.20C).

145 Aerosol particles were deposited during daytime (between 10:00 and 16:00) on Ppolytetrafluoroethylene (PTFE) filters (Zefluor PTFE membrane, 2 μm pore size, 25 mm diameter, Pall Corp.), which were prebaked at 200 °C in an oven overnight and stored in clean filter slides, ~~were deposited during daytime (between 10:00 and 16:00)~~ using a stainless steel filter holder connected to a PM₁₀ head (flow rate 1 m³ h⁻¹, Comde-Derenda GmbH) via a stainless steel tube and conductive tubing of 2.85 m length (flow rate 8.7 L min⁻¹ (summer) or 10 L min⁻¹

(winter), residence time 0.75 s (summer) or 0.72 s (winter)). Deposition times were varied (20–260 min) based on ambient organic mass concentrations in order to achieve similar organic mass loadings concentrations deposited on the filter (summer: $3.5 \pm 1.4 \mu\text{g}$; winter: $4.0 \pm 1.0 \mu\text{g}$ based on concurrent AMS measurements during the deposition period) and to avoid mass loading effects (Huang et al., 2018; Wang and Ruiz, 2018). A total of 21 filter samples were collected in the summer and 10 in the winter. After deposition, each filter sample was stored in a filter slide, wrapped in aluminium foil, and then stored in a freezer at $-20 \text{ }^\circ\text{C}$ until analysis in the laboratory by a filter inlet for gases and aerosols coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (FIGAERO-HR-ToF-CIMS, Aerodyne Research Inc., hereafter CIMS) deploying iodide (I^-) as reagent ion. Particles collected on the filter were thermally desorbed by a flow of ultra-high purity (99.999 %) nitrogen heated to $200 \text{ }^\circ\text{C}$ over the course of 35 min. The resulting mass spectral desorption signals are termed thermograms (Lopez-Hilfiker et al., 2014). For individual compounds, signals that peak at distinct desorption temperatures (T_{max}) correlate with their saturation vapor pressure (Lopez-Hilfiker et al., 2015; Mohr et al., 2017); however, interference from isomers with different vapor pressures or thermal fragmentation of larger oligomeric molecules can lead to more complex, multimodal thermograms (Lopez-Hilfiker et al., 2015). Integration of thermograms of individual compounds yields their total particle-phase signal. We assume the sensitivity to be the same for all compounds measured by CIMS (Huang et al., 2019) and convert the signal to mass so that the molecular weight of a compound is taken into account. In this study we do not attempt to derive any atmospheric mass concentrations from these filter measurements, since the actual deposited area of aerosol particles on the filter was larger than the area of the desorption flow, and the deposition was not evenly distributed across the filter. We therefore focus on the molecular composition and volatility distributions of OA particles, their seasonal variations, and the interpretation of these observations for potential sources. In order to correct for filter backgrounds, we collected prebaked clean filters from the measurement site without deposition flow for both winter and summer. Field blank samples for winter and summer were analyzed by CIMS in the laboratory and used for background subtraction.

3 Results and discussion

3.1 Particulate OA mass loadings

We observe higher total non-refractory $\text{PM}_{2.5}$ mass concentrations measured by AMS in winter ($27.0 \pm 11.9 \mu\text{g m}^{-3}$, average ± 1 standard deviation) than in summer ($7.1 \pm 3.3 \mu\text{g m}^{-3}$) at this measurement site (Figure S1). Similar observations were also made for other central European locations, e.g. Zurich, Switzerland (Jimenez et al., 2009; Zhang et al., 2007). Reasons for this observation are differences in emission sources between the seasons, boundary layer height dynamics, and/or meteorological conditions (Canonaco et al., 2015; Daellenbach et al., 2019; Baumbach and Vogt, 2003). The surface inversion, which develops by radiative cooling of the ground and is dissolved from the bottom up by solar radiation and heating up of the ground (Baumbach and Vogt, 2003), is expected to be stronger in winter due to lower ambient temperature and global radiation (Figure S2), weaker air circulation (i.e. wind speed, Figure S3), and less precipitation. Air pollutants are therefore more likely to be kept beneath this inversion and have longer local residence time in the atmosphere in winter. While the average organic mass loadings measured by AMS are lower in summer ($5.1 \pm 3.2 \mu\text{g m}^{-3}$) than in winter ($8.4 \pm 5.6 \mu\text{g m}^{-3}$; see Fig. S1), organics contribute relatively more mass to total non-refractory $\text{PM}_{2.5}$ measured by AMS in summer ($68.8 \pm$

190 13.4 %) compared to winter (34.8 ± 9.5 %; see Fig. S1). Contributions of fragments containing only C and H atoms
(CH)_x or also one oxygen atom (CHO₁)_x or more than one oxygen atoms (CHO_{gt1})_x to total OA measured by AMS
are similar ~~for both seasons, with slightly higher contributions of CH and CHO₁ in summer~~ (CH: 29.4 ± 3.9 % ~~for
summer and 27.9 ± 4.6 % for winter~~; CHO₁: 15.7 ± 1.6 % ~~for summer and 15.3 ± 1.9 % for winter~~; CHO_{gt1}: 14.0
 ~~± 2.6 % for summer and 15.8 ± 2.8 % for winter~~) ~~compared to winter (CH: 27.9 ± 4.6 %; CHO₁: 15.3 ± 1.9 %) and~~
195 ~~slightly lower contributions of CHO_{gt1} in summer (14.0 ± 2.6 %) compared to winter (15.8 ± 2.8 %).~~ This is also
~~reflected in the higher elemental oxygen-to-carbon (O:C)-ratios (O:C) measured by AMS were observed~~ in
winter (0.61 ± 0.12) than in summer (0.55 ± 0.10). ~~The results implying~~ that OA is more oxygenated in winter.
Due to fragmentation of organic molecules during the ionization process in the AMS, molecular information of
OA is lost. This information is able to retrieve from the filter samples analyzed by CIMS. Due to the fact that the
200 iodide CIMS is selective towards polarizable and thus oxygenated compounds (Lee et al., 2014), the organic
compounds measured by CIMS are oxygenated organic aerosol (OOA). In the next section we will discuss the
molecular composition of OOA measured by CIMS.

3.2 Molecular composition of OOA

Figure 1a and 1c show a comparison of CIMS mass spectral patterns of all CHOX compounds ($C_{x \geq 1}H_{y \geq 1}O_{z \geq 1}X_{0-n}$
205 detected as clustered with I⁻, with X being different atoms like N, S, Cl, or a combination thereof; 1808 out of a
total of 2138 identified compounds and accounting for >96 % of total signals), and CHON compounds only for
summer and winter (panels b, d). Mass spectra shown were normalized to the sum of the deposited mass of all
detected CHOX compounds. Although the absolute CHOX mass concentrations are uncertain, the time series of
the sum of the deposited mass of all detected CHOX compounds follows the trend of the OA concentrations
210 measured by AMS quite well (Pearson's R: 0.95 for summer and 0.96 for winter). CHO compounds (compounds
containing only C, H, and O atoms) are the dominating group and make up 79.4 ± 3.3 % of total CHOX in summer
and 74.6 ± 2.2 % of total CHOX in winter, followed by CHON compounds with 20.1 ± 3.4 % of total CHOX in
summer and 24.6 ± 2.4 % of total CHOX in winter. CHON compounds contribute relatively more mass in winter
(also reflected in the organic bound nitrate fraction (OrgNO₃, i.e., organonitrates) from AMS data (summer: $0.3 \pm$
215 $0.2 \mu\text{g m}^{-3}$; winter: $1.7 \pm 1.1 \mu\text{g m}^{-3}$), determined assuming an NO₂⁺/NO⁺ ratio of OrgNO₃ of 0.1; Farmer et al.,
2010; Kiendler-Scharr et al., 2016; see Figure S4 and S5), while CHO compounds contribute relatively more mass
in summer. This is possibly due to the higher daytime O₃ concentrations in summer and higher daytime NO₂
concentrations in winter (Figure S6) as well as different emission sources. Contributions of some biogenic marker
compounds are higher in summer (Fig. 1a–b), particularly C₈H₁₂O₅ (molecular formula corresponding to 2-
220 hydroxyterpenylic acid identified in α-pinene SOA by Claeys et al., 2009; Kahnt et al., 2014) and C₈H₁₁O₇N
(identified in the laboratory as α-pinene oxidation product by Lee et al., 2016). We also observe good correlations
(Pearson's R: 0.85; Figure S7a) between our summer mass spectra and the summer daytime mass spectra acquired
in 2016 near Karlsruhe (a city in southwest Germany, about 70 km northwest of Stuttgart; Huang et al., 2019),
indicative of the regional nature of sources and/or chemistry in summer. We therefore conclude that the majority
225 of the precursor VOC for OOA presented here in summer are most likely of biogenic origin, despite the urban
location of the measurement site.

Significantly higher contributions of C₆H₁₀O₅ (molecular formula corresponding to levoglucosan, a tracer for
biomass burning; Saarnio et al., 2010) are observed in winter compared to summer (Fig. 1c). Besides, higher
contributions of C₆H₅O₃N, C₇H₇O₃N, C₆H₅O₄N, and C₇H₇O₄N (molecular formulae corresponding to nitrated

230 phenols, tracers for biomass burning identified by Mohr et al., 2013) are also observed in winter (Fig. 1d). Some
of these compounds were also observed in the central European city of Zurich, Switzerland in winter (Daellenbach
et al., 2019). We cannot completely exclude that these compounds may have contributions from vehicular
emissions (Tong et al., 2016). However, significantly higher contributions of levoglucosan and nitrated phenols
indicate that biomass burning emissions are a dominant contributor to OOA in Stuttgart in winter. In addition to
235 compounds from biomass burning, we also observe similar patterns of contributions of CHON compounds with
 m/z between 300–400 Th (also dominated by $C_8H_{11}O_7N$), and high contributions of $C_8H_{12}O_4$ (molecular formula
corresponding to terpenylic acid identified in α -pinene SOA by Claeys et al., 2009) and $C_8H_{12}O_6$ (molecular
formula corresponding to 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) in α -pinene SOA identified by
Szmigielski et al., 2007; Müller et al., 2012) in winter. After removing the five biomass burning tracer compounds
240 ($C_6H_{10}O_5$, $C_6H_5O_3N$, $C_7H_7O_3N$, $C_6H_5O_4N$, and $C_7H_7O_4N$), good correlations (Pearson's R: 0.70; Figure S7b) are
observed between summer mass spectra and winter mass spectra, indicating that biogenic emissions may also
contribute significantly to the OOA particulate mass in winter. In addition, in both summer and winter,
contributions of $C_7H_8O_5$ (identified in the laboratory as toluene oxidation product by Hinks et al., 2018; Molteni
et al., 2018) are also observed, with relatively-higher contributions in winter-summer (when the main wind direction
245 was from the inner city of Stuttgart, see Fig. S3) than in summer-winter, indicating anthropogenic influences related
to traffic or industrial activities (EPA, 1994).

In the following we will have a closer look at the bulk molecular composition for winter and summer daytime
OOA measured by CIMS. Consistent with the O:C ~~ratios~~-measured by AMS (winter: 0.61 ± 0.12 ; summer: $0.55 \pm$
0.10), higher O:C ~~ratios~~ are also observed by CIMS in winter (0.89 ± 0.06) compared to summer (0.82 ± 0.02),
250 despite lower ambient temperature and weaker global radiation in winter (see Fig. S2). The AMS O:C ~~ratios~~ are
expected to be lower than those of the organic compounds measured by iodide CIMS, as the latter is selective
towards oxygenated compounds (Lee et al., 2014). Mass contributions of CHO and CHON with different number
of oxygen atoms per molecule to total CHOX compounds as a function of the number of carbon atoms are shown
in Figure 2. C_8HO compounds exhibit the highest mass contributions in summer, while C_6HO compounds surpass
255 C_8HO compounds in winter due to the large contributions of levoglucosan ($C_6H_{10}O_5$; see Fig. 2a and 2c). The mass
distribution of CHO compounds in winter also exhibits higher contributions from compounds with 1–6 carbon
atoms and 4, 5 (levoglucosan), 7–9 oxygen atoms, while in summer higher contributions from compounds with 7–
10 carbon atoms and 5–7 oxygen atoms are observed. This indicates that the slightly higher oxidation levels (or
O:C ~~ratios~~) in winter are related to both shorter carbon chain lengths and higher number of oxygen atoms of the
OOA compounds compared to summer (see also Figure S8). In addition, relatively higher contributions of
260 compounds with larger number of carbon atoms (C16–23) are also observed in winter (Fig. 2). A similar pattern
can be found for CHON compounds (Fig. 2b and 2d). $C_{9-10}HON$ compounds exhibit the highest mass contributions
in summer, similar to what we observed in 2016 in summer near the city of Karlsruhe, where these compounds
were determined to originate from biogenic VOC emissions (Huang et al., 2019). ~~However, †~~The filters in Stuttgart
265 were deposited during daytime, therefore the chemistry involved in the formation of these CHON compounds is
likely involves-dominated by the reaction of organic peroxy radicals (RO_2) with NO_x ; contributions of oxidation
products formed via night-time instead of night-time- NO_3 radical chemistry cannot be ruled out. In winter, C_6HON
relative contributions exceed those from $C_{9-10}HON$ compounds, similar to the pattern of CHO compounds,
indicative of similar sources (biomass burning emissions). Furthermore, in summer CHON compounds are
270 dominated by compounds with 6–9 oxygen atoms, while in winter significantly higher contributions from

compounds with 5–7 carbon atoms and 3–4 oxygen atoms are observed, mostly due to nitrated phenols (C_{6–7}H₅,
O_{3–4}N; see also Fig. 1d).

The results imply the importance of non-fossil OA formation from biogenic and/or biomass burning influences
in different seasons even in a city with high traffic emissions mainly based on fossil fuel combustion (LUBW,
2019). This is similar to previous studies in other European cities such as Barcelona, Spain (Mohr et al., 2012) and
some megacities in China (Ni et al., 2019). In the next section, we investigate the volatility of OOA compounds
measured by CIMS, which can influence their lifetime in the atmosphere and thus air quality.

3.3 Seasonal changes of volatility of OOA

3.3.1 Volatility distribution

Effective saturation mass concentrations (C_{sat}), a measure for volatility of a compound, were parameterized for
each CHO and CHON compound using the approach by Li et al. (2016):

$$\log_{10} C_{\text{sat}}(298 \text{ K}) = (n_{\text{C}}^0 - n_{\text{C}})b_{\text{C}} - n_{\text{O}}b_{\text{O}} - 2 \frac{n_{\text{C}}n_{\text{O}}}{n_{\text{C}}+n_{\text{O}}} b_{\text{CO}} - n_{\text{N}}b_{\text{N}} \quad (1)$$

and then corrected for the summer (24 °C) and winter (2 °C) periods (Stolzenburg et al., 2018; Donahue et al.,
2011; Epstein et al., 2010):

$$\log_{10} C_{\text{sat}}(T) = \log_{10} C_{\text{sat}}(298 \text{ K}) + \frac{\Delta H_{\text{vap}}}{R \ln(10)} \left(\frac{1}{298} - \frac{1}{T} \right) \quad (2)$$

$$\Delta H_{\text{vap}}(\text{kJ mol}^{-1}) = -5.7 \cdot \log_{10} C_{\text{sat}}(298 \text{ K}) + 129 \quad (3)$$

We stress here that isomers cannot be differentiated with the C_{sat} parameterization (Donahue et al., 2011) and that
thermal fragmentation of organic compounds (Lopez-Hilfiker et al., 2015; Huang et al., 2018) during particle
desorption with the FIGAERO can bias the C_{sat} results towards higher volatilities. This will be discussed later. The

CHO and CHON compounds were then grouped into a 25-bin volatility basis set (VBS; Donahue et al., 2006)
based on their log₁₀C_{sat} values (Figure 3). Organic compounds with C_{sat} lower than 10^{-5-4.5} μg m⁻³, between 10^{-4.5-}
10^{-20.5} μg m⁻³, between 10^{-0.5-}10^{2.5} μg m⁻³, and higher than between 10^{-2.5-}10^{6.5} μg m⁻³ are termed extremely low
volatile organic compounds (ELVOC), low volatile organic compounds (LVOC), ~~and~~ semi-volatile organic
compounds (SVOC), and intermediate volatile organic compounds (IVOC), respectively (Donahue et al., 2009).

As shown in Fig. 3a, organic compounds with C_{sat} between 10²⁻10³ μg m⁻³ make up the biggest mass contributions
during daytime in both summer and winter, ~~suggesting that SVOC is the dominating group in both seasons
(summer: 74.2 ± 3.4 %; winter: 66.7 ± 4.9 %; see Fig. 3ab–e)~~. The dominating compounds in these volatility bins
come from the group of C_{8–12}HO compounds in summer and from the group of C_{1–7}HO compounds with relatively
higher O:C ~~ratios~~ in winter (Figure S9a and S9c). Dominant compounds are 2-hydroxyterpenylic acid (C₈H₁₂O₅)
and levoglucosan (C₆H₁₀O₅) for summer and winter, respectively (compare also to Fig. 1a and 1c). Non-negligible
contributions from C_{1–7}HON compounds are also observed in these volatility bins in winter (Fig. S9b and S9d),
mainly from nitrated phenols (C_{6–7}H₅, O_{3–4}N; compare also to Fig. 1d). In winter we ~~also~~ observe significant-much
lower contributions of SVOC with C_{sat} between 10⁵⁻10⁶ μg m⁻³ in the particle phase. Since winter is much colder
compared to summer (Fig. S2), compounds of higher volatility are expected to be able to condense in winter.

However, we may also have contributions from thermal decomposition products of oligomers to ~~some of~~ these
low-molecular weight compoundsSVOC (also reflected in the multi-mode thermograms for CHOX compounds
with 1–5 carbon atoms; see Figure S10). But for the larger compounds, such as dimers and trimers, contributions
of thermal decomposition products become negligible (i.e. thermograms are unimodal; Huang et al., 2018; Wang

and Ruiz, 2018). LVOC and ELVOC, which include compounds with larger molecular weight, exhibit higher mass contributions in winter (LVOC: $26.437.0 \pm 3.12.2$ %; ELVOC: $6.915.9 \pm 1.93.5$ %) than in summer (LVOC: $21.722.6 \pm 2.5$ %; ELVOC: 4.81 ± 1.24 %; see Fig. 3b–c). The average mass-weighted $\log_{10}C_{\text{sat}}$ value is $1.050.97 \pm 0.28 \mu\text{g m}^{-3}$ for summer and $0.63.1.2 \pm 0.484 \mu\text{g m}^{-3}$ for winter.

The results indicate that even though the lower ambient temperatures in winter may lead to increased partitioning of SVOC into the particle phase, the bulk winter OOA is less volatile. Similar results were also observed in Zurich, Switzerland by Canonaco et al. (2015) based on AMS data. The lower volatility of OOA in Stuttgart in winter compared to summer can be partially explained by the higher contributions of compounds with shorter carbon chain lengths and higher number of oxygen atoms in winter (i.e. higher O:C-ratios; see Fig. S8), and the relatively higher contribution of larger molecules (number of carbons atoms >16; see also Fig. 2). Differences in aging processes (functionalization, fragmentation, and oligomerization; Jimenez et al., 2009) between the seasons may also play a role, since Keller and Burtscher (2017) found that aging processes reduce the volatility of OA from biomass burning.

3.3.2 Variation of the maximum desorption temperatures (T_{max})

Thermograms resulting from the thermal desorption of the filter samples were analyzed. T_{max} , the maximum desorption temperatures at which the signals of a compound peak, were compared for summer and winter. Figure 4a–b shows the campaign-average high resolution two-dimensional (2D) thermogram of CHOX compounds, a framework developed recently to investigate the OOA thermal desorption behavior over the entire m/z and T_{max} range (Wang and Ruiz, 2018). Each thermogram of each individual compound in the 2D space was normalized to its maximum signal. Due to the CHOX compounds containing at least 1 carbon atom, 1 hydrogen atom, and 1 oxygen atom, and being detected as clustered with I (m/z 126.9050 Th), the smallest m/z in the 2D thermogram is 168 Th. As shown in Fig. 4a–b, the majority of the OOA compounds exhibit higher T_{max} with a wider spread across different CHOX compounds in winter (114.4 ± 17.1 °C, average ± 1 standard deviation) compared to summer (96.8 ± 18.2 °C; see also Figure S11). For the summer period, T_{max} decreases from 160 °C to 60 °C for m/z 168–280 Th, stays relatively constant at 60–110 °C for m/z 280–550 Th, and increases from 60 °C to 120 °C for m/z >550 Th; for the winter period, T_{max} decreases from 160 °C to 80 °C for m/z 168–280 Th, stays relatively constant at 2 T_{max} regions (one region at 80–100 °C and the other one at 110–130 °C) for m/z 280–550 Th, and increases from 80 °C to 130 °C for m/z >550 Th (see also Fig. S11). The high T_{max} values for m/z <280 Th (SVOC range) result from multi-mode thermograms with thermal decomposition of larger molecules (Lopez-Hilfiker et al., 2015). A similar picture can be seen in the campaign-average thermograms for the sum of the signals of all CHOX, CHO, and CHON compounds detected (normalized to the maximum; Fig. 4c). The pattern of the summer 2D thermogram in Stuttgart, particularly the “zigzag”-like behavior of e.g. m/z 280–380 Th (see Figure S12a), is comparable to that from alkane-Cl SOA at high RH (67 %) and high NO_x conditions observed by Wang and Ruiz (2018), and was explained by increased hydroxyl functionalization over ketone functionalization. The winter 2D thermogram in Stuttgart also has a “zigzag”-like pattern but less pronounced and at higher T_{max} (see Fig. S12b).

The results indicate a generally lower apparent volatility (i.e. higher T_{max}) of bulk OOA in winter, in agreement with the results based on the C_{sat} parametrization (see also Fig. 3). Recent studies show that T_{max} of a compound can be influenced by isomers (Thompson et al., 2017), thermal fragmentation of larger molecules during the heating of the filter (Lopez-Hilfiker et al., 2015), variations in filter mass loading (Huang et al., 2018; Wang and Ruiz, 2018), and/or differences in particles' viscosity (Huang et al., 2018). Since deposited organic mass loadings

on the filter samples were similar for summer and winter, we can exclude a mass loading effect on the T_{\max} results presented here. However, we also observed by eye that the filter samples in winter were more blackish, possibly due to the higher black carbon (BC) concentrations during daytime (10:00–16:00) in winter ($1247 \pm 112 \text{ ng m}^{-3}$) compared to summer ($1032 \pm 311 \text{ ng m}^{-3}$). If (and how) the higher BC concentrations can affect the desorption behaviors of organic compounds (i.e. interactions between organic compounds and BC) is still unknown and requires further laboratory studies. Higher O:C ratios (Buchholz et al., 2019), and/or higher oligomer mass fractions (Huang et al., 2019; compare to LVOC and ELVOC mass contributions in Fig. 3b–c) have been shown to be correlated with higher T_{\max} , which is in agreement with our mass spectral observations in winter. Besides, higher inorganic sulfate concentrations in winter (see Fig. S1) might also play a role in the formation of low volatile but thermally unstable organic compounds which can only be detected as their decomposition products with FIGAERO-CIMS (Gaston et al., 2016; Riva et al., 2019). If assuming that the winter thermograms are more influenced by thermal decomposition of oligomers than the summer thermograms, which artificially shifts the molecular formula-based volatility distribution towards higher volatility, the winter OOA are expected to be even less volatile.

4 Conclusions and atmospheric implications

In this paper, chemical composition and volatility of OA particles were investigated during July–August 2017 and February–March 2018 in the city of Stuttgart, one of the most polluted cities in Germany. The average organic mass loadings measured by AMS are lower in summer ($5.1 \pm 3.2 \mu\text{g m}^{-3}$) than in winter ($8.4 \pm 5.6 \mu\text{g m}^{-3}$), but the relative contributions of OA to total non-refractory $\text{PM}_{2.5}$ mass measured by AMS are higher in summer ($68.8 \pm 13.4 \%$) compared to winter ($34.8 \pm 9.5 \%$). This can be explained by the differences in emission sources between the seasons, boundary layer height dynamics, and/or meteorological conditions (Canonaco et al., 2015; Daellenbach et al., 2019; Baumbach and Vogt, 2003). CIMS mass spectra from filter samples collected at the measurement site during daytime (10:00–16:00) show OOA compounds in summer have O:C ratios of 0.82 ± 0.02 and are more influenced by biogenic emissions (as shown by e.g. tracers of α -pinene oxidation products), while OOA compounds in winter have slightly higher O:C ratios (0.89 ± 0.06) and are more influenced by biomass burning emissions (as shown by e.g. signals of levoglucosan and nitrated phenols).

The apparent volatility of the OOA compounds varies between the two seasons. OOA in winter is found to be less volatile, which is reflected in the higher contributions of LVOC and ELVOC in the VBS, as well as in the higher maximum desorption temperatures (T_{\max}) of the organic compounds desorbing from the particles deposited on the filter samples. Potential possible reason for the lower apparent volatility of winter OOA is the increased residence time of air masses over Stuttgart due to the stronger surface inversion and thus longer atmospheric aging time of the OOA compounds, leading to a reduction in volatility (Keller and Burtscher, 2017; Jimenez et al., 2009). This is also consistent with the higher O:C ratios and the higher mass contributions of larger molecular-weight LVOC and ELVOC in winter. Since the OOA observed in the winter period also shows influence from biogenic emissions, the sources for the LVOC and ELVOC may partly be biogenic. In addition, interactions between different species and/or particles (particle matrix; Huang et al., 2018) due to higher BC, OA and inorganic concentrations, such as the intermolecular interactions between biomass burning compounds and biogenic/anthropogenic organic compounds and/or the interactions between organic compounds, inorganic compounds, and BC, might also play a role in the reduction of volatility of aerosol particles in winter. Overall, the

lower apparent volatility of the winter OOA compounds could be caused by higher O:C-ratios, but may also be related to the higher particle viscosity due to the higher mass contributions of larger molecular-weight LVOC and ELVOC, interactions between different species and/or particles deposited on the filter (particle matrix; Huang et al., 2018), and/or thermal decomposition of large molecules.

The results suggest that whereas lower temperatures in winter may lead to increased partitioning of SVOC into the particle phase, this does not result in a higher overall volatility of OOA in winter, and that the difference in sources and/or chemistry between the seasons plays a more important role. Our study provides insights into the seasonal variation of molecular composition and volatility of ambient OA particles during daytime, and into their potential sources, which is important for air pollution mitigation in urban locations. Our study shows the important contributions of non-fossil OA from biogenic and biomass burning even in an urban area with high traffic emissions mainly based on fossil fuel combustion (LUBW, 2019). As a consequence, in addition to mitigating traffic emissions, reducing emissions of anthropogenic OOA precursors from e.g. industry and biomass burning may contribute to reducing the environmental and health effects of air pollution.

Data availability

Data are available upon request to the corresponding author.

Author contributions

WH operated AMS and took the filter samples during the two field campaigns, analyzed the filters by CIMS in the laboratory, did the CIMS and AMS data analysis, produced all figures, and wrote and edited the manuscript; HS organized the campaign, did the trace gas, CPC, and black carbon data analysis, and provided suggestions for the data interpretation and discussion; XS operated AMS and took the filter samples during the field campaigns; RR took the filter samples during the summer campaign; TL gave general advice and comments for this manuscript; CM provided suggestions for the data analysis, interpretation, discussion, and edited the manuscript. All authors contributed to the final text.

Competing interests

The authors declare no conflict of interest.

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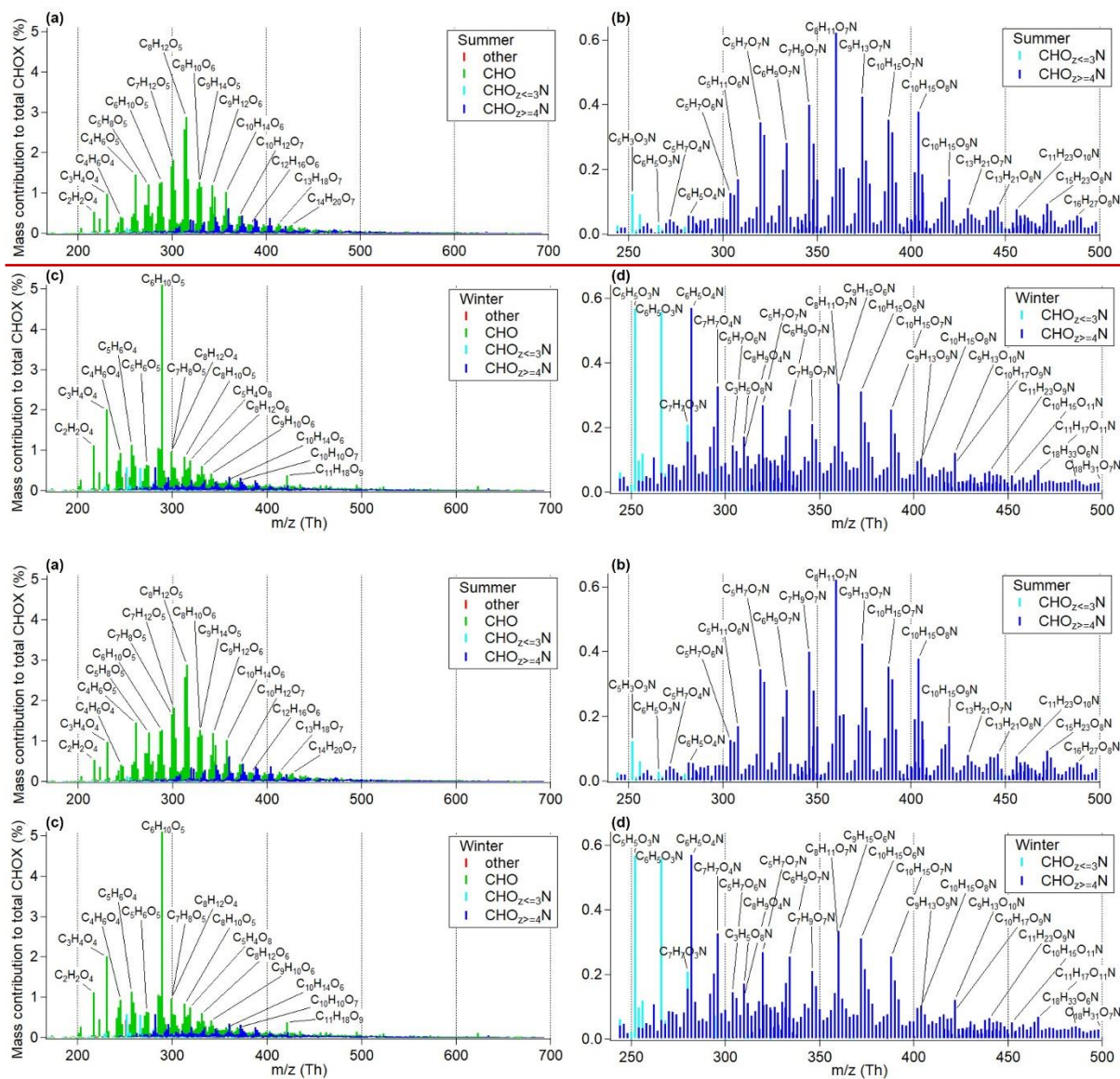
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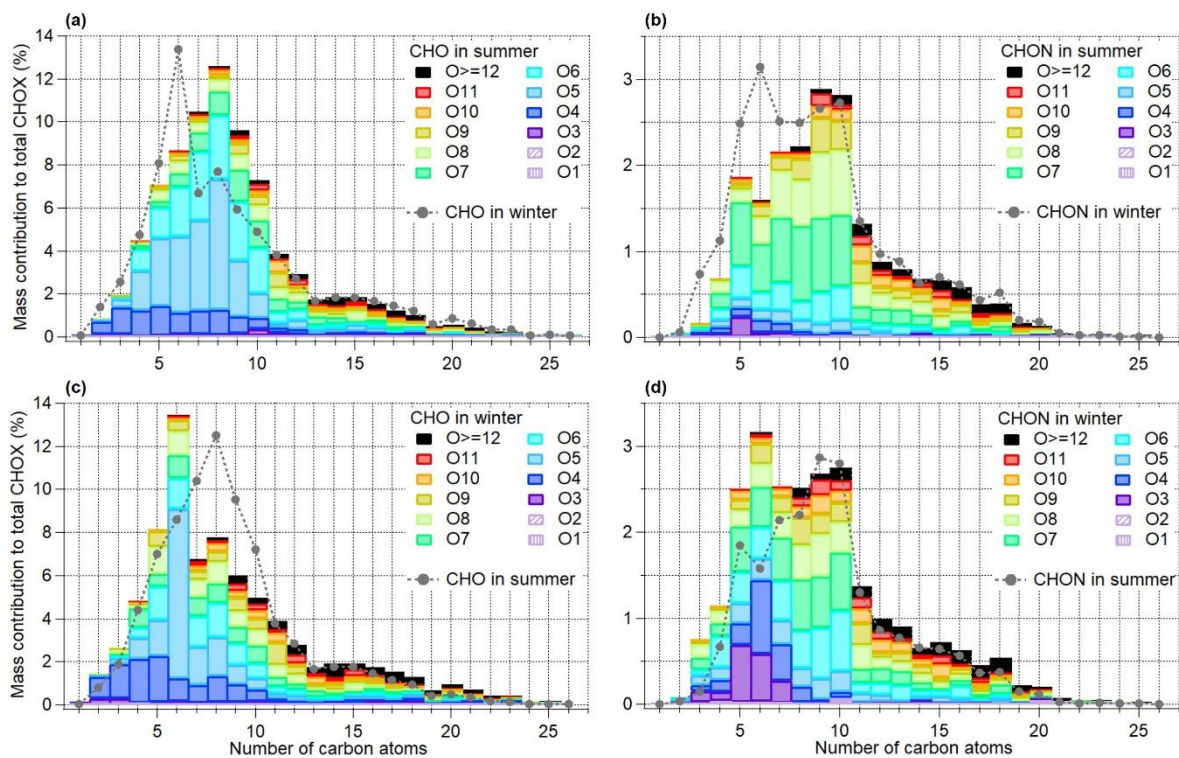


Figure 2. Mass contribution of CHO and CHON compounds with different number of oxygen atoms as a function of the number of carbon atoms to total CHOX compounds for the summer (a, be) and winter (bc, d) periods. The corresponding distribution for the other season is plotted as a gray dotted line.

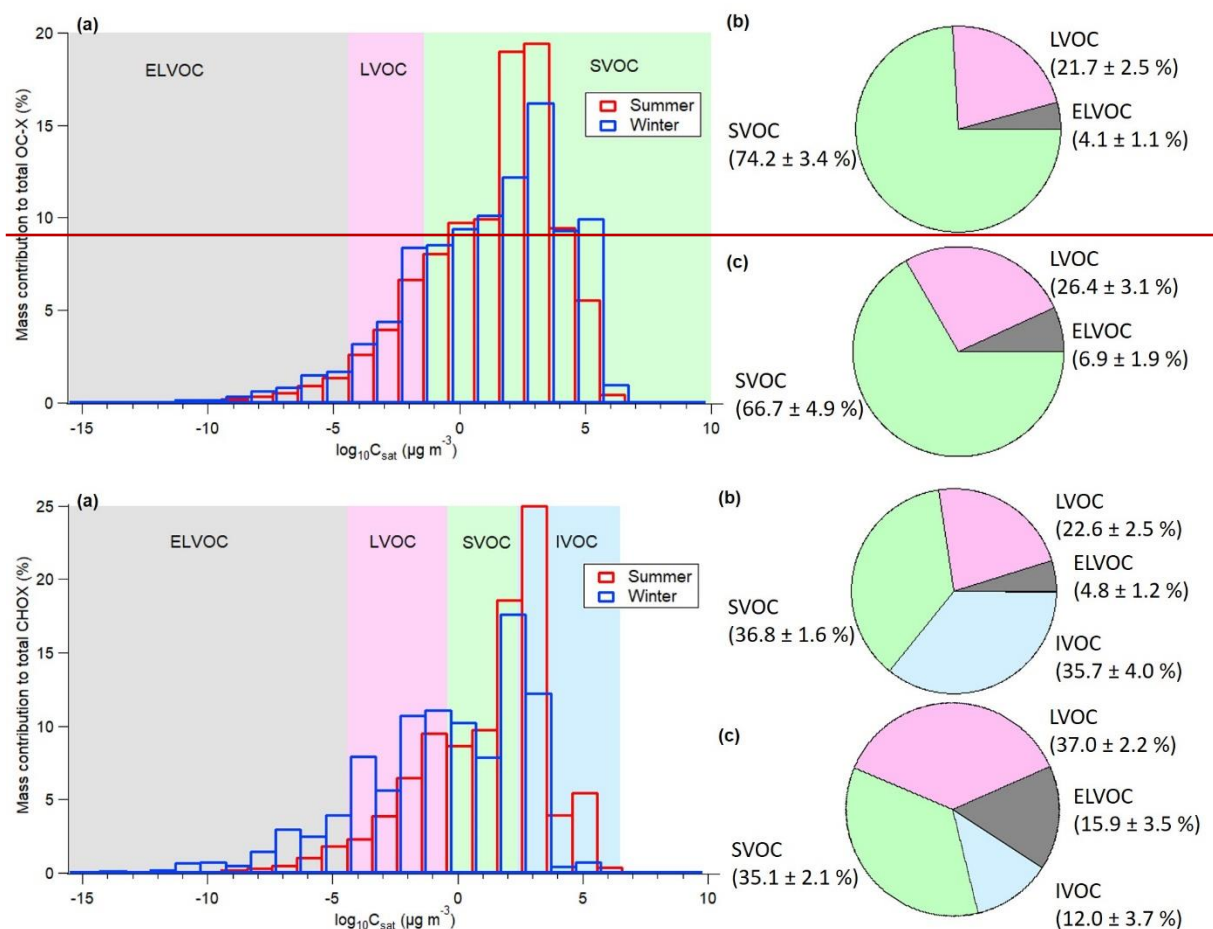


Figure 3. (a) Volatility distribution for the summer (24 °C) and winter (2 °C) periods based on the molecular formula parameterization by Li et al. (2016); resulting pie chart for the mass contributions of SVOC, IVOC, LVOC, and ELVOC in the summer (b) and winter (c) periods. Compounds more volatile than IVOC with C_{sat} higher than $10^{6.5} \mu\text{g m}^{-3}$ (summer: $0.1 \pm 0.0 \%$; winter: $0.0 \pm 0.0 \%$) are not labeled in the pie chart.

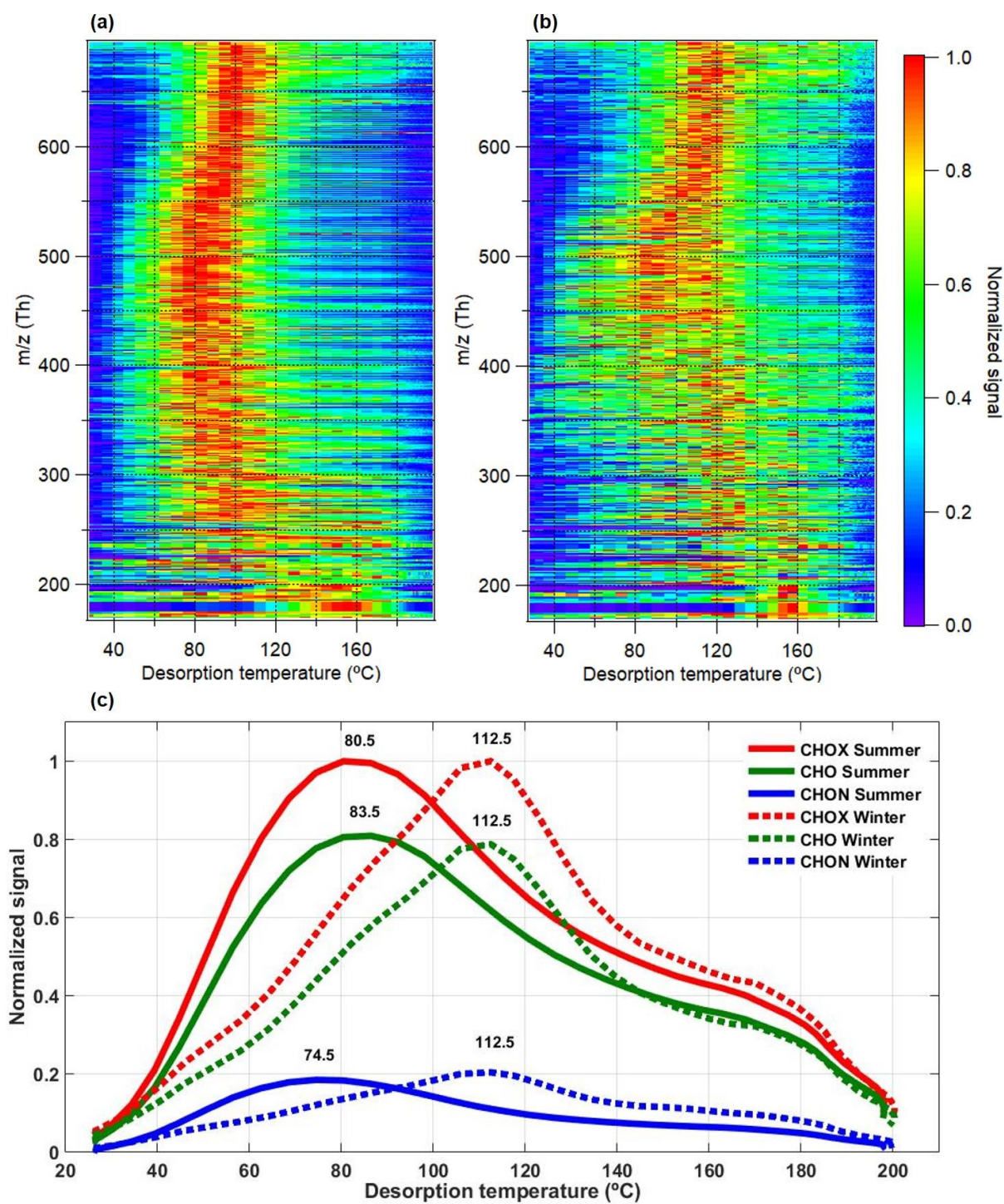


Figure 4. Comparison of campaign-average high resolution two-dimensional (2D) thermograms of CHOX compounds for the summer (a) and winter (b) periods vs m/z (includes mass of I⁻ ion; m/z 126.9050 Th), and the sum thermograms of CHOX, CHO, and CHON compounds (c). The 2D thermograms and sum thermograms were normalized to their maximum values.

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Table S1. Instruments installed in the measurement container.

Measured parameter	Instrument	Data period	
		Summer 2017	Winter 2018
Ambient temperature	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Container temperature	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Dew point temperature	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
RH	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Pressure	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Wind speed	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Wind vertical	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Wind direction	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Rain	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Rain type	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Rain rate	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Radiation	WS700 (Lufft GmbH)	July 7–August 17	February 5–March 5
Particle number concentration (>7 nm)	CPC3022 (TSI Inc.)	July 5–August 17	February 5–March 5
Particle number concentration (>2.5 nm)	CPC3776 (TSI Inc.)	July 5–August 17	February 5–March 5
O ₃	O341M (Environment SA)	July 5–August 17	February 5–March 5
CO ₂	NGA2000 (Rosemount Inc.)	July 5–August 17	February 5–March 5
SO ₂	AF22M (Environment SA)	July 5–August 17	February 5–March 5
NO ₂	AS32M (Environment SA)	July 5–August 17	February 5–March 5
Particle optical diameter (0.18–18 µm)	OPC FIDAS200 (Palas GmbH)	July 5–August 17	February 5–March 5
Particle size (10–410 nm, d _m)	NanoScan-SMPS (TSI Inc.)	July 5–July 26	/
Black carbon (BC)	AE51 Aethalometer (Aethlabs Inc.)	July 5–August 17	February 5–March 5
Single particle composition and size (0.2–2.5 µm, d _{va})	LAAPTOF (AeroMegt GmbH)	July 5–August 17	February 5–March 5
Particle mass and size (0.07–2.5 µm, d _{va})	AMS (Aerodyne Research Inc.)	July 5–August 17	February 5–March 5
Particle-phase oxygenated organic molecules (offline filters)	FIGAERO-CIMS (Aerodyne Research Inc.)	July 5–August 14	February 8–March 5

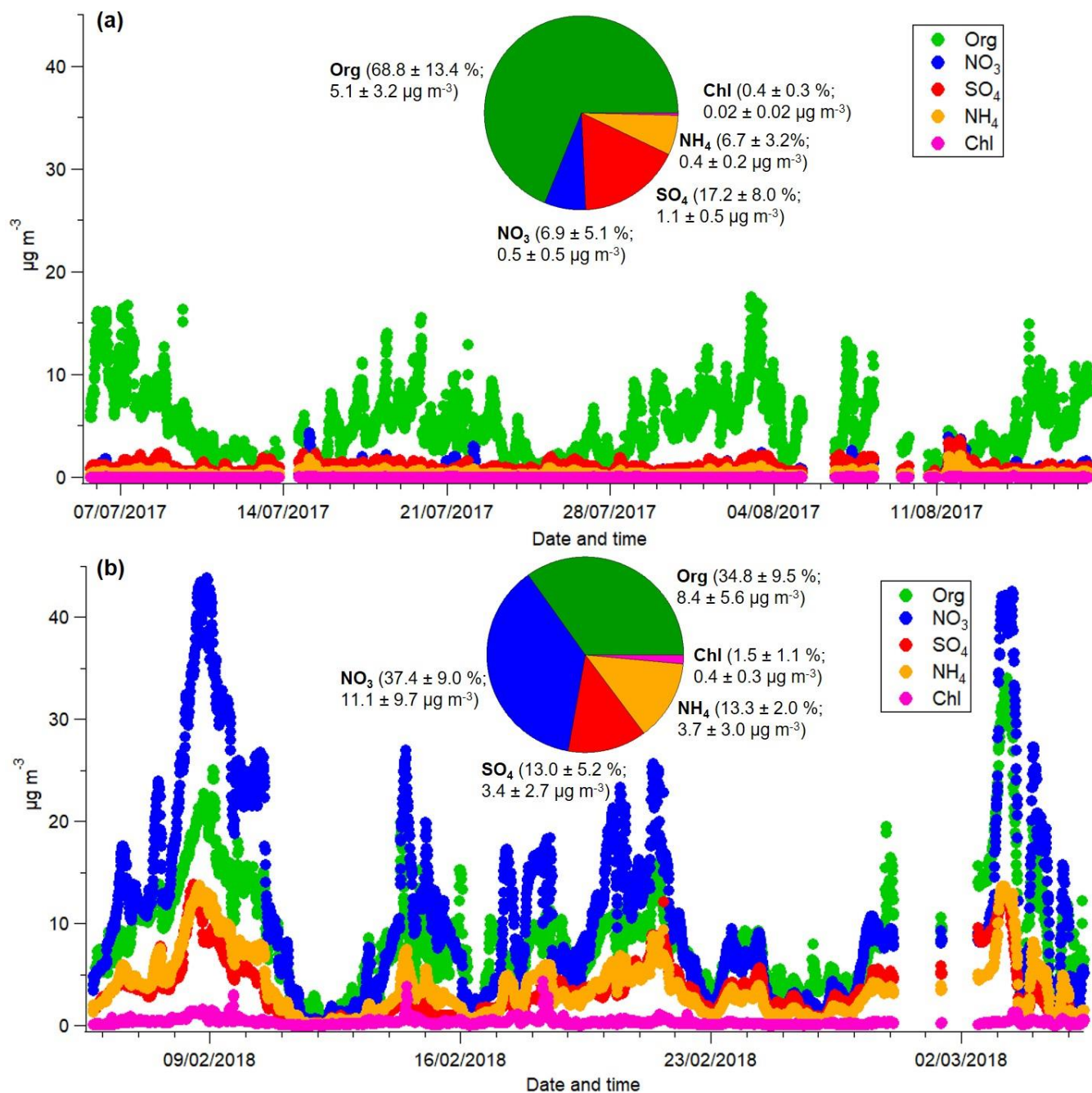


Figure S1. Time series of aerosol composition measured by AMS (Organics (Org), Nitrate (NO₃), Sulfate (SO₄), Ammonium (NH₄), and Chloride (Chl)) in the summer (a) and winter (b) periods.

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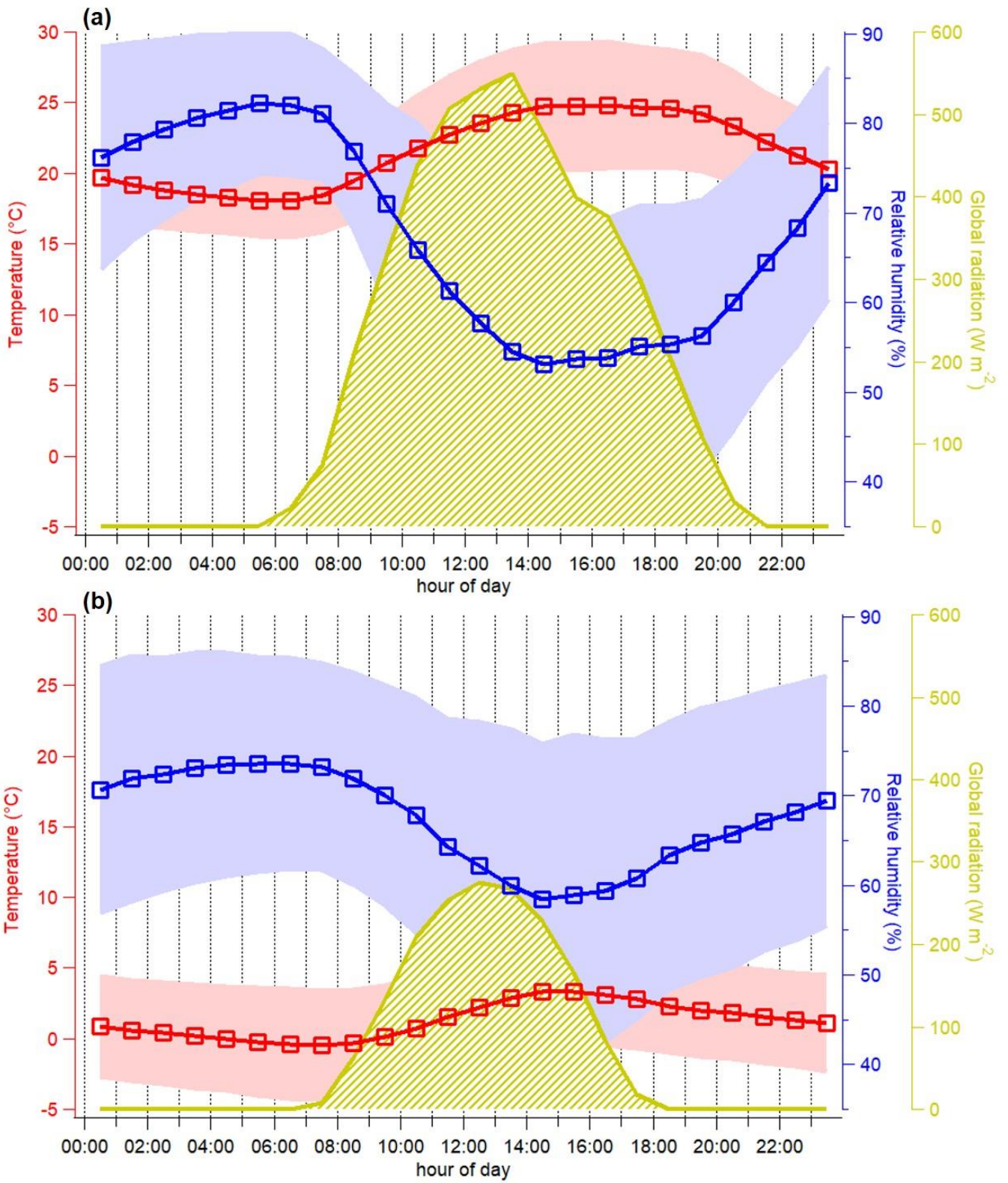
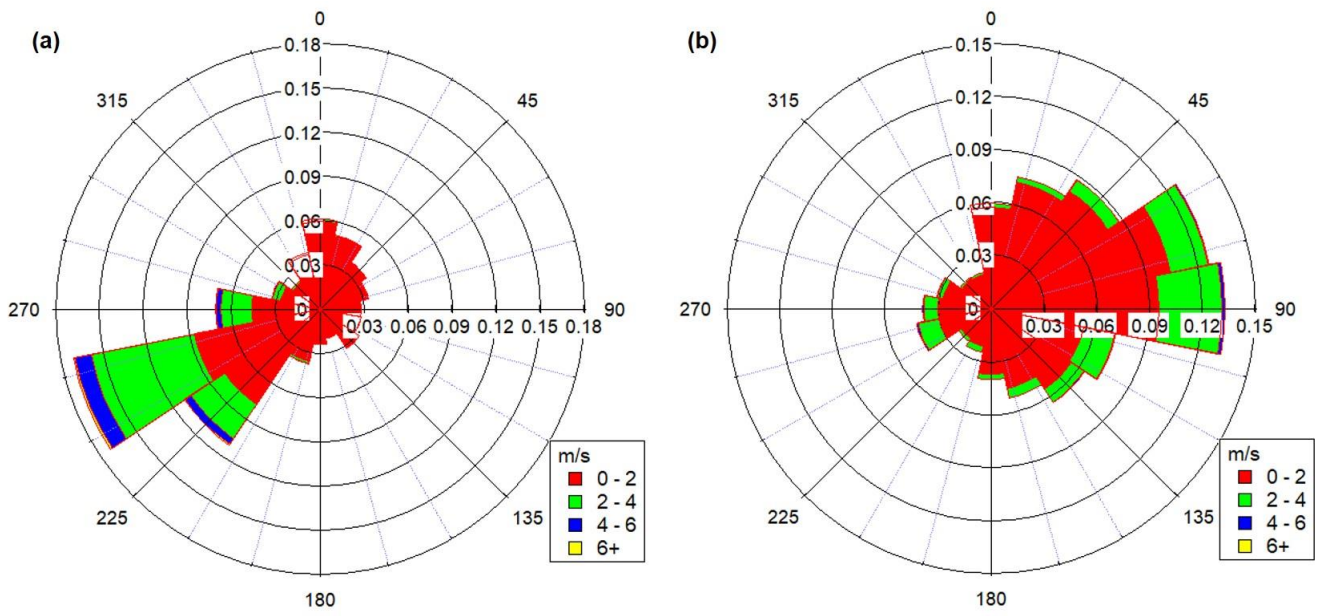


Figure S2. Mean diel patterns of ambient temperature, relative humidity, and global radiation in the summer (a) and winter (b) periods. The shaded areas represent ± 1 standard deviation.



10 **Figure S3.** Wind speeds and directions for the summer (a) and winter (b) periods.

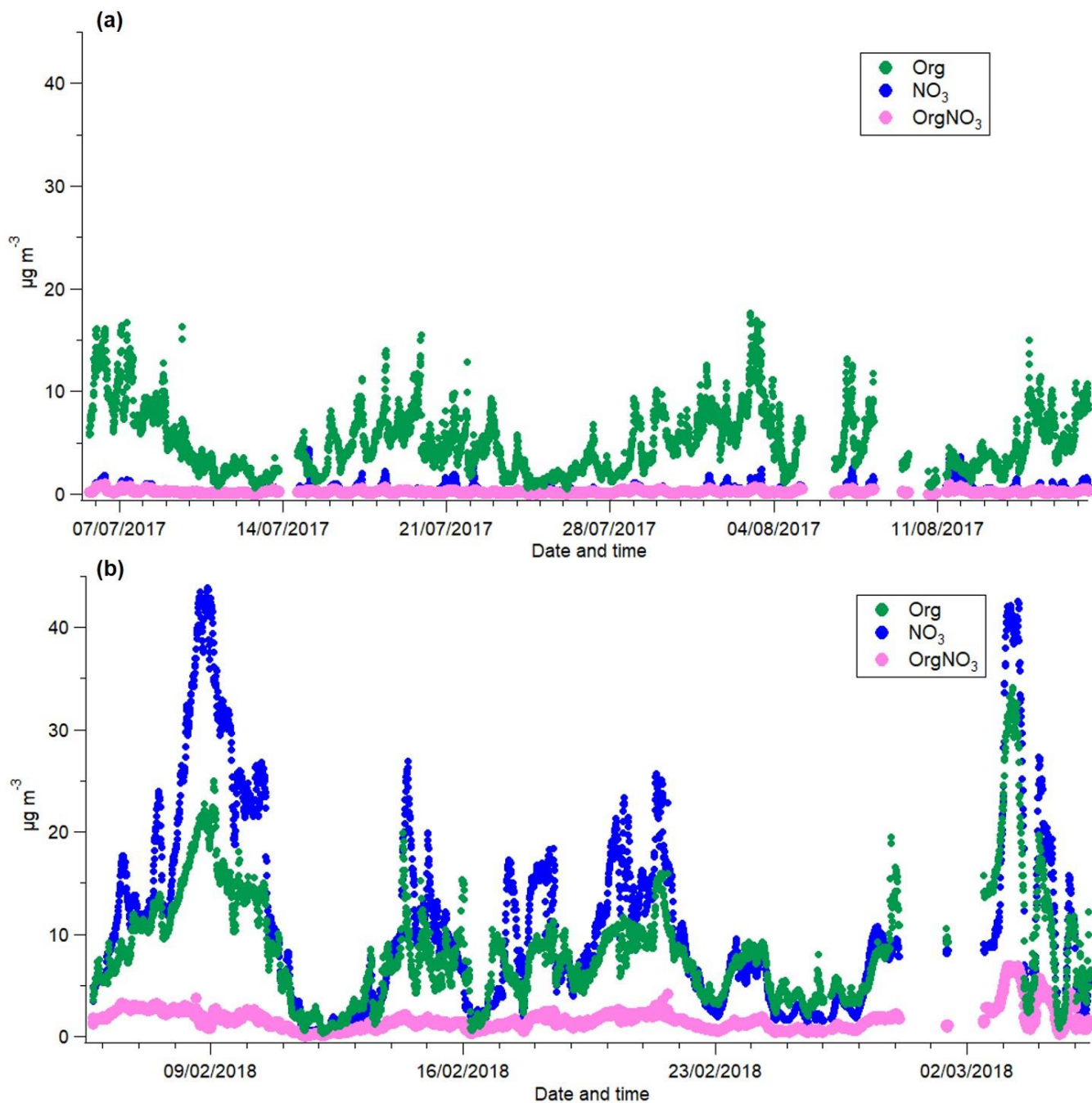


Figure S4. Comparison of time series of Organonitrates (OrgNO₃) with Organics (Org) and Nitrate (NO₃) by AMS for the summer (a) and winter (b) periods. OrgNO₃ concentrations were estimated based on the NO₂⁺/NO⁺ ion ratio measured by AMS and assuming a ratio of 0.1 for OrgNO₃ (Farmer et al., 2010; Kiendler-Scharr et al., 2016).

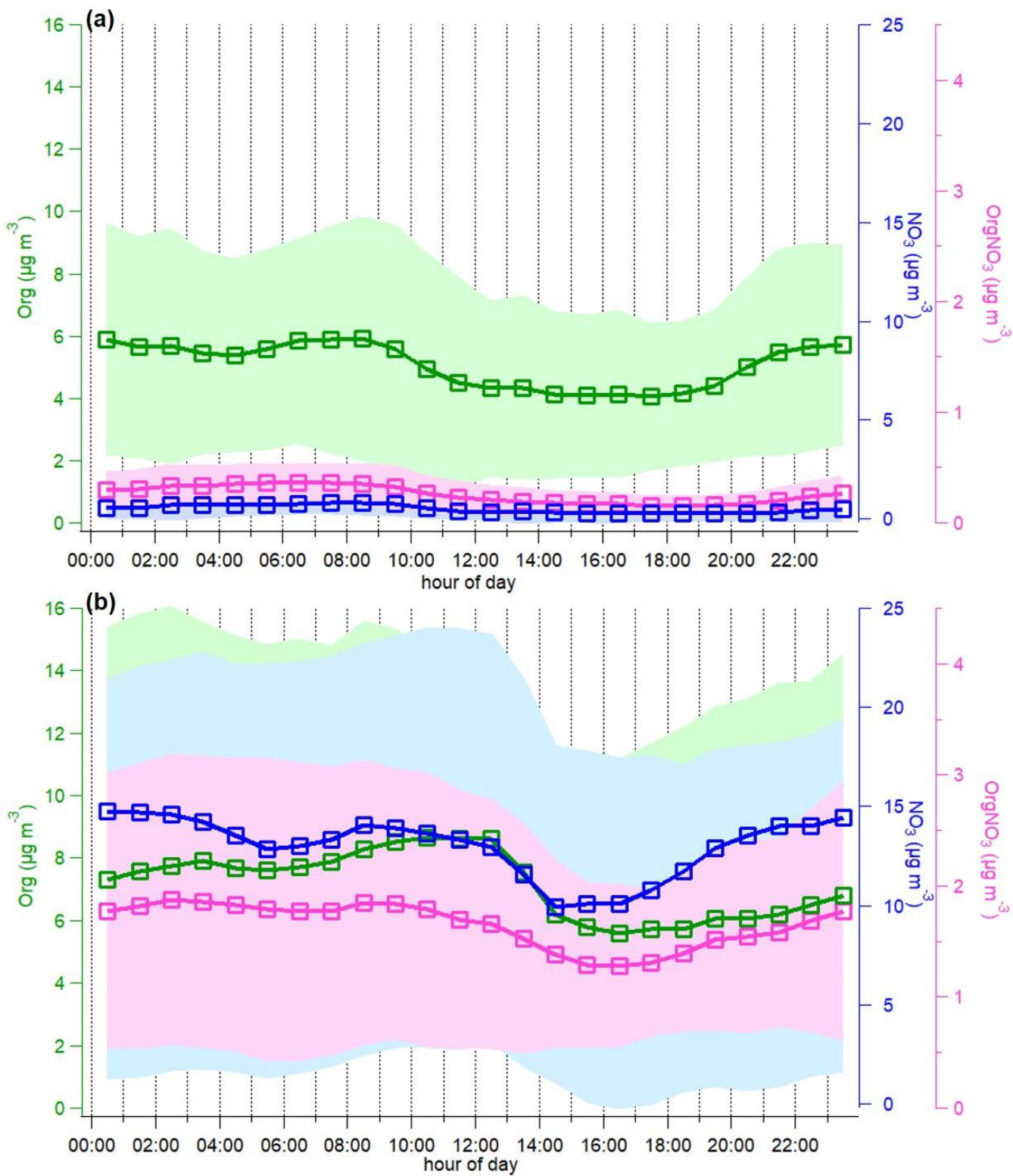
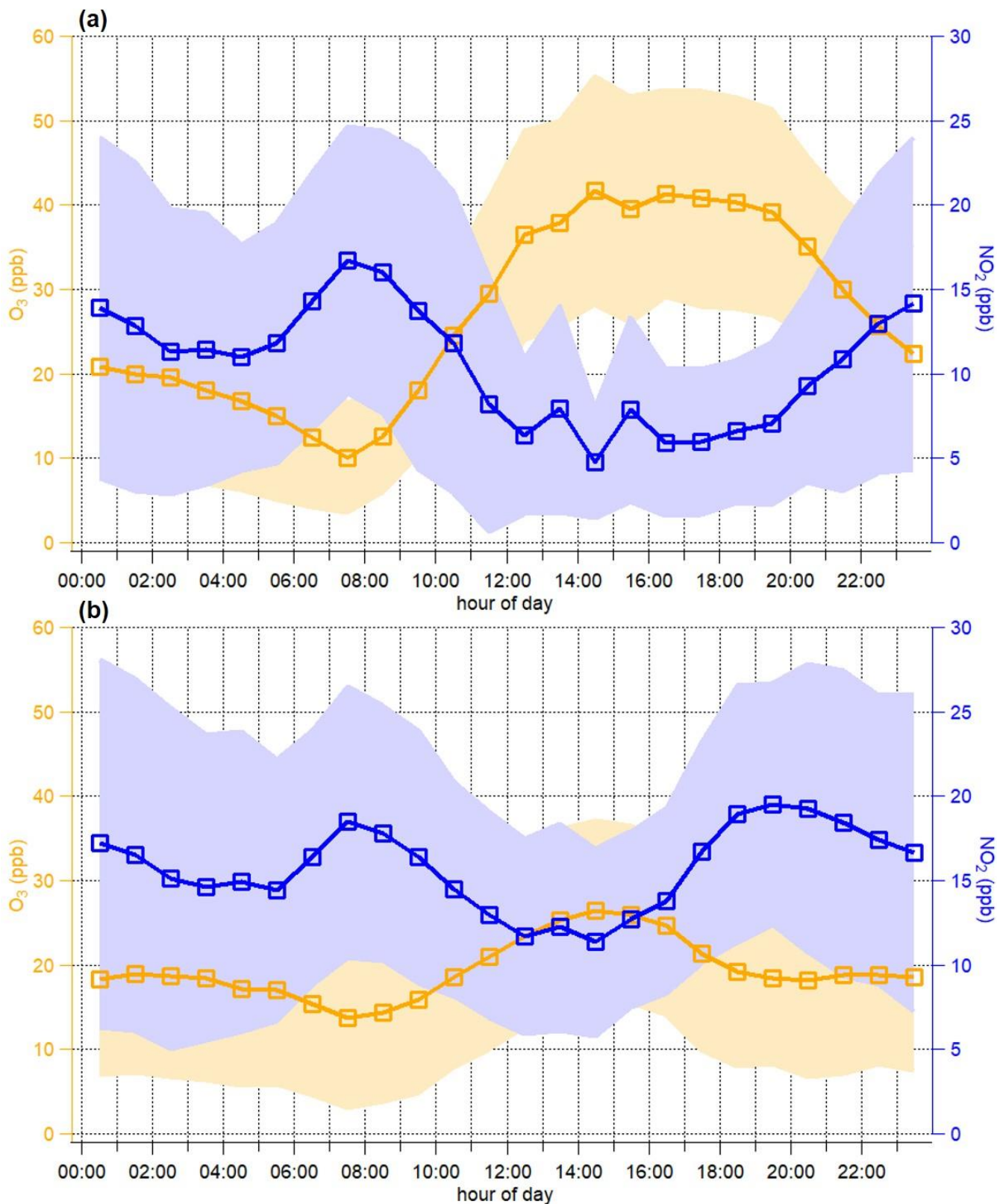


Figure S5. Mean diel patterns of Organics (Org), Nitrate (NO_3), and Organonitrates (OrgNO_3) by AMS for the summer (a) and winter (b) periods. The shaded areas represent ± 1 standard deviation.



20 **Figure S6.** Mean diel patterns of O₃ and NO₂ mixing ratios for the summer (a) and winter (b) periods. The shaded areas represent ±1 standard deviation.

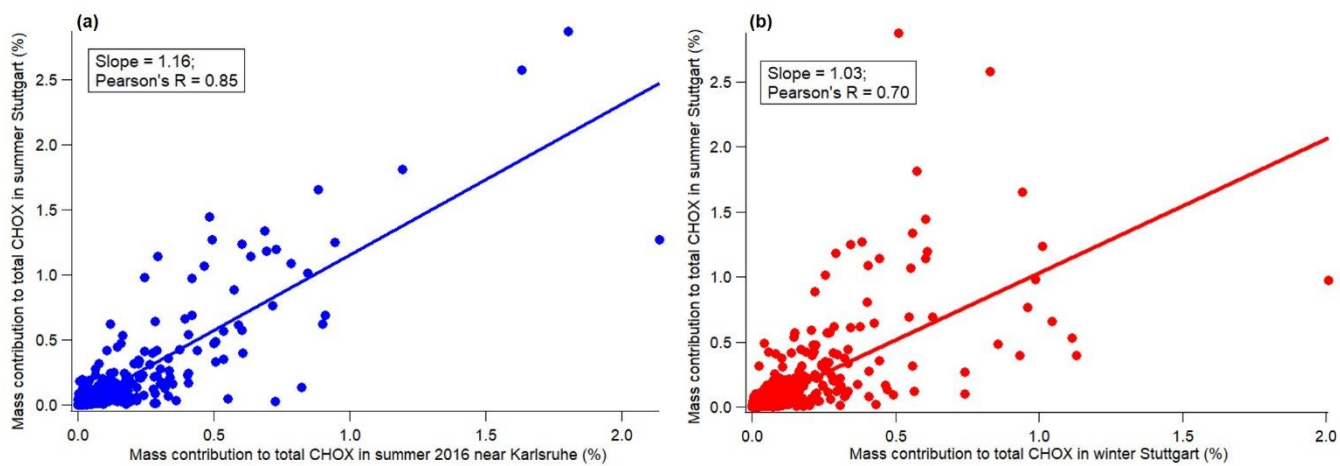


Figure S7. Correlations of CHOX compounds in summer 2017 in Stuttgart (a) with CHOX compounds in summer 2016 near Karlsruhe (Huang et al., 2019) and (b) with CHOX compounds in winter 2018 in Stuttgart after removing five prominent biomass burning tracer compounds ($C_6H_{10}O_5$, $C_6H_5O_3N$, $C_7H_7O_3N$, $C_6H_5O_4N$, and $C_7H_7O_4N$).

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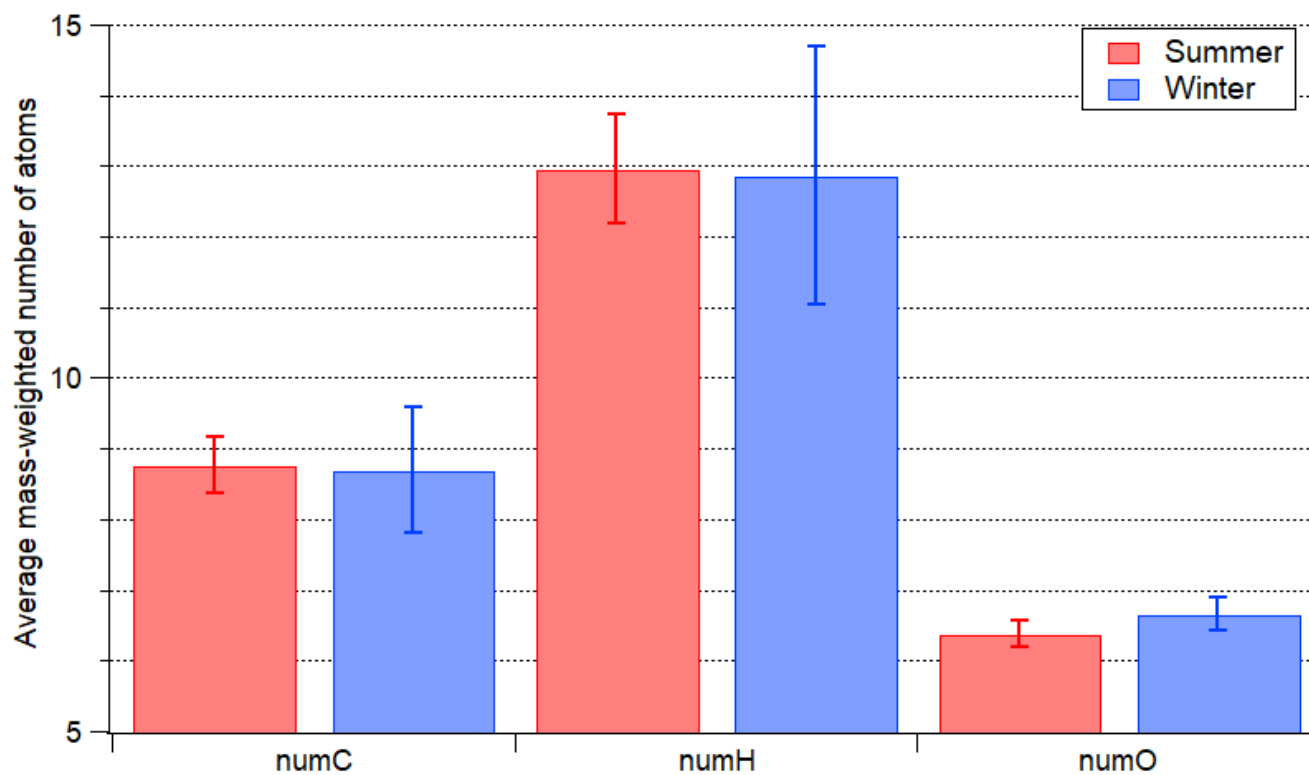


Figure S8. Average mass-weighted number of carbon atoms (numC), hydrogen atoms (numH), and oxygen atoms (numO) of the CHOX compounds for the summer and winter periods.

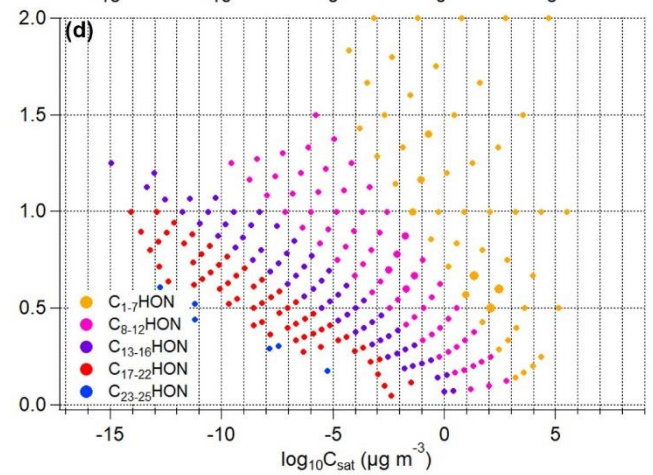
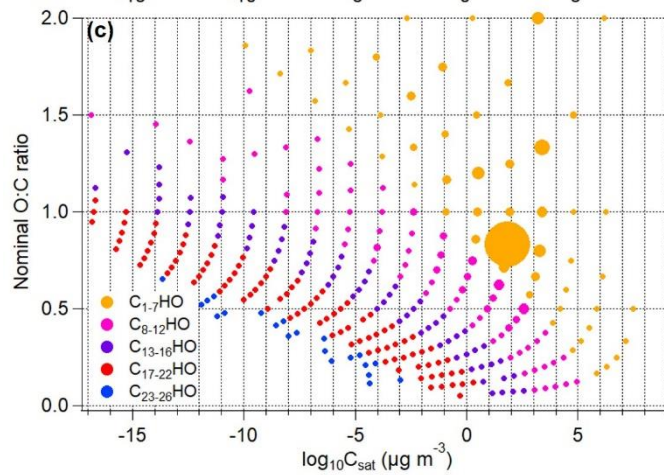
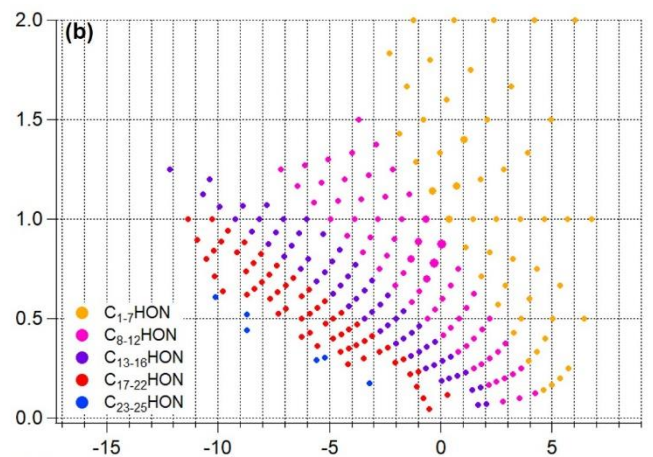
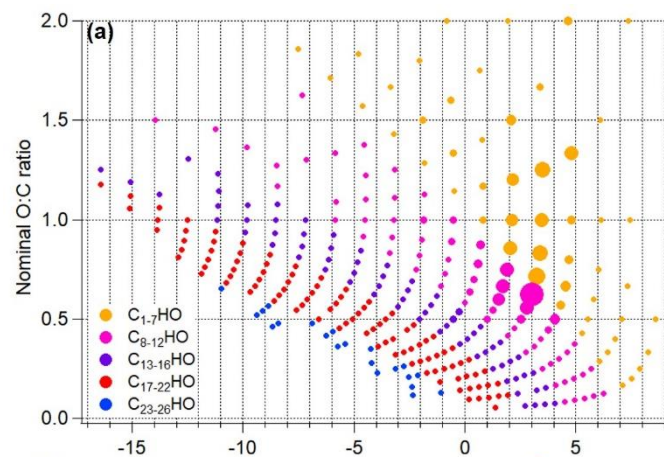
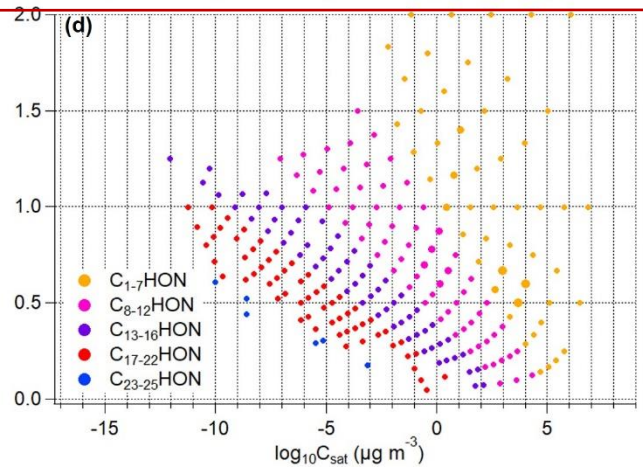
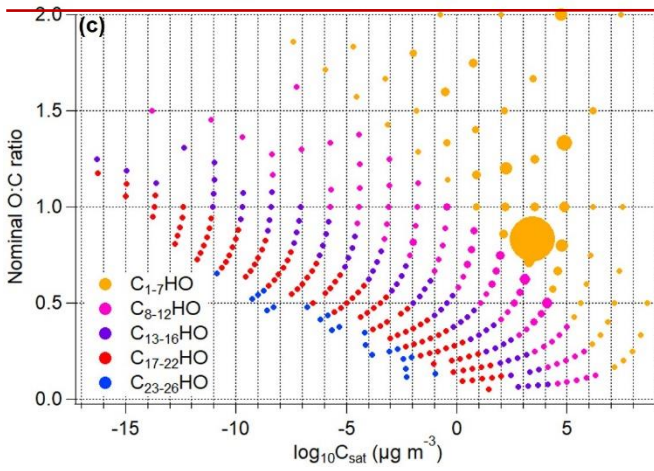
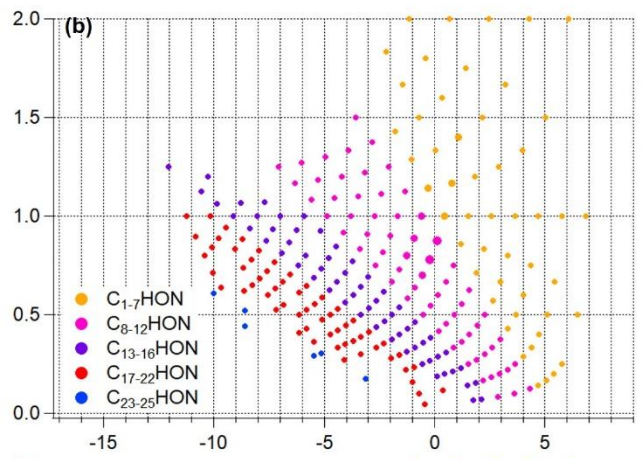
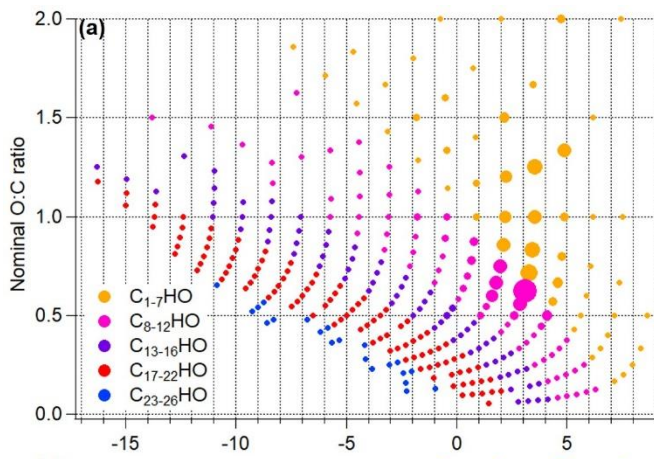
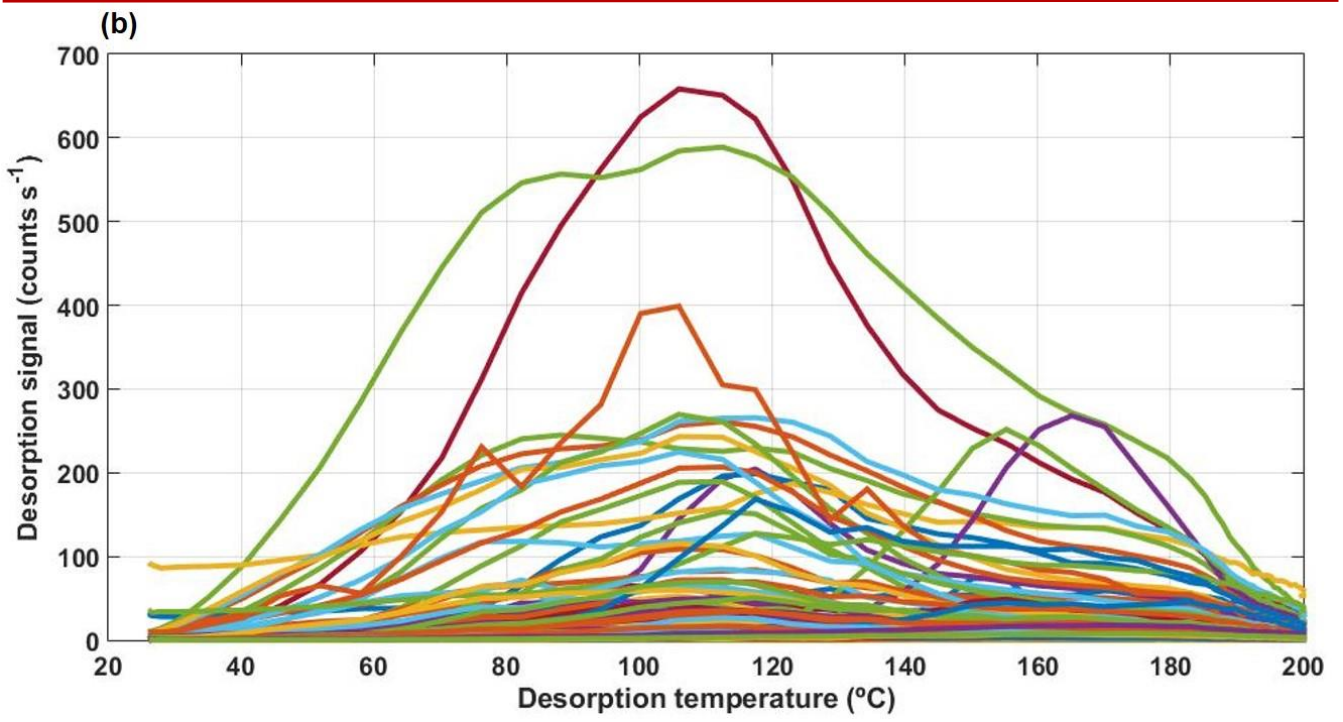
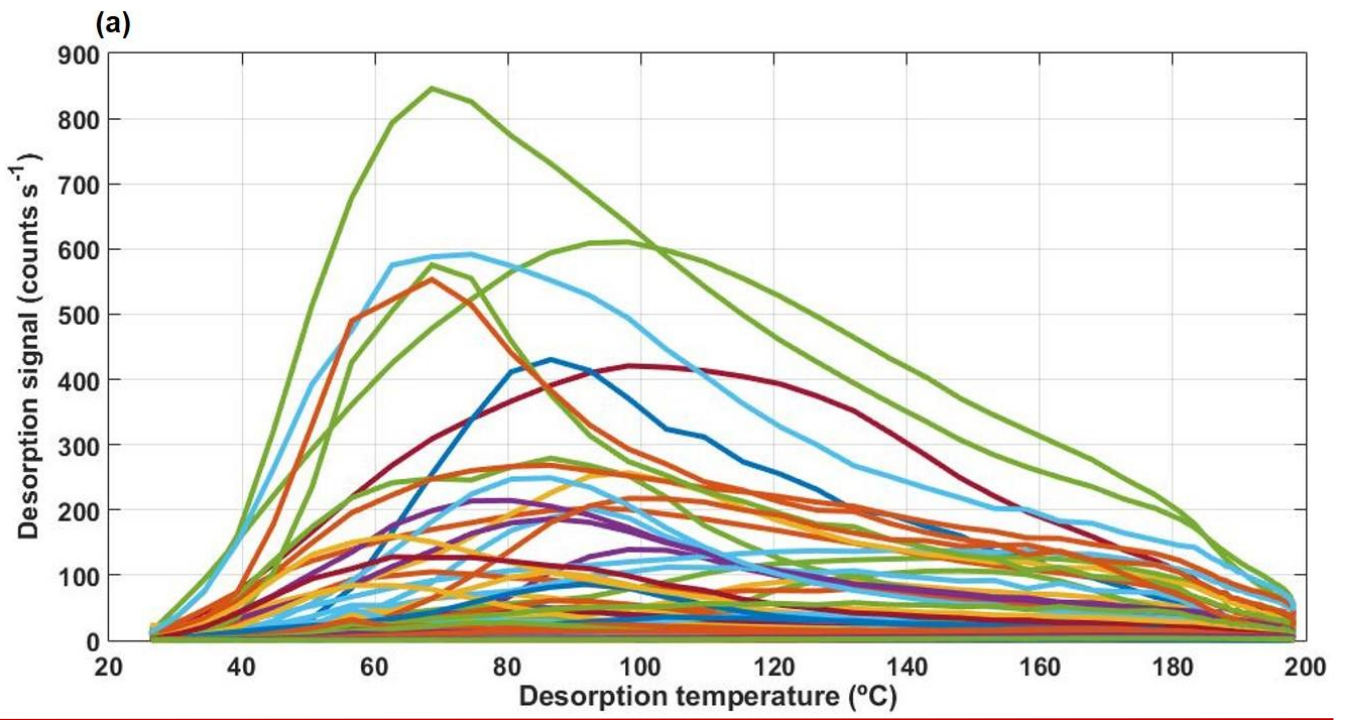


Figure S9. Volatility distribution of CHO compounds (a) and CHON compounds (b) in the summer period (24 °C), CHO compounds (ac) and CHON compounds (bd) in the winter period (2 °C) vs their corresponding nominal O:C ratio. Markers were colored by different number of carbon atoms and sized by their corresponding mass contributions to total CHOX compounds.



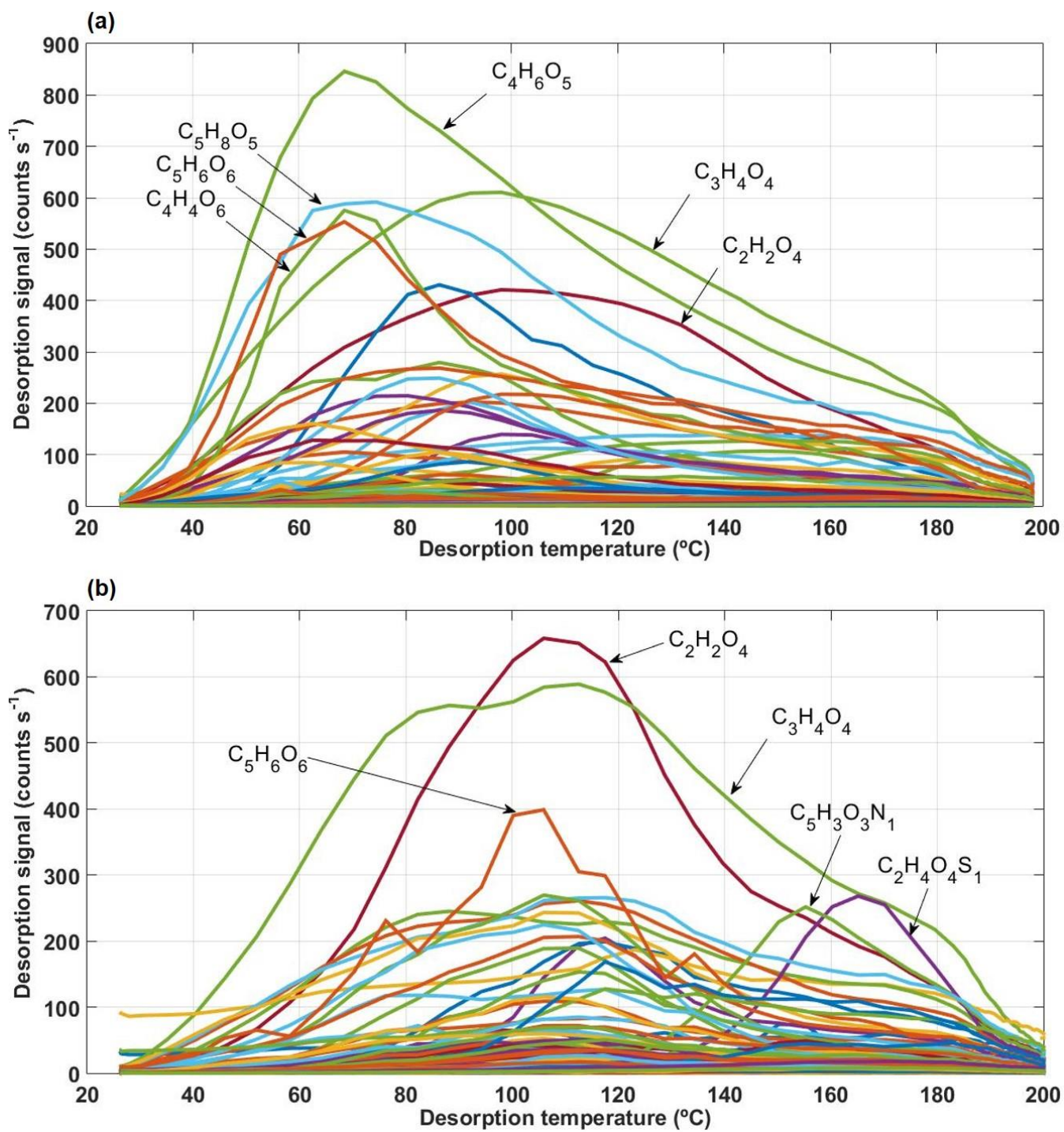
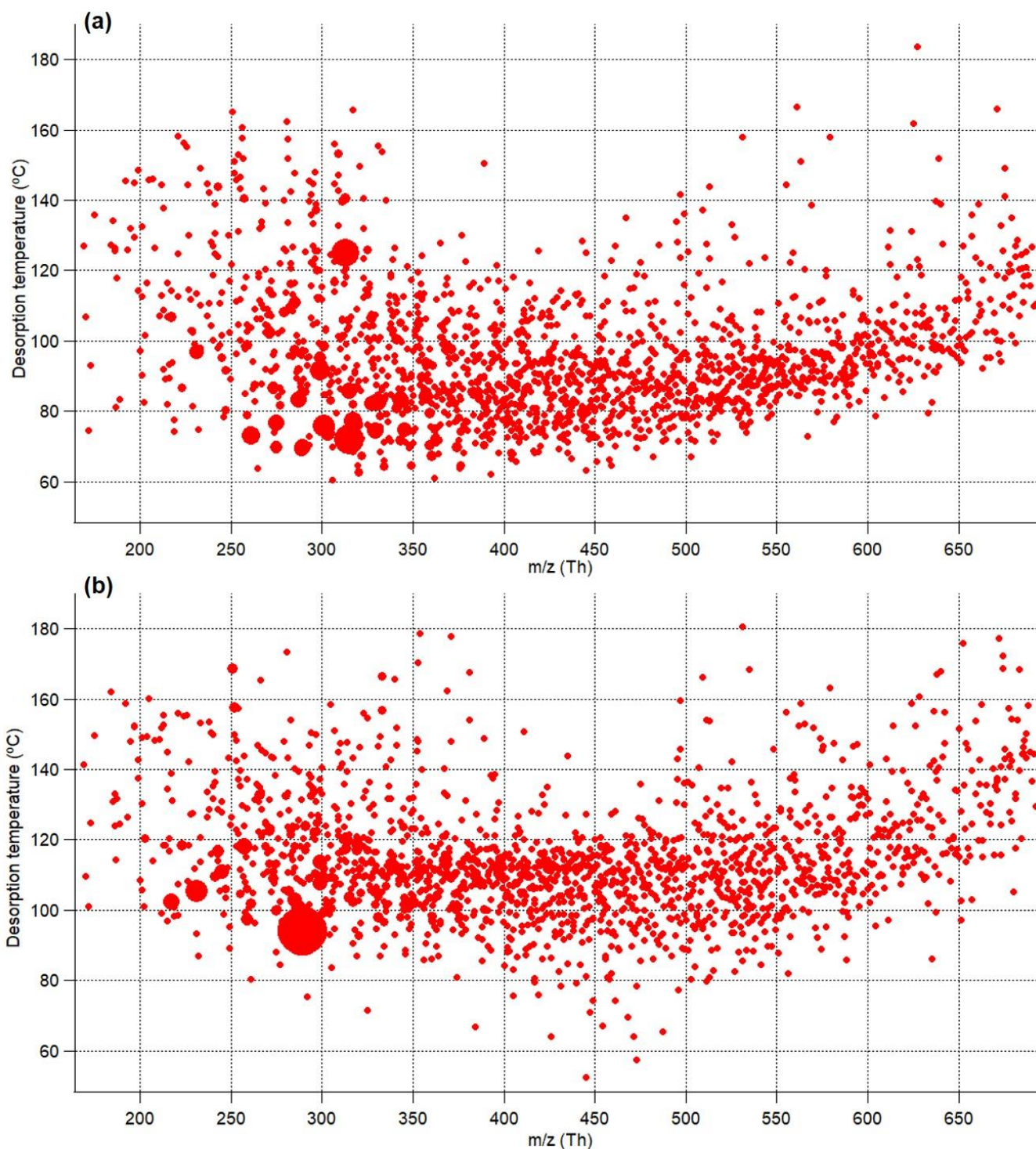
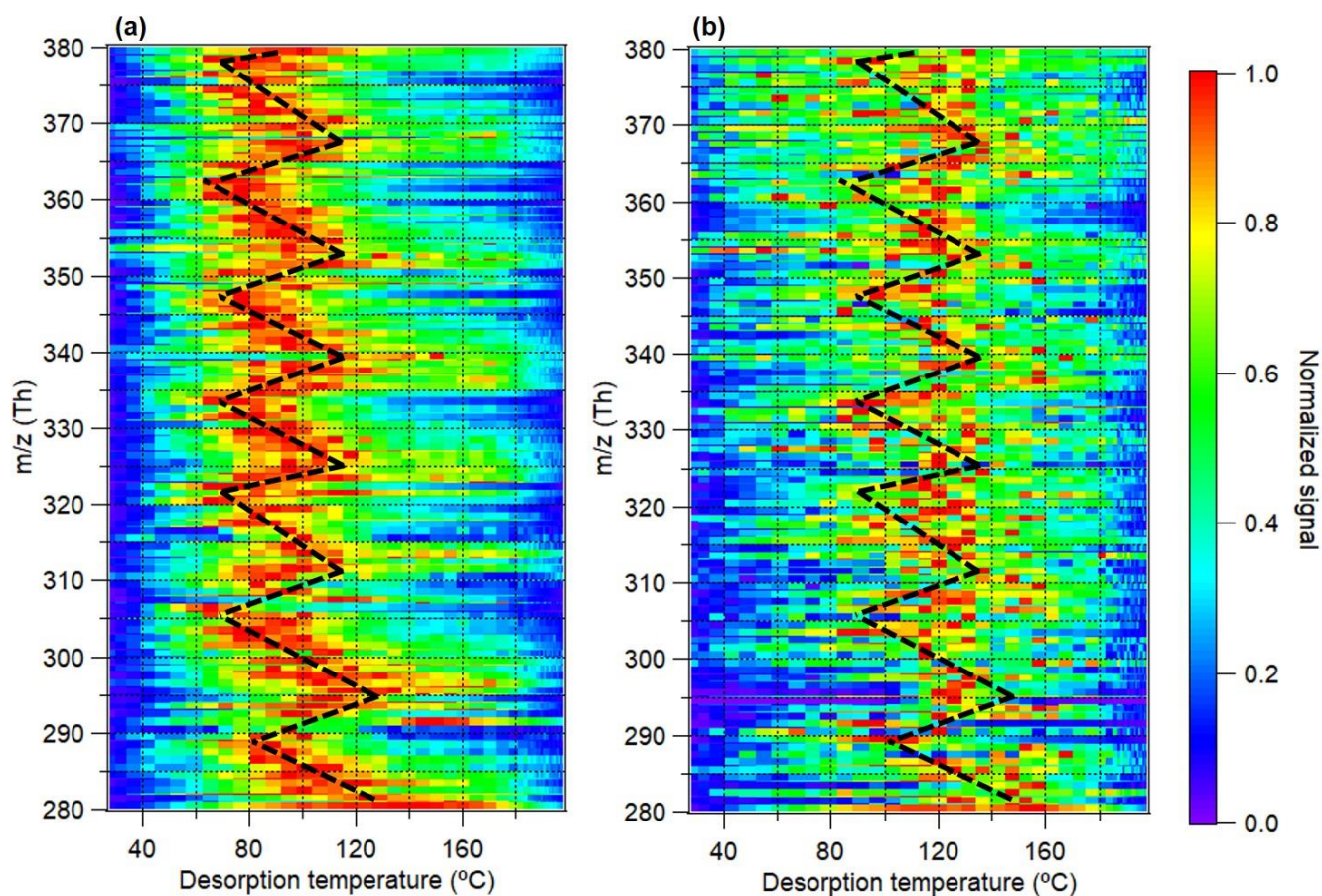


Figure S10. Thermograms of CHOX compounds with 1–5 carbon atoms for the summer (a) and winter (b) periods.



40 **Figure S11.** Mean T_{\max} distribution of CHOX compounds as a function of m/z (includes mass of Γ ion; m/z 126.9050 Th) for the summer (a) and winter (b) periods. Markers were sized by their corresponding mass contributions to total CHOX compounds. Mean T_{\max} were calculated as the campaign-average of the T_{\max} for each CHOX compound.



45 **Figure S12.** Comparison of high resolution 2D thermograms of CHOX compounds for mass range 280–380 Th of Figure 4 for the summer (a) and winter (b) periods. The 2D thermograms were normalized to their maximum values. A black dotted line was plotted by hand to guide the eye.

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