

Anonymous referee #1

Daellenbach et al. propose a comprehensive characterization of the molecular composition of aerosols sampled at an urban site in Central Europe (Zurich, Switzerland). Chemical composition is retrieved using an ultra-high resolution mass spectrometry (Orbitrap) and further compare with aerosols sampled during wood burning emissions from Alpine valleys and chamber investigations of wood smoke. Finally, samples from the boreal forest were also used to evaluate the influence of biogenic emission in aerosol formation in Zurich. The results presented in this work are interesting and provide important information on source apportionment of aerosol in Central Europe. The comparison lab and field data is particularly valuable. Overall, the interpretation and the results are well sustained. Therefore, I think the paper should be publishable after some comments are addressed.

We thank the reviewer for the positive feedback and will answer the comments point-by-point below.

General comments:

page 2, lines 31-33: the authors mentioned that ESI coupled to a UHR-MS is a promising technique. It is now an established technique and cannot be classified as promising. Indeed many studies in atmospheric sciences and analytical chemistry have demonstrated the capabilities of the UHR-MS including the Orbitrap technology (commercialized by Thermo 15 years ago).

We reformulated the sentence to:

"The use of soft ionization techniques, such as electrospray ionization coupled to ultra-high-resolution mass spectrometry (ESI-UHR-MS) is a powerful technique that may help bridging such existing gaps (Nizkorodov et al., 2011)."

page 3, 1-3: Another major limitation of any offline technique compare to the AMS is the time resolution, which is worth mentioning.

We added this information, on page 3, line 10-12:

"However, the typical number of samples analyzed remains very limited with low temporal resolution in comparison to online measurement techniques."

page 3, 27-30: How many samples were analyzed? Different sizes (e.g., PM₁₀, PM₁,...) were chemically characterized and compared. However, the authors never mentioned the influence of the size, how would that impact the interpretation?

We performed the following Orbitrap analyses:

- 1) 15 PM₁₀ filter samples from Zurich, Switzerland (24h sampling time), covering the entire year of 2013 (Daellenbach et al., 2017).
- 2) 1 composite of 4 PM₁₀ filter samples from Magadino, Switzerland (24h sampling time), highly influenced by biomass burning for wintertime residential heating.
- 3) 1 composite of 4 PM₁₀ filter samples from S. Vittore, Switzerland (24h sampling time), highly influenced by biomass burning for wintertime residential heating.

- 4) 1 composite of 16 PM10 filter samples of fresh biomass burning emissions from laboratory experiments (30mins sampling time)
- 5) 1 composite of 11 PM10 filter samples of 10h equivalent atmospherically aged biomass burning emissions from laboratory experiments (30mins sampling time)
- 6) 1 composite of 15 PM10 filter samples of 30h equivalent atmospherically aged biomass burning emissions from laboratory experiments (30mins sampling time)

Additionally, we included 2 average spectra from Hyytiälä (PM1, summer 2011: 12h sampling time, summer 2014: 48 to 64h sampling time) representing biogenic SOA published in Kourtchev et al. (2016). Biogenic SOA is mostly in PM1 (Vlachou et al., 2018), thus comparing PM1 samples from Hyytiälä to PM10 samples from Zurich doesn't affect the conclusions related to biogenic SOA.

We added the following information in the new version of the manuscript:

“

The field samples at the 3 sites in Switzerland were daily collected in 2013 using a High Volume samplers (500 l min⁻¹, quartz-fiber filter, 14.7 cm filter diameter). Zurich is located on the northern Swiss plateau and the site is classified as urban background. The sites in Magadino and S. Vittore are in Alpine valleys in Southern Switzerland. While the 15 samples collected in Zurich were analyzed individually, the 4 samples from Magadino and 4 samples from S. Vittore were grouped and analyzed as composites (10.12.2013, 14.12.2013, 18.12.2013, 22.12.2013).

Samples from smog chamber experiments were analyzed to examine the composition of wood burning emissions from the stable flaming phase and their evolution with aging (Bruns et al., 2016; 2017). During these experiments, fresh emissions were first injected into a 6 m³ Teflon smog chamber (Platt et al., 2013; Bruns et al., 2016, 2017). After 30 min of mixing, particles were sampled onto quartz-fiber filters (UV-lights off, sampling time 30 mins at ~30 l/min). Then, emissions were photochemically aged in the smog chamber, by injecting HONO at a flow rate of 1-2 l/min, which generates OH radicals upon photolysis. Samples were collected before aging (fresh) and at equivalent atmospheric aging times of 10 and 30 h (determined by the Barmet et al. (2012) method, assuming a winter time OH concentration of 10⁶ molec cm⁻³). All samples were grouped and measured as three composites: fresh wood burning emissions (16 samples), 10h equivalent atmospheric aging (11 samples) and 30h equivalent atmospheric aging (15 samples).

Further, we included 2 average spectra from the SMEAR-II station (Station for Measuring Ecosystem Atmosphere Relations, Hari and Kulmala 2005) at Hyytiälä (PM1, summer 2011: 12h sampling time, summer 2014: 48 to 64h sampling time, both quartz-fiber filters) previously published in Kourtchev et al. (2016). The SMEAR-II station (Station for Measuring Ecosystem Atmosphere Relations, Hari and Kulmala 2005) at Hyytiälä is a rural background site in Finland, strongly influenced by biogenic SOA (vegetation dominated by Scots pine and Norway spruce). The PM₁ aerosol was collected between 16 and 25 August 2011 and between 7 July and 4 August 2014 using a low volume sampler (35 l min⁻¹). Since biogenic SOA is mostly in PM1 (Vlachou et al., 2018), comparing PM1 samples from Hyytiälä to PM10 samples from Zurich does not affect the conclusions related to biogenic SOA.

In addition, we collected samples from Frauenfeld (PM₁₀), Payerne (PM₁₀), Bern (PM₁₀), Zurich (PM_{2.5}) from the same year to complement the dataset with further chemical analyses (Section 2.3).

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page 4, analytical procedure: The authors decided to use the Orbitrap in negative mode. Why didn't they explore the positive mode as well? As recently highlighted by e.g., Lin et al. (Anal Chem, 2018 10.1021/acs.analchem.8b02177) the positive mode can provide additional valuable information. The positive mode is generally less selective than the negative mode. Therefore for a global screening, both modes should be used.

With the specific interest of this study in SOA sources and the large contribution of acids to SOA, we opted for analyzing the aerosol in the negative mode. However, in the light of recent publications we agree with the reviewer and will in future studies use both positive and negative mode analyses. We have added the following information:

"Recent results show that the positive mode ESI, which is less selective, can provide additional valuable information, especially regarding fresh emissions (Lin et al., 2018). Here, to compare with previous results and as the main aim is to characterize SOA, we have focused on the negative mode ESI analysis."

page 4, lines 20-21. While replicate/triplicate measurements were performed the authors never mentioned the variability of their measurements. Screening analysis might bring large variability. Therefore, the authors should provide some statistical analysis in order to better validate their results/findings.

We added an assessment of the variability among the replicate measurements in the supplementary information and mention it in the main text:

Text added in manuscript:

"Two or three replicate measurements were conducted for each extract (variability assessed in Fig. S9), and field blank extracts were analyzed in the same way."

Text added in the supplementary information:

variability among replicate measurements

In order to estimate the relative error we performed replicate measurements of all samples (here computed as: $(x_{i,max} - x_{i,min})/x_{i,avg}$), with $x_{i,max}$, $x_{i,min}$, $x_{i,avg}$ being the maximum, minimum, and average peak (i) intensity measured for a respective sample. While the relative error varies considerably for a constant median peak intensity, overall typically the relative error of peaks ranges between 8 and 27%.

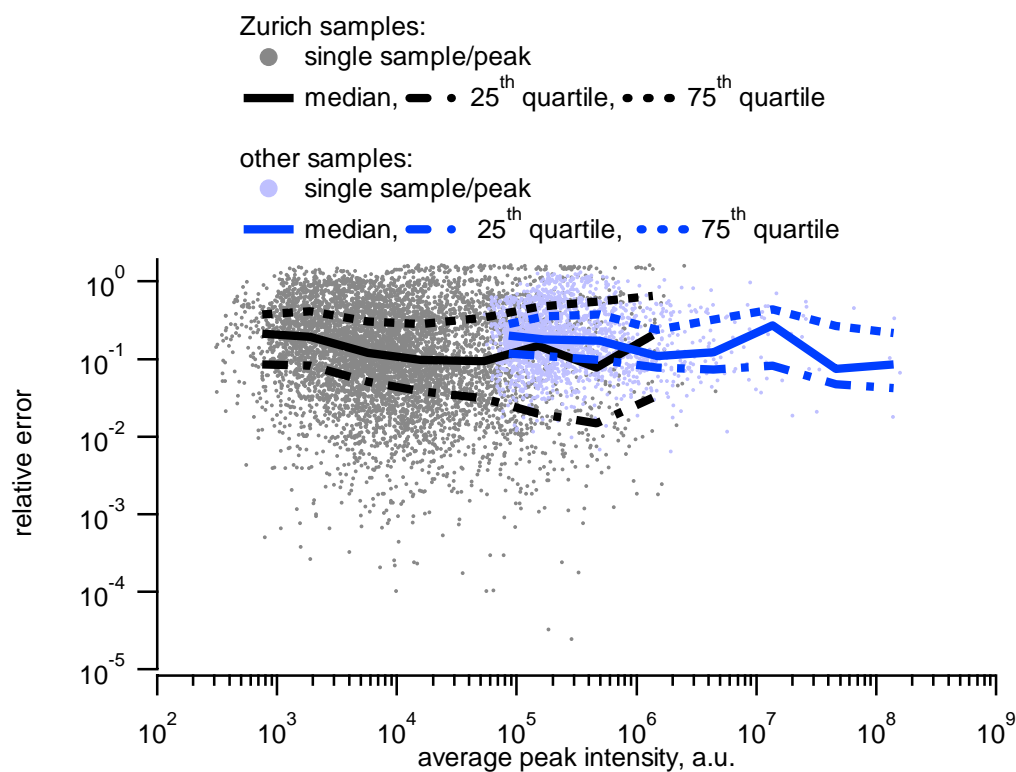


Figure S9: relative error as a function of the average signal intensity displayed for all samples and peaks.

page 7, lines 21-23: As it is presented it is hard to see any correlation. Please provide the r or r^2 for the different species to support the discussion (e.g., a table showing all the r^2 should be added). The authors mentioned that they measured the concentration of CO. How does CO correlate with other anthropogenic pollutants?

In the present study we analyzed 15 samples from Zurich from a larger study with 91 samples from the same site. This paragraph introduces the bigger picture and the correlations are presented in Daellenbach et al. (2017). We now state the correlations and cite the publication more explicitly:

“WOOA correlated with anthropogenically-influenced inorganic ions like NH_4^+ and was for this reason interpreted as being formed from anthropogenic VOC emissions. SOOA in contrast showed a positive non-linear relation to temperature, consistent with the temperature driven enhancement of biogenic terpene emissions (Daellenbach et al., 2017, for entire dataset from Zurich $R_p^2(\text{WOOA}, \text{NH}_4^+, n=90)=0.79$, $R_s(\text{SOOA}, \text{temp}, n=91)=0.65$).”

page 8, lines 4-15: It was already acknowledged by the authors that the relative contribution of a compound cannot be directly linked to its concentration (lines 1-3, page 3). However, it would be worth mentioning this point in this paragraph as it is an important aspect. Indeed, nitroaromatics are highly sensitive using ESI (-) but their large contribution to the MS doesn't imply that they are the most abundant species.

We have added the following content to the manuscript:

“We present the average summer ($T > 11^\circ\text{C}$, 18.04.2013, 12.05.2013, 05.06.2013, 29.06.2013, 23.07.2013, 16.08.2013, 09.09.2013, 03.10.2013, 27.10.2013) and winter ($T < 6^\circ\text{C}$, 12.01.2013, 05.02.2013, 01.03.2013, 25.03.2013, 20.11.2013, 14.12.2013) spectra from (-)ESI-UHR-MS at the urban background site in Zurich (mass spectral signature and van Krevelen diagrams in Fig. 2). We note that peak intensities, x_i , are not directly linked to concentrations and only relative differences can be interpreted. The summer and winter

average spectra exhibited a strong seasonal difference. During summer, peaks related to compounds only containing carbon, hydrogen and oxygen (CHO) dominated the spectrum. The majority of these compounds had a ratio H/C around 1.5 and O/C between 0.4 and 1.4 (Fig. 2). These compounds were either absent or had a much lower intensity during winter. "

page 9, lines 18-19: Are the ratios (e.g., H/C or O/C) weighted by the area of the individual peak?

Yes they are weighted by the peak intensity. We would like to refer to section 2.2.3 in the manuscript where we describe the computation of the properties in detail:

All properties, molar ratios, and chemical formulae presented in this manuscript refer to neutral molecules. Literature data was additionally also filtered with criterion (2) for comparability. Bulk elemental ratios (H/C, O/C, N/C and S/C) and the number of carbons of the organic aerosol were computed as follows (Nizkorodov et al., 2011, Bateman et al., 2012):

$$(O/C)_{bulk} = \frac{\sum_i x_i * N_{O,i}}{\sum_i x_i * N_{C,i}} \quad (2)$$

$$(H/C)_{bulk} = \frac{\sum_i x_i * N_{H,i}}{\sum_i x_i * N_{C,i}} \quad (3)$$

$$(N/C)_{bulk} = \frac{\sum_i x_i * N_{N,i}}{\sum_i x_i * N_{C,i}} \quad (4)$$

$$(S/C)_{bulk} = \frac{\sum_i x_i * N_{S,i}}{\sum_i x_i * N_{C,i}} \quad (5)$$

$$C_{bulk} = \frac{\sum_i x_i * N_{C,i}}{\sum_i x_i} \quad (6)$$

page 9, line 22: Accretion products imply aerosol processes (i.e., IUPAC definition). However, the chemistry describes by Berndt et al is a gas phase process. In addition, it is unlikely that these compounds arise from isoprene-RO₂ + monoterpene-RO₂ as isoprene concentration is very low in the Boreal forest and contributes overall to a small fraction of the OH and O₃ reactivities (e.g., Hakola et al., 2012).

We adapted the paragraph in question to:

" ...

The C13-C16 compounds are thought to consist mainly of sesquiterpene oxidation products, but may also be produced through reactions of monoterpene and isoprene RO₂ radicals (Berndt et al., 2018), which is less probable in the boreal forest due to the low isoprene concentrations.

"

page 10, lines 1-5: Those products were also formed from the oxidation of isoprene (e.g., Surratt's group). Please check the literature and provide some information on the concentration of isoprene within the studied areas.

We added that also isoprene can form such small compounds and refer to section 3.4.2 where we studied the isoprene/monoterpene emission ratios in the region around Hyytiälä and Zurich (Fig. S2):

"Some of these compounds were related to OH radical induced atmospheric aging of monoterpene SOA, especially at high NO_x conditions, in ambient as well as in laboratory experiments (Zhang et al., 2018; Mutzel et al., 2015) but could also originate from other biogenic precursors such as isoprene (see section 3.4.2)."

We highlight the information on page 10, L25-27:

"

Modelled biogenic emissions showed a higher isoprene (ISO, C₅H₈) to monoterpene (MT, C₁₀H₁₆) ratio in Switzerland than in Finland (Fig. S2, Jiang et al., 2018). The higher ISO/MT ratio in BVOC emissions in Zurich could contribute to the higher C3-C7 CHO compound contribution at this site (see above, Fig. 4, 5, 7).

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Supplementary Figure S9:

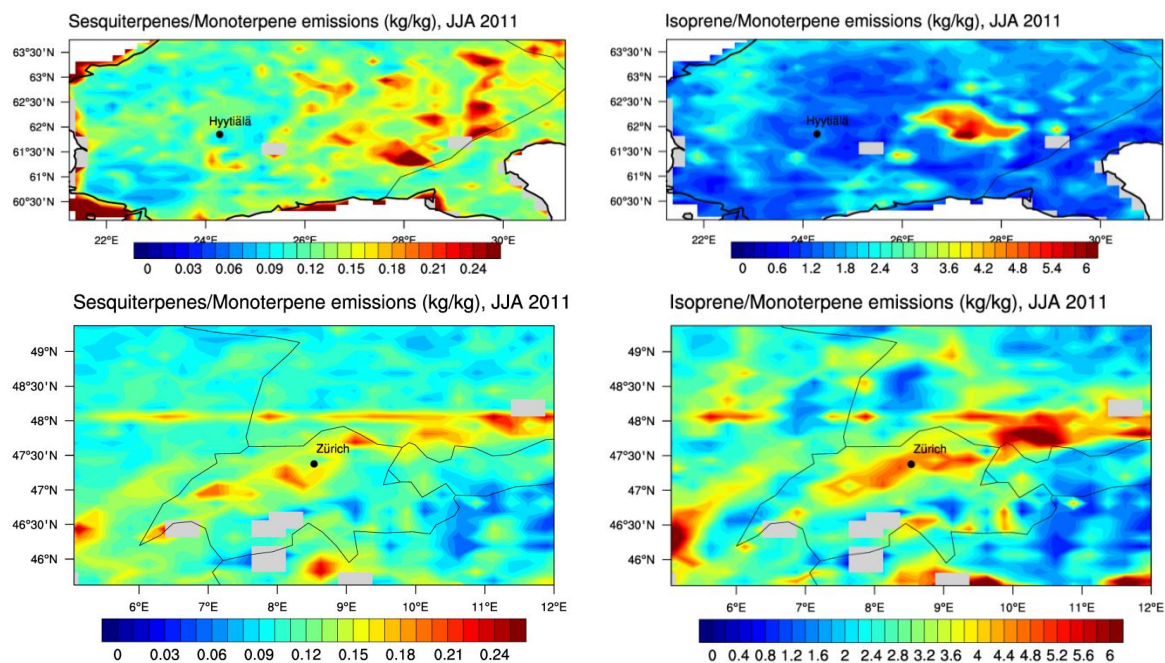


Figure S2: biogenic emissions of isoprene (ISO), monoterpene (MT), and sesquiterpenes (SQT) displayed as ratios SQT/MT and ISO/MT for the area (approx. 450 km x 450 km) surrounding Zurich, Switzerland, and Hyytiälä, Finland, calculated for summer 2011 using the MEGAN biogenic emission model (Jiang et al., 2018)

page 10, 3.4.2: The discussion of this paragraph is not consistent with the previous section. For instance, as it is written the authors suggest that the C4 & C5 compounds are formed from the aging of monoterpene-derived SOA but in the paragraph 3.4.2 they mention that the isoprene emissions are larger in Zurich than in Hyytiälä, implying that isoprene chemistry plays a bigger role in Zurich. Please clarify and make the discussion more consistent.

As detailed in the manuscript C4-C5 can be enhanced in Zurich compared to Hyytiälä for different reasons: 1) higher NO_x concentrations (Zurich>Hyytiälä) lead to enhanced fragmentation of monoterpenes (detailed in 3.4.4), and 2) higher isoprene/monoterpene emission ratio in Zurich than Hyytiälä (detailed in section 3.4.2).

We refer to the discussion in the manuscript.

Section 3.4.1, page 10, L16-21:

Meanwhile, small molecules such as C₄H₆O₅ (possibly related to malonic acid) and C₅H₈O₅ (possibly related to hydroxyglutaric acid) exhibited a higher fractional contribution in Zurich during summer than in Hyytiälä 2014 (Fig. 4, 6, 7, 8). Some of these compounds were related to OH radical induced atmospheric aging of monoterpene SOA, especially at high NO_x conditions, in ambient as well as in laboratory experiments (Zhang et al., 2018; Mutzel et al., 2015) but could also originate from other biogenic precursors such as isoprene (see section 3.4.2). In the following, we will discuss the possible reasons for the differences.

Section 3.4.2, page 10, L27-28:

The higher ISO/MT ratio in BVOC emissions in Zurich could contribute to the higher C3-C7 CHO compound contribution at this site (see above, Fig. 4, 5, 7).

Section 3.4.3, page 11, L20-24:

The increase in the proportion of smaller compounds (C3-C7) occurs despite their increasingly higher evaporation rates. This could be related to a higher fraction of 1st generation products residing in the gas-phase where they are prone to further oxidation, possibly also promoting fragmentation. Since the average temperature in Zurich during summer is 17°C (average T_{max}=21°C) this would partially explain the enhancement of the fraction of lower molecular weight compounds (C3-C7) compared to Hyytiälä.

Section 3.4.4, page 11, L26-31:

While laboratory monoterpene experiments show an important influence of functionalized monomeric oxidation products, ambient measurements have revealed an enhancement of fragmentation over functionalized products with increasing NO_x concentrations (Zhang et al., 2018). Fragmentation products of RO₂ + NO reactions and subsequent autooxidation could explain such observation. Since we observe a similar behavior (Fig. 7b) in this study, the higher (C3-C7)/(C8-C12) ratio in summertime Zurich than in Hyytiälä can be related to enhanced NO_x concentrations at the urban site (NO_x summertime Zurich: 15 ppb, Hyytiälä: 0.5 ppb).

page 13, lines 33-34: Based on the molecular signature of this group, can the authors propose a potential source? Could it be the VCP recently highlighted by McDonald et al. (2018, science)?

The question refers to the unexplained compound class characterized by carbon numbers between 9 and 12 and H/C between 1.5 and 2.0. Volatile chemical products, VCP, might contribute to the observed unexplained compound class. However, in absence of VCP laboratory aging experiments to compare our ambient SOA signatures to, we are unable to hypothesize on the origin of these compounds.

Figure 3b: Why is the dendrogram not symmetric? For instance, hyytiala 2011 vs hyytiala 2014 is different than hyytiala 2014 vs hyytiala 2011. It should not be like that, or should it be (if so, please explain)? In addition, the axes are not consistent compare to Figure 3a. Please revise Figure 3b to be consistent with Figure 3a.

Figure 3a presents a 2D clustergram and is sorted in both dimension and figure 3b only in one dimension, a 1D clustergram. The cells in Figure represent the fraction of peaks that a certain spectrum has in common with the sample indicated on the right axis of the figure.

Given 2 samples i and ii , the correlation R is the same for $R(i,ii)$ and $R(ii,i)$. The fraction of peaks that a sample i has in common with ii (number of peaks k) $k(i \cap ii)/k(i)$ is not the same as $k(ii \cap i)/k(ii)$. Therefore, only a 1D analysis can be performed.

We added more information in Section 2.4:

"

In approach B, we computed the number of peaks k that a sample i had in common with another sample ii normalized to the total number of peaks detected in sample i ($k(i \cap ii)/k(i)$)

"

We now added more information to the figure caption apply the same sorting also to the other dimension for easier readability.

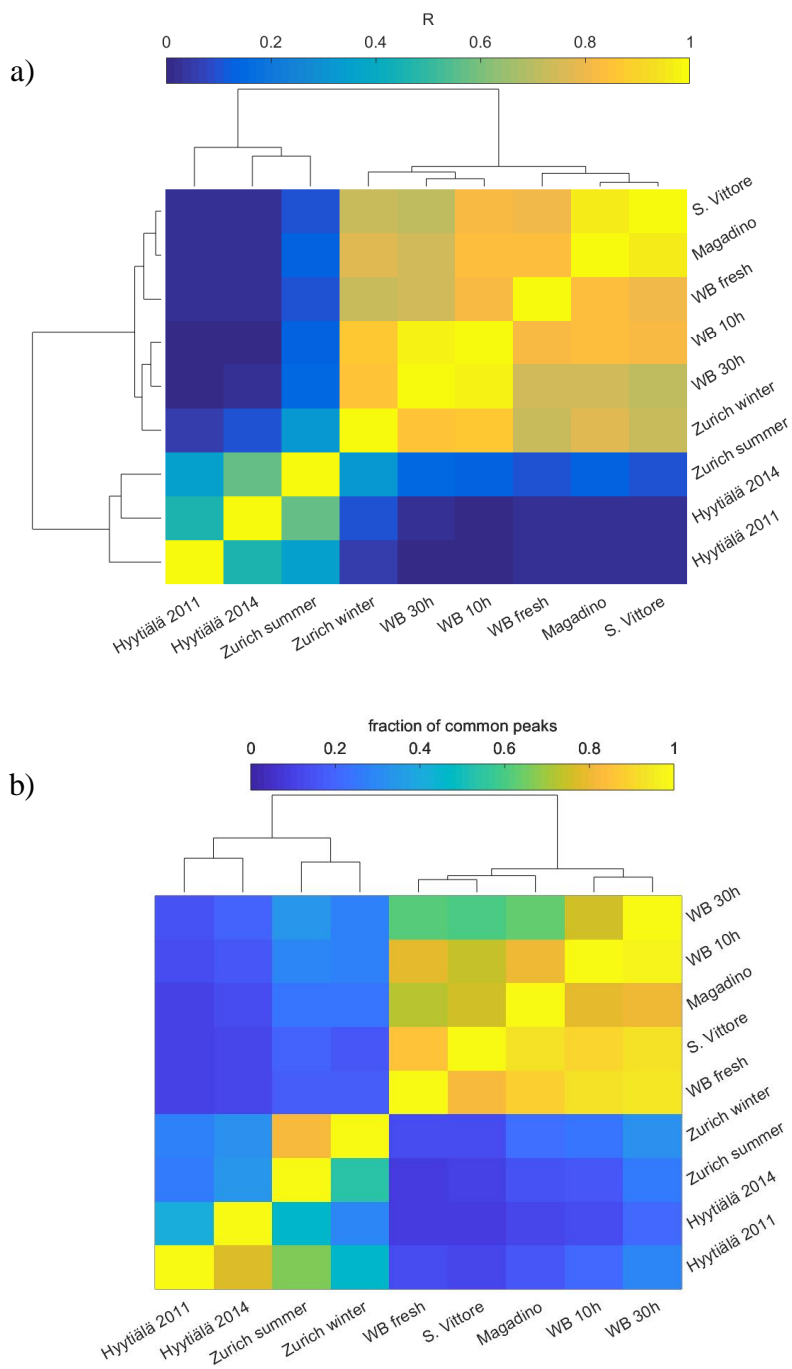


Figure 3: a) correlation matrix of mass spectra sorted by hierarchical cluster analysis also depicting the similarity as dendrograms, b) number of common peaks of a sample with the sample indicated on the y-axis normalized to the total number of peaks of the respective sample sorted by hierarchical cluster analysis also depicting the similarity as dendrograms.

"

Figure 5 (and S3) is hard to read. Please make all the graphs bigger. Another option would be to split the figure and have one figure for biogenic conditions with Zurich summer, Hyytiala 2011/2014 and possibly Zurich winter. Another figure will include wood burning experiments and episodes as well as Zurich winter.

The figures cannot be enlarged within the panel but we agree with the reviewer that the subpanels need to be well visible. This figure should be a full page figure in the final manuscript (we adapted the manuscript in this sense).

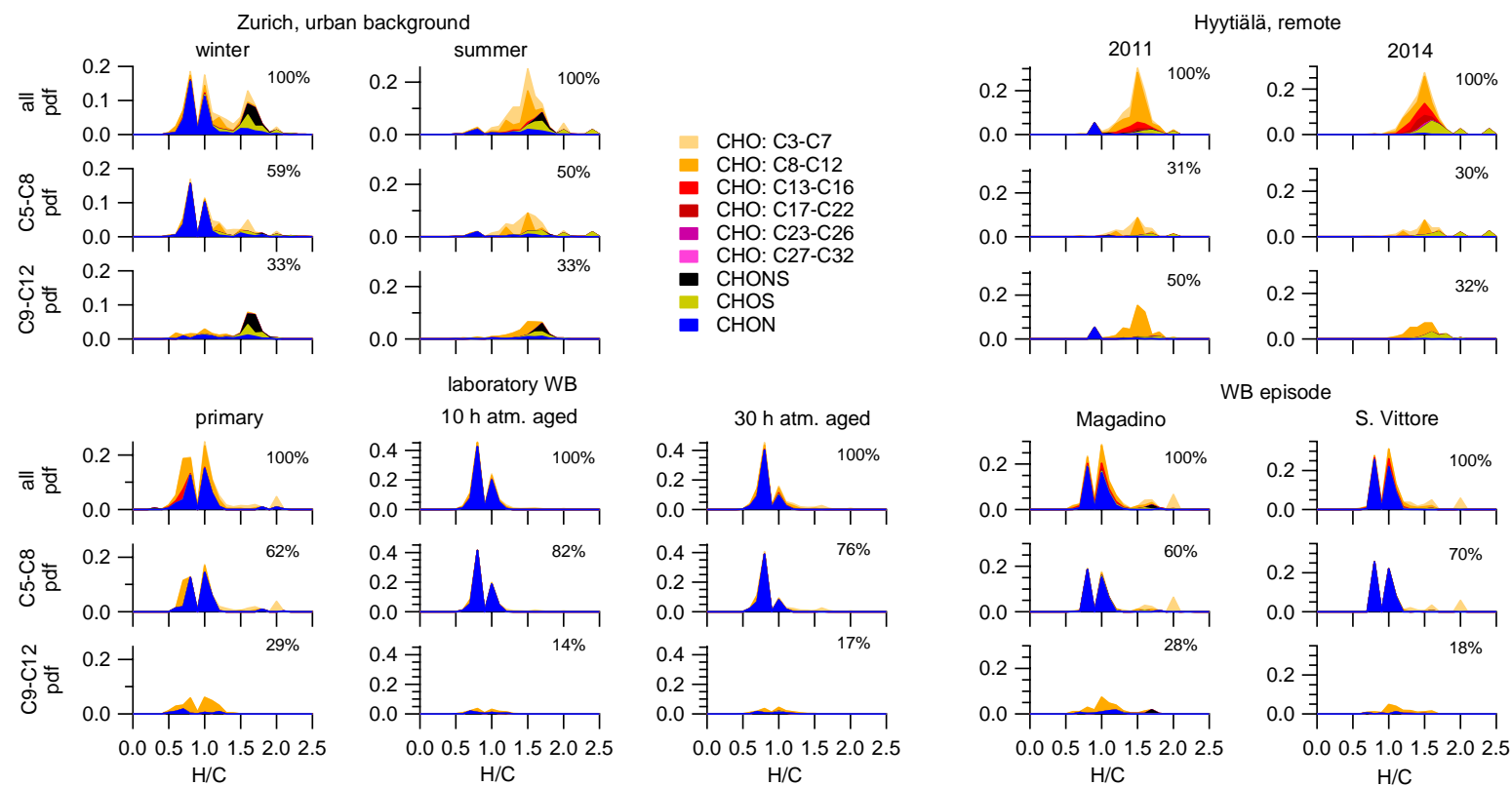


Figure 5: Probability density functions (pdf) and contributions of different molecule families to H/C for all molecules (neutral composition based on (-)ESI-ultra-high resolution mass spectra), molecules with 5 to 8 carbon atoms, and 9 to 12 carbon atoms for the ambient samples collected in Zurich, Magadino, S. Vittore, and wood burning smog chamber experiments. The area of the histograms is proportional to the percentage of the total signal explained for each data set.

Figure 7a is really hard to read and does not bring much information, as it is. It can be one separate figure and once again split between biogenic and wood burning SOA.

For a better readability we split Figure 7a from 7b, c, and d:

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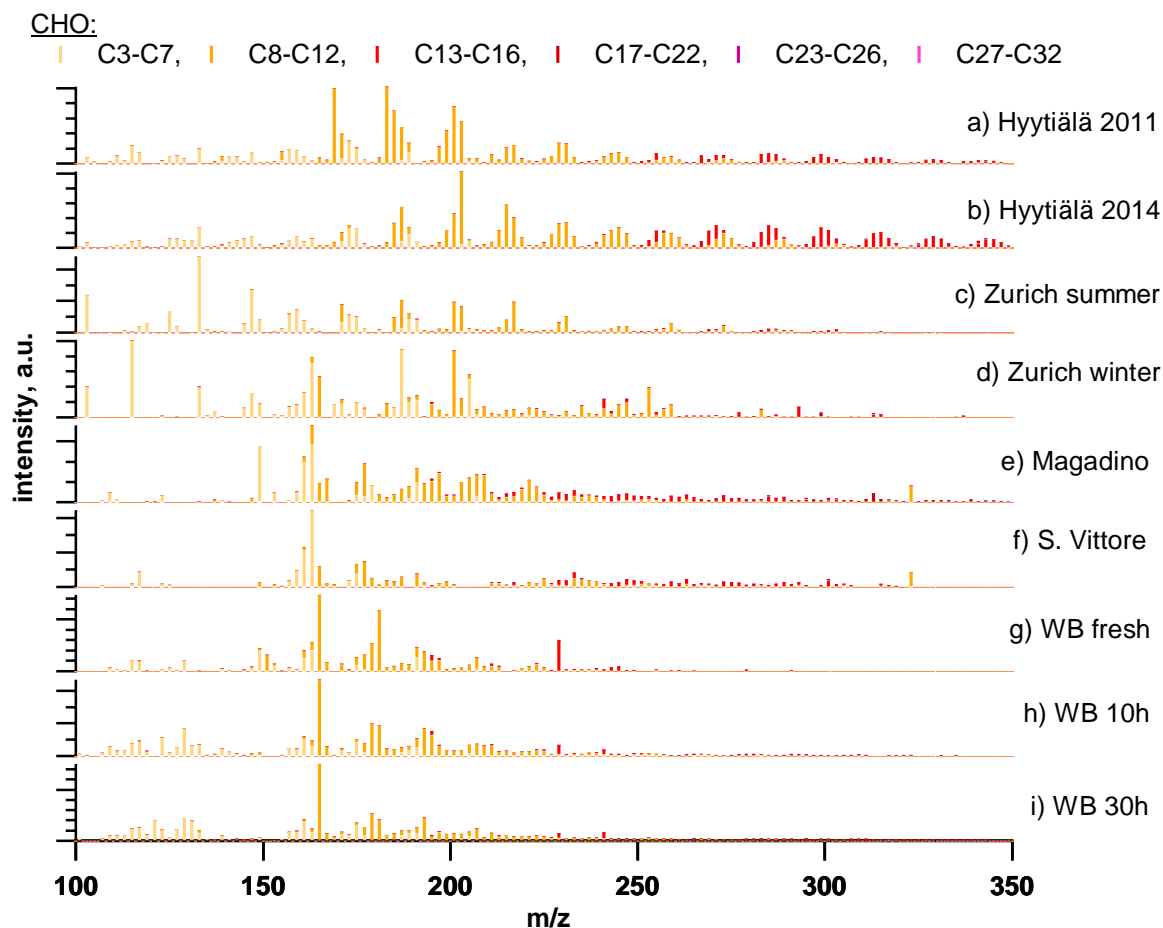


Figure 7: Ultra-high-resolution mass spectra of CHO compounds integrated to unit-mass resolution in the negative mode for the organic aerosol for Zurich during summer ($T > 11^\circ\text{C}$) and winter ($T < 6^\circ\text{C}$) 2013 (PM_{10} , OA-weighted average), for the Hyytiälä during campaigns in 2011 and 2014, during wood burning episodes in S. Vittore and Magadino and laboratory wood burning experiments (fresh emissions, 10h and 30h atmospherically aged),

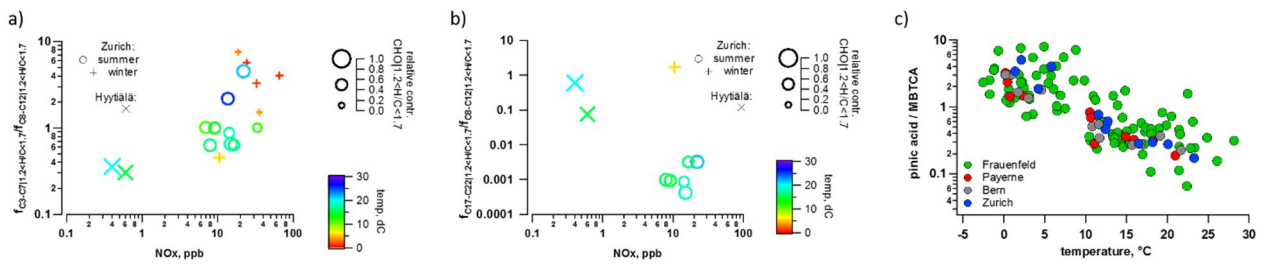


Figure 8: impact of NOx on fraction of (a) C3-C7 and (b) C17-C22 relative to C8-C12 compounds, c) ratio of pinic acid to MBTCA from LC-MS as a function of temperature.

Figure 9 (and S4) doesn't include Zurich winter. Why?

Equivalent figures are presented in Fig. 2 and Fig. S5.

technical comments:

page 1, line 19: define OA page 2, line 22: Marseilles should be Marseille

We corrected the mistake.