Reply to reviewers II (acp-2020-1244)

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The authors would like to thank the reviewers for their minor comments and suggestions, which helped improving the quality of this work. Once more, a new version of the manuscript has been prepared following the suggestions from the reviewers and replies for each comment are addressed in a point-by-point manner.

Anonymous Reviewer #1

I commend authors for such thorough and detailed revision that has addressed all my concerns. I recommend the manuscript for publication after few technical corrections listed below, are maid:

1. **Title: I do not think that 'interannual increase' is a correct term, 'interannual variation', maybe? Or, since you did provide a better proof for the trend, you could refer to an increase in secondary aerosol fraction due to potential growth in atmospheric oxidation potential, just a suggestion.**

The title was changed as follows:

Increase of secondary aerosol fraction in an urban background.

2. **Reply to comment No 4: 'In Zurich, for instance, f44 during summer afternoons, when photochemical processes are most vigorous as indicated by high oxidant – OX (O3 + NO2) was found similar or lower than f44 on days with low -OC, while f43 (less-oxidized fragment) tended to increase (Canonaco et al., 2015). The SOA is often divided into two factors: less oxidized oxygenated OA (LO-OOA) and more oxidized ozygenated OA (MO-OOA)'. Is this really correct - f44 lower for days with higher oxidation? Or this is a mistake, and the opposite was meant?**

This sentence is in accordance with the findings from (Canonaco et al., 2015), although it was rephrased for better understanding as follows:

In Zurich, however, f44 during summer afternoons, when photochemical processes are most vigorous as indicated by high oxidant – OX (O_3 + NO_2), was found similar or lower than f44 on days with low – OX, while f43 (less oxidized fragment) tended to increase (Canonaco et al., 2015). The SOA, also referred as Oxygenated OA (OOA), is often divided into two factors: less-oxidized oxygenated OA (LO-OOA) and more-oxidized oxygenated OA (MO-OOA).

3. **Reply to comment No 7: 'There are evident differences in meteorological variables from one period to the other (Fig. S7). In summer A, temperature (24.0° C) and solar radiation (259 W) are lower and average relative humidity (71%) and wind speed (2.0 m/s) are higher than in period B (27° C, 280W, 70.0%, 1.7m/s), indicating a probably rainier or cloudier summer in period A.' Check units for B, I assume 1.7 is m/s? Also,**

are such differences in RH (70% and 71%) as well as WS (2 vs. 1.7 m/s) significant? Otherwise, just state that they were similar.

The units of the meteorological variables for period B were corrected as follows:

(27.0^{o} C, 280W, 70%, 1.7m/s)

Neither relative humidity (RH) nor wind speed present significant variations. In the case of the relative humidity, a month-by-month Mann-Kendall test revealed a decreasing trend, which would be in line with the slight decrease that shows the period-average figures. The same statistic for wind speed does not support the decrease from period A to B, so the text was modified as follows:

There are not significant differences in meteorological variables from one period to the other (Fig. S7). In summer A, temperature (24.4^{o}C) and solar radiation (259 W) are lower, and relative humidity and wind speed (2.0 m/s) is similar compared to period B (27.0^{o} C, 280W, 70%, 1.7m/s, respectively). These results are in line with a colder and cloudier summer in A as is depicted in Meteocat (2020a, 2020c, 2020b).

4. **Reply to comment No 7: 'The composition-dependent collection efficiency (CE) correction (Middlebrook et al., 2012) correction was applied (minimum, maximum) for Period A and B respectively; (0.45±0.68), (0.50, 0.99), exceeding CE=0.6 a 0.13% and a 1.5% of data).' Is period B data missing here? I see the average, SD and range for the A period only?**

The authors were referring to minimum and maximum values, therefore, not averages nor SD were provided. The actual text was written as follows:

The composition-dependent collection efficiency correction (CE) (Middlebrook et al., 2012) was applied for the two periods with minimum and maximum values of 0.45 and 0.68 for period A and 0.50 and 0.99 for period B, exceeding CE=0.6 a 0.13% and a 1.5% of data, respectively.

Anonymous Reviewer #2

The authors did remarkable work in revising their manuscript and taking care of the comments which were properly addressed.

1. **However, I still have some concerns regarding the conclusion which does not contain the main message of the work and appears poorly structured.**

The conclusion was restructured as follows:

Characterization of non-refractory fine aerosol (NR-PM_1) in the urban background of Barcelona including organic aerosol (OA) source apportionment was performed regarding two nearly one-year periods between 2014 and 2018. Period-averaged PM_1 concentrations were 10.1 and 9.6 $\mu g \cdot m^{-3}$ respectively for the so-called periods A (May 2014 - May 2015) and B (September 2017 - October 2018). Slopes between total mass concentration of Q-ACSM species and BC and PM_1 retrieved by a Scanning Mobility Particle Sizer were near one, but Q-ACSM overestimation caused by the use of the default relative ionization efficiency for OA, probably lower than the actual one, cannot be discarded.

Average contributions of the inorganic NR-PM_1 were 19% and 18% for SO_4^{2-}, 16% and 13% for black carbon (BC), 10% and 13% for NO_3^-, 11% and 11% for NH_4^+ and <1% for Cl^- for periods A and B, respectively. Hence,

SO_4^{2-} and BC concentrations decreased from A to B, while NO_3^- ascended. Seasonal NR-PM_1 cycles consist of the maximization of OA and SO_4^{2-} in the warmer subperiods and NO_3^- (high volatility in hot conditions) and BC in the coldest. NO_x were also reduced on average from A to B, as well as O_3 and SO_2. Nevertheless, O_3 became more reactive on period B.

The OA was the major component in both periods under study, accounting for a 42% of total PM_1 in both periods. Five organic sources were identified by PMF: Cooking-like OA (COA), Hydrocarbon-like OA (HOA), Biomass Burning OA (BBOA), Less-Oxidized Oxygenated OA (LO-OOA) and More-Oxidized Oxygenated OA (MO-OOA). BBOA was only present in the subperiod November-March and only one OOA (Oxidized OA) factor was apportioned in this cold subperiod in 2014-2015. Secondary OA (SOA, comprised by the sum of OOAs) proportion and absolute concentrations increased from the first period to the second, while primary OA (POA) concentrations were reduced. In turn, LO-OOA and MO-OOA changed its relevance in OOA contributions, being the most oxidized the promoted one from 2014-2015 towards 2017-2018. The oxidation could be partially attributed to the action of solar radiation and temperature, in warm months both higher in period B, as the ratio LO-OOA-to-MO-OOA is also lower in summer. Nevertheless, the decreasing trend of NO_x and the increase of O_3 reactivity would position the increasing potential oxidation as a feasible cause as many other urban studies have reported. Seasonal variation of OA contributions was also affected by air masses origin. Northern flows and stagnation episodes induced primary pollution events, although high-SOA events were driven by long-range episodes, comprising Mediterranean and European advections (mainly MO-OOA), and regional breeze-driven recirculation (mainly LO-OOA).

Studies of NR-PM1 chemical composition and OA sources have been performed extensively in urban background sites, although to the authors' knowledge, this is one of the first in which the approach benefits of interannual comparison and airmass origin determination in the western Mediterranean basin. The results obtained highlight the role of SOA as the main source of OA and its permanency even if POA is reduced in this site. Moreover, the most aged-SOA airmasses are related with long-range European and Mediterranean circulations which drag pollutants accumulated during several days. However, some gaps remain unsolved about the oxidation of the urban-background atmosphere of Barcelona such as possible pathways of production and transformation of SOA and their interconnection with O_3 processes could be the objective of further investigations.

Minor comments:

2. The authors must reconsider the notation of their fitting parameters. Do they need to include 4 digits like lines 198-199 and Tab S1, while only 2 digits are used for the rest of the manuscript?

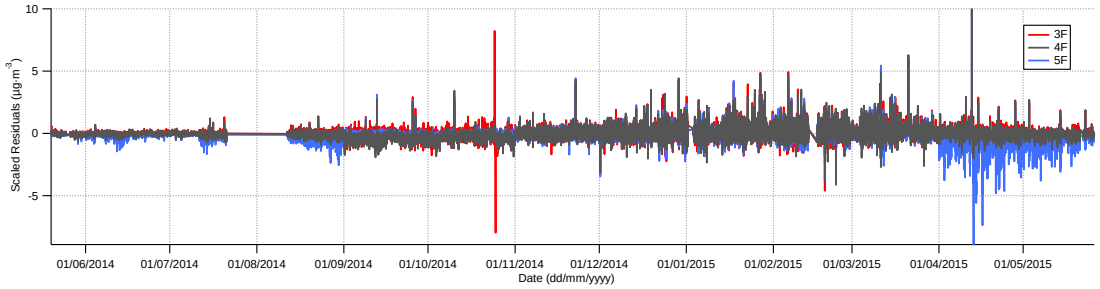
In the new version of the manuscript, the decimal digits are set to two in all of the squared correlation coefficient mentions, including Tables and Figures.

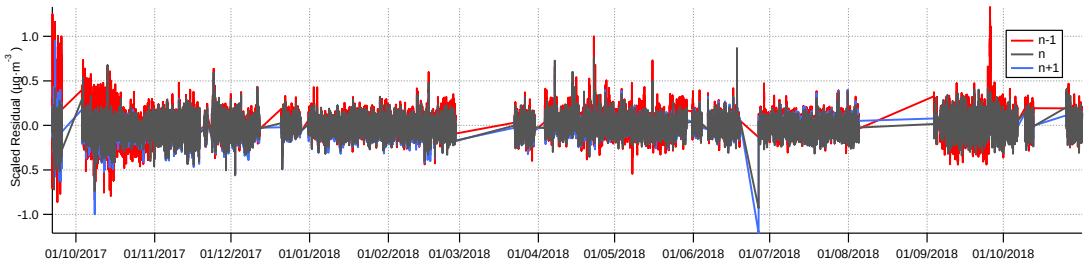
3. Line 433: replace "hydro-carbon-like" with "hydrocarbon-like".

This change was implemented on the manuscript.

4. Fig. S3: The three different colors of grey are not easy to distinguish.

These figures were improved for the sake of readability as follows:


Scaled Residuals (µg·m-3)
10
5
0
-5
3F
4F
5F
01/06/2014
01/07/2014
01/08/2014
01/09/2014
01/10/2014
01/11/2014
01/12/2014
01/01/2015
01/02/2015
01/03/2015
01/04/2015
01/05/2015
Date (dd/mm/yyyy)


Scaled Residual (µg·m-3)
1.0
0.5
0.0
-0.5
-1.0
n-1
n
n+1
01/10/2017
01/11/2017
01/12/2017
01/01/2018
01/02/2018
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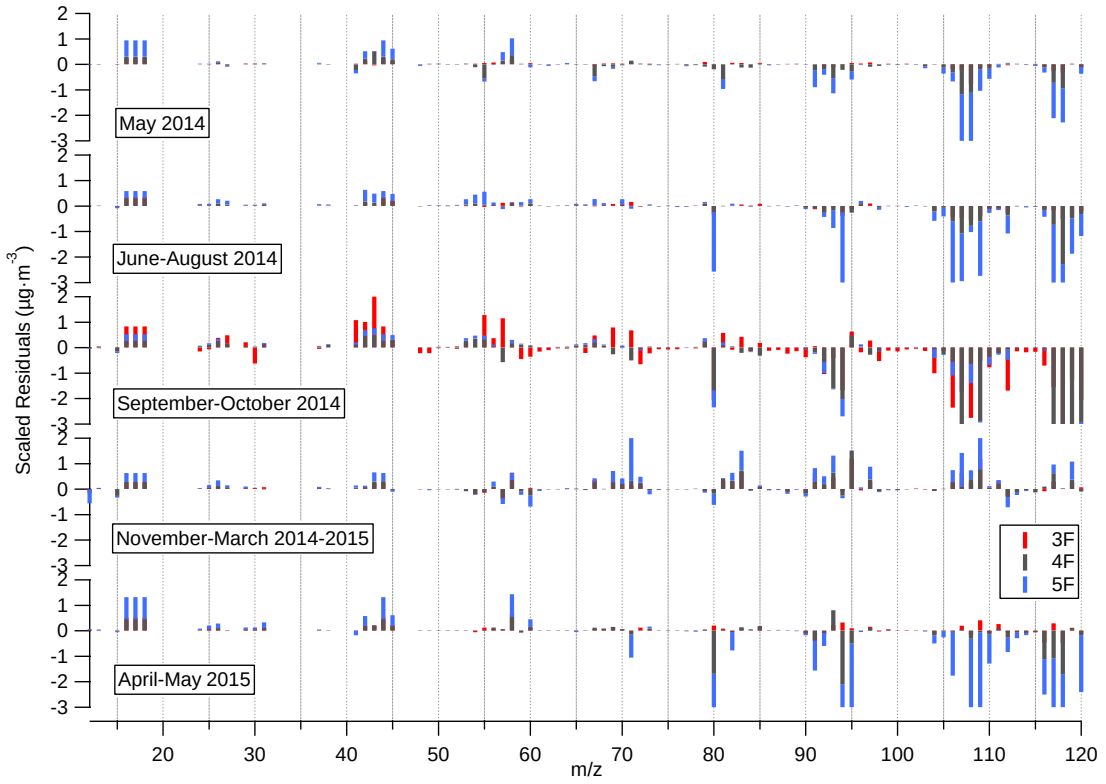
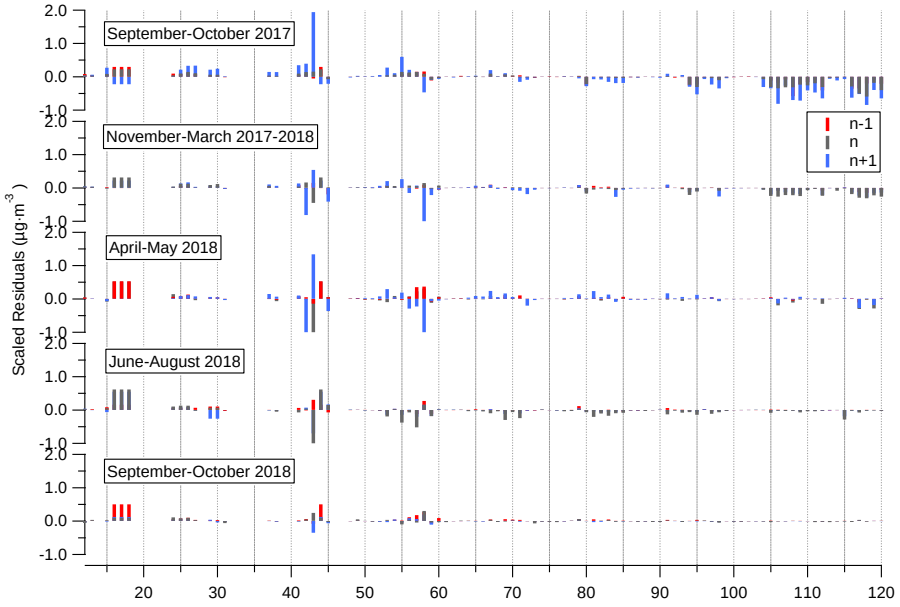
01/05/2018
01/06/2018
01/07/2018
01/08/2018
01/09/2018
01/10/2018


Scaled Residuals (µg·m-3)
May 2014
June-August 2014
September-October 2014
November-March 2014-2015
April-May 2015
3F
4F
5F
20
30
40
50
60
70
80
90
100
110
120
m/z



5. Figure S5: It would be better if all axes intercepted at zero.

Figure S5 was modified according on the reviewer's suggestion.