We thank all the constructive comments from two reviewers. The following texts are the response to the reviewers.

The normal italic font is original *reviewer comments,* smaller green font is authors' responses, and the small blue italic font is *the changes in the revised version.*

Anonymous Referee #2

Received and published: 6 March 2021

Review comments, This manuscript reports the analysis of one year of ACSM mass spectral data obtained from a polluted rural Swiss site using ME-2 implemented in the time-rolling scheme. Five factors were resolved, including two POA factors (traffic-related HOA and BBOA), one local OA (LOA) factor, and two oxygenated OA factors (a less oxidised LO-OOA and a more oxidised MO-OOA). The diurnal cycles, seasonal variations, sources and processes of the OA factors were discussed and the statistical and rotational uncertainties for the modelled OA factors were assessed. In addition, the rolling PMF analysis results were compared to the results from the conventional PMF analysis on the data segregated by seasons and the source apportionment of offline AMS filter samples. This is a valuable study that demonstrates the utility and strength of applying rolling PMF analysis to the long terms ACSM data. This paper is an important contribution to the field of aerosol source apportionment and should be accepted for publication after the following review comments are addressed.

This study is extensive and the amount of information given in the manuscript is massive. However, the texts can sometimes be a bit hard to follow and confusing. I suggest more efforts are made to organise the contents more effectively, streamline the discussions, and improve the paper's general readability. For example, the descriptions of various aspects of the PMF analysis are lengthy and somewhat lack of coherence. Compiling a summary table of the key information and parameters used in the analysis could be useful. Many figures in the manuscript and the supporting information are hard to read and the figure captions are ineffective. Font size should be increased to be legible under normal page view. Figure captions should be sufficiently detailed to make the figures understandable.

We thank the reviewer for the positive feedback. We also think this study will be very important to the community and will be a good role model for similar analyses.
Our apology for the poor presentation quality, therefore, we have put in an extensive effort to reorganise the structure of the manuscript in the revised version for both the main text and the SI. Specifically, we moved most of the methodologies and settings into the SI as suggested, and we have added a table of content for the SI to provide a good overview of the paper. Also, sequences of the figures in the SI were reordered to follow the storyline for both the main text and the SI. All the figures were reconstructed in the revised version based on the reviewer's specific comments.

The LOA factor appears to be an artifact arising under certain instrumental condition, thus is not a real ambient OA factor per se. Calling it Local OA implies that it is an OA component associated with certain local emission. This could be misleading, so are the discussions about the ambient behaviors of this factor.

We agree that LOA could lead to a misunderstanding of its source, therefore, we took the reviewer's suggestion and changed the name from LOA to *m/z* 58 related OA (58-OA) factor. The surface ionization changes due to the switch of the filament in the middle of the campaign and constraining of this factor during PMF analysis led to an overestimation of its mass concentration. The time series of it should be always considered as the upper limit of this source contribution, and the real mass concentration of it could be substantially lower. However, since the mass concentration remains low, we still consider it as a minor factor. Therefore, we only include it in the PMF analysis without further exploration of its potential source. To better explain the 58-OA factor, we therefore modified the introduction of this factor in Section 2.5 (revised version) as follows: "*The 58-OA was dominated by nitrogen-containing fragments (at m/z 58, 84, and 98). In general, ACSM estimates organic m/z 98 signal by dividing organic m/z 84 to a factor of 2 according to the* *fragmentation table of organic species that was provided by Allan et al. (2004). Thus, the intensity of m/z 98 is always half of the intensity of m/z 84 in each factor. This 58-OA only appeared after the filament was switched on 14 April 2014. The instrument setup thus strongly influenced the sensitivity of these components (likely due to influences of surface ionizsation). The nitrogen-containing ion, m/z 58, was also observed in Hildebrandt et al. (2011) due to the enhanced surface ionisation in a certain period. In addition, the potassium signal enhanced at the same time, which further corroborated our hypothesis of the enhanced surface ionisation. Also, since this factor was constrained through the whole dataset, the PMF model overestimated the mass concentration of this factor significantly, which leads to high uncertainties for the 58-OA. Therefore, the time series of this source should be considered as the upper limit, and the real mass concentration of it could be substantially lower. However, with the low mass concentration of the 58-OA during the whole campaign, we considered it as a minor factor. Thus, this factor was considered in the PMF analysis, but no further interpretation of its potential source will be attempted in this manuscript.*"

The effort to determine statistical and rotational uncertainties for the OA factors is commendable. One question however is since the PMF solutions are selected, the average a-value is calculated to be fairly low (around 0.2). The errors for the OA factors are then determined based on the selected PMF solution. Aren't this approach somehow circular?

The averaged employed *a*-value is around 0.2, but the upper *a*-value we allowed the model to vary is 0.4. Also, the employed *a*-value only give us a sense of the variabilities of OA source profiles. It does not necessarily mean the higher the averaged *a*-value, the higher the errors are. In addition, it is always worthwhile to check the distribution of employed *a*-values of these constrained factors. Because it can help us to cross-validate if the constrained factors have rather small errors, for example, when the error of BBOA is rather big, and there are quite many selected runs distributed at the highest a-value range, it could suggest that the upper *a*-value applied during bootstrap and rolling analysis is not sufficient. More freedom is required to obtain a better resolved BBOA factor. Moreover, this study combined the bootstrap re-sampling and rolling technique, therefore, it is also very important to understand the uncertainty in a more quantitative way using the time series of OA factors. Thus, we think both approaches are essential, and we would like to keep them both.

Line 22, Change "cite" to "site".

Corrected

Line 21 - 22, it is not appropriate to claim this study "the first ever application of rolling PMF analysis for a rural site . . ." The data analysed by Parworth et al. (2015) came from a rural site in Central United States and that study was the first to report the application of rolling window PMF analysis on long term ACSM data.

We appreciated the comment from the reviewer. We rephrased the sentence as follows: "*As the first-ever application of rolling PMF with ME-2 analysis on a yearlong dataset that is collected from a rural site,…."*

Section 2.2, it is useful to provide information about ACSM operation and quality control measures, such as the ACSM measurement time resolution, the detection limits for NR species.

We have added a sentence in the line 140, P 7 of Section 2.2 (revised version): "*In this study, we recorded the data with a time resolution of 30 minutes."* We did not conduct a detection limit analysis in this study. However,the mass closure analysis was described in the second paragraph of this section. Also, Section 1 of the SI described the quality of the CE corrected data using scatter plots (Fig. S1) vs collocated independent measurements.

Line 148, change "doesn't" to "don't"

We have moved this part into Section 1 of the SI, but of course, the typo has been corrected.

Line 179, what's the reason for the ion signals at m/z 12 and 13 being mostly negative? Is this an issue specific to this study?

It is not unusual for *m/z* 12 and 13 to be problematic in Q-ACSM data. To our knowledge, a conclusive reason for this has not been reported, but we speculate it may be due to electronic instability at the beginning of the quadrupole scan. However, their concentration is in any case quite low, and their exclusion from PMF therefore does not affect the results.

Line 179 -180, why is m/z 15 "affected by high biases due to potential interference with air signals"? ACSM determines particle signals as the difference between the filter-off and filter-on modes. So, aren't the air influences on the ACSM diff signals removed from the diff signals?

Some organic ions still need to correct some air interferences even after the subtraction of sample and filter signals, *m/z* 15 is one of them. In general, ACSM/AMS uses the fragmentation table created by Allan et al. (2004). The *m/z* 15 from the organic matrix is calculated using the following equations:

frag_organic[15]=[15]-frag_NH_4[15]-frag_air[15]

frag_air[15]=0.00368*frag_air[14]

frag_air[14]=[14]-frag_nitrate[14]

When we refer to the potential air interference, the coefficient (0.00368) we used to estimate frag_air[15] could vary from different environments because of the different proportions of the N15 isotope in the air in different environments. A similar phenomenon could also be observed for *m/z* 29 organic signal due to a similar issue. However, the lack of resolution in *m/z* of the ACSM makes it difficult to perfectly isolate the air interference. Therefore, we have to remove it before PMF analysis.

Line 251, the meaning of "within a range of 0.4" is vague. Spell out the range. What exactly does "random" mean in "a random a-value"?

We appreciate the input from the reviewer. We have moved this section (PMF Window settings) into the Section 3.2.3 of the SI, and the sentence has been changed to: *"To allow the factor profile to adapt itself over time, we applied an a-value randomly from a set of a-values, including 0, 0.1, 0.2, 0.3, and 0.4 (so-called random a-value approach)."* Here, "random" means that with 50 repeats per PMF window, the PMF window can apply *a*-values randomly within the range of 0-0.4 (Δ*a*-value=0.1).

Section "2.6.1 Window settings", many discussions within this section do not seem closely related to the topic of setting the proper rolling window size.

We have changed the section name to "PMF window settings". Here, we mention that we test the optimum window size using different window lengths (1, 7, 14, and 28 days) in this section. But of course, we do not mention the optimum window size yet, since it would be covered in Section 4 of SI.

Line 254- 255, it is mentioned that different a-values were chosen to constrain the fitting of LOA. is there any significance with the specific value?

Not really, we can get this 58-OA even from unconstrained PMF. The changes of different *a*-values do not have significant influence on the PMF solutions. However, since the factor profile is always stable and unique, we did not attempt the random a-value approach during rolling analysis to save some computational time. Specifically, let's say we had an upper a-value for 58-OA of 0.4 with the Δ*a*-value of 0.1. Then, it would have 5 possible a-values for 58-OA. When we consider HOA and BBOA in this study, we will end up with 5*5*5=125 possibilities. In order to cover all the possibilities during the bootstrap process, we have to set the iterations of each time window to more than 125. In the end, the total PMF runs will be 2.5 times more than the current PMF runs. Therefore, we did not consider applying a random *a*-value approach for this factor.

Line 257, does this sentence suggest surface ionisation enhances the production of N-containing ions? Are there reference(s) to support this?

Yes, we do suggest that. But we can only speculate on the potential chemical fingerprints of these three ions (*m/z* 58, 84, and 98) based on the NIST database. But we cannot make a strong statement with the poor *m/z* resolution of the ACSM.

As the LOA factor appeared after a filament change, it is a factor associated with a certain instrument condition. ME-2 analysis that constraints the LOA profile may lead to the retrieval of this factor may be forced even when it was not supposed to be present.

The 58-OA is always present for the spring, summer, and fall 2014 seasons during unconstrained PMF. Therefore, we do believe the presence of it after the filament change. Regarding the fall 2013 and winter seasons, it is true that we cannot identify 58-OA from unconstrained PMF, but the contribution of this factor is so small (1.2% and 0.7% in Fig. 4) that we think it is OK to leave it in for the yearlong rolling analysis. We do not want to run rolling PMF separately with a different number of factors to avoid an inconsistent transition period. Therefore, we decided to keep this factor for the whole year although its contribution before the filament change was negligible.

Line 277, what is eBCtr ?

Thanks a lot for the notice, we have added the descriptions for this acronym and eBCwb at the place where they first occur.

Line 282, isn't the measurements done with Q-AMS, how was it known that m/z 43 is C2H3O+?

We removed (Canonaco et al., 2015) from the citation. Ng et al. (2010) used Q-AMS datasets for the analysis, and they did conclude that *m/z* 43 of OOA factors is mainly from $C_2H_3O^+$. In addition, we added (Crippa et al., 2014) to the citation. This overview study includes quite a bit of HR-AMS measurements, they also clearly stated that *m/z* 43 of OOA factors is mainly from $C_2H_3O^+$.

Line 287 – 288, what do 4th and 5th position reference to?

In total, we have 5 facotrs with two unconstrained factors (MO-OOA and LO-OOA) at either 4th or 5th position in all 20750 PMF runs.Therefore, we need to put the MO-OOA factor into the same position (4th position in this study) for all 20750 runs before averaging. But of course, we need to explain it better. Therefore, the sentence has been rephrased to: "*Since we left two factors unconstrained (4th and 5th factor), MO-OOA can be at either at the 4th or the 5th position in these 20750 runs.*"

Line 316, define BLH

Modified.

Line 325-328, this sentence is awkward and difficult to understand. Consider to revise.

We thank the suggestion from the reviewer, we have modified it to: *"It was due to advection within the shallow boundary layer as both primary and secondary pollutants increased simultaneously. At the same time, the local wind speed near the ground was very low. One potential explanation was that the locally and regionally induced orography influenced winds, including vertical diffusion processes, caused these delayed midday peaks. However, these processes remain difficult to track without spatially distributed measurements."*

Line 398, the small seasonal differences in HOA% is interesting. What's the explanation? Since HOA is mainly a POA factor whose concentration should be influenced strongly by BLH, it loading tends to be much higher during winter than in summer. In contrast, stronger photochemistry tends for lead to higher SOA in the summer. So the seasonal difference in HOA% is expected to be strong in winter.

It is true that BLH heavily influences the seasonal variabilities of HOA mass concentration. Also, it is true that the HOA mass concentration is higher in winter (0.74 µg·m^{-3}) than in summer (0.57 µg·m^{-3}) because of the higher OA loadings in the winter, which was due to the fact that the lower temperature in winter favors components partitioning into the particle phase and and also higher biomass burning related OA sources (BBOA and LO-OOA in winter). However, we cannot state that the HOA contribution was higher in the winter when both HOA and OA mass concentration increased.

Line 428, what are the standard deviations for the a values?

The standard deviations have been added in the sentence: *"HOA and BBOA have averaged a-values of 0.207±0.036 and 0.195±0.050, respectively."*

Line 483, is dimethyl disulphide sufficiently low volatility to be in the particle phase? Are there HR-AMS or other analytical results to support the presence of this compound? As pesticide application is usually seasonal, did you see evidence from this perspective?

Thanks to the comment from the reviewer. We modified the sentence to *"In July, a potential source of these distinct ions was some oxidation products of dimethyl disulphide, which shows signals at m/z 94, m/z 95, and m/z 96 (NIST Mass Spectrometry Data Center, 2014)."* Despite the high volatility of dimethyl disulphide, considering the monitoring station is literally in the middle of a farmland, we still believe there were possibilities that oxidation products of it could be detected by our online instrument. However, again, this can only be speculated with the poor *m/z* resolution of the ACSM. Nevertheless, it is a potential explanation of this event.

Line 519 – 521, are there references to support this statement?

We have changed the statement to*:" This was most likely due to the increase of biogenic sources and the increasing photochemistry (high O_3 and NO_2 concentration) at high temperature (>20 °C), which caused the complexity of the OOA sources."* These high-temperature points were mainly from summer, and the O_3 concentration was also very high at the same time (Figure. R1 (b)). Therefore, we changed the statement by explained it in a better way as the reviewer suggested.

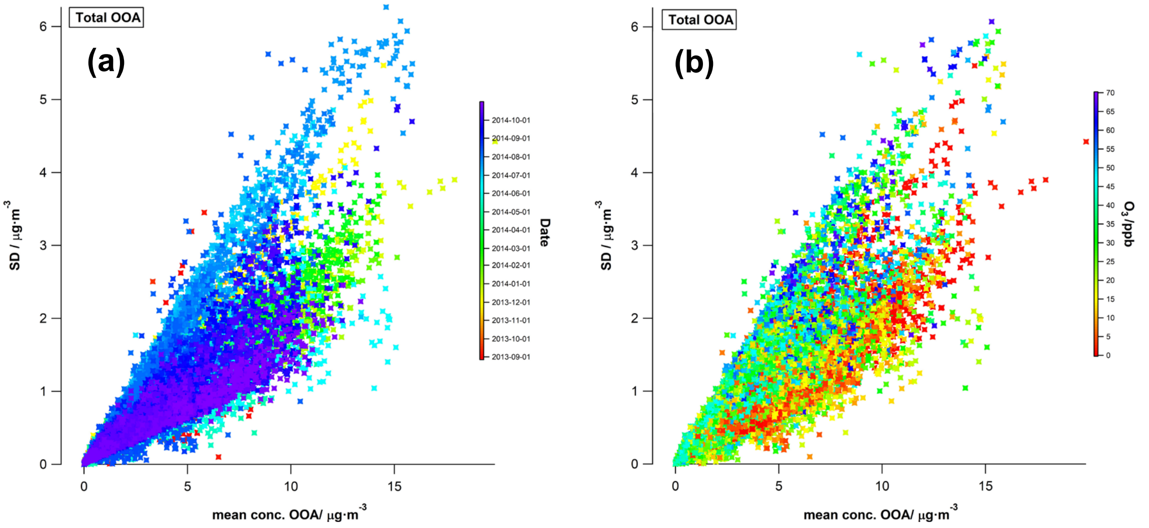

Figure. R 1 Absolute statistical uncertainties of PMF for Total OOA (LO-OOA+MO-OOA) for all data: (a) The data points are colour-coded by date and time and (b) the data points are colour-coded by O_3 concentration (ppb).

Fig 3, what do BCtr, BCwb stand for?

These are equivalent black carbon from traffic source (eBCtr), equivalent black carbon from wood burning source (eBCwb), we have added a spelling out the description in the main text. Moreover, we make sure all these terms, eBC, eBCtr, and eBCwb are consistent.

Fig. S6, explain the error bars in the caption

Modified to:"***Fig. S4*** *Averaged factor profiles from seasonal bootstrap solutions for five different periods. The error bars of each factor represent the standard deviation of the averaged bootstrapped solution, the thick dark sticks are the variabilities that each variable allowed to vary with the corresponding averaged a-value. SON = September, October and November, DJF = December, January and February, MAM = March, April, and May, JJA = June, July, and August.*"

Fig S8, how exact was the probabilities calculated?

Each PMF time window has 50 repeats, while only part of these 50 repeats would be selected. The probabilities were calculated using the employed *a*-values from selected PMF runs for each time window.

Fig. S9, the key is difficult to understand, what are the dots exactly, what does it mean "clouds of measured f44 vs. f43 in SOA factors"?

We added Eq. S11 and Eq. S12 into the SI to describe how these small dots are calculated.

$$subtracted\ f_{44} = \frac{mass\ conc.of\ OOA\ @[m/z\ 44]}{mass\ conc.of\ OOA + residual\ of\ total\ OA} \tag{11}$$

$$subtracted\ f_{43} = \frac{mass\ conc.of\ OOA\ @[m/z\ 43]}{mass\ conc.of\ OOA + residual\ of\ total\ OA} \tag{12}$$

Fig. S10, figure caption hard to understand. What are the "Missing time points"?

Modified to: "***Fig. S10*** *Non-modelled time points (due to criteria-based selection) and $Q/Q_{exp.}$ vs rolling window size.*"

Reference

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