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Revised manuscript with all changes highlighted

Revised supplement with all changes highlighted

Reply to:

Anonymous Referee #1

Referee comments in black, author replies in blue

This article presents a fourteen-month dataset of the chemical composition of submicron aerosols at a high altitude site in the Swiss Alps. Long-term datasets at high time resolution are rather new, as well as the instrumentation used (TOF-ACSM), which makes this study unique and very interesting. The topic is obviously within the scope of ACP. I recommend publication in ACP after all major and minor comments listed below are addressed by the authors.

Major concerns.

First, I suggest the authors to reorganize the introduction. In its current form, I find it pretty hard to follow. I would have expected a thought process like: Why is it important to measure in FT? Why long term measurements? Why MS techniques rather than filters? Why ACSM? Why TOF? All of these questions were not clearly answered.

The introduction was rearranged according to the suggestion and a few sentences were added to clarify and answer the stated questions.

1. Why measure in the FT

"Knowledge of the aerosol concentrations and properties in the lower FT is important due to its impact on cloud formation and to validate model results from the FT."

2. Why long-term?

"Long-term measurements are essential to capture long-term trends, inter-season variations or other effects taking place on longer time scales. Furthermore, increasing data coverage allows for a more reliable determination of the typical aerosol conditions at a specific site."

Second, I have serious concerns about the organic mass spectra analysis, which I found too weak to be published as is. - ME-2 was performed seasonally, because the use of fixed factor profiles over long term periods is conceptually inappropriate (and I fully agree with this). It would have been appreciated to clearly see the benefit of this approach compared to one single PMF run (leading to unidentified factors, or high seasonal residuals for example?). Seasonal PMF of OA is a new topic, the authors need to provide more information.

Since in many regions distinctively different sources for primary aerosol or precursors for secondary aerosol formation exist during the various seasons (especially winter/summer) it is generally advised to perform separate PMF source apportionment due to the nature of inflexible source profiles within one analysis. This is investigated on the basis of the OOA factors in Canonaco et al. (2015) (doi:10.5194/acp-15-6993-2015, in the manuscript the discussion version of that paper is referenced because the final version was not yet available at the time of submission) and the authors conclude that “PMF analysis of multiseason data employing only two OOA factors cannot capture the seasonal variability of OOA.” Additionally, a primary source which is not present during the whole period (e.g. BBOA) is likely to not be extracted properly by a multi-season PMF. It becomes more and more likely that e.g. a non-physical splitting of a factor present during the whole year reduces the PMF residuals more than the addition of a small but real primary factor making it impossible to retrieve this factor. In their guidelines for PMF on AMS data Ulbrich et al. (2009) state that factors contributing less than 5% are often difficult to extract effectively. Seasonal PMF for long-term datasets was also performed before by Minguillon et al. (2015) (doi:10.5194/acp-15-6379-2015) and Tiitta et al. (2014) (doi:10.5194/acp-14-1909-2014). Parworth et al. (2015) (doi:10.1016/j.atmosenv.2015.01.060) even took it one step further and ran separate PMF on shifting two-week windows (which they call “rolling window technique”) over a full period of 19 months to capture changes in the OOA and BBOA factors. Hence, a separation into seasons increases the chances to find factors only present during part of the year. Since these limitations have already been discussed elsewhere and are reviewed in our manuscript (addition of a paragraph after P18247 L 9) we don’t expect to be able to draw additional conclusions from our dataset and did not perform additional multi-season PMF.

eBC data are available. Why this hasn’t been used to optimize a values, as presented in Frohlich et al., 2015?

Yes, eBC data is available but due to the very low concentrations no reliable eBC source apportionment is possible at the JFJ. Additionally, while an optimisation of the a value with correlation to external tracers like eBC usually is an adequate and reliable way to constrain a solution we do not think that this holds true in the case of the JFJ. At the JFJ, aerosol of all sources (except POAloc) is transported vertically to the JFJ at the same time resulting in similarly good correlations of all sources with eBC, see e.g. Fig1c. The JFJ specific challenges are discussed on P18247. As mentioned there, we were unable to select an optimal solution (i.e. optimal a values) and instead report the mean result of all solutions from a range of reasonable a values. This can be called a form of “extended chemical mass balance” where a range of fixed profiles is considered while leaving the OOA unconstrained.

More globally, some papers (Crippa et al., 2014; Frohlich et al., 2015) clearly give guidelines for OA source apportionment, that don’t seem to be followed in this study. Is the JFJ site too specific, so that these guidelines don’t apply?

We are well aware of these guidelines and tried to follow them as much as possible but due to the specific conditions at the JFJ high elevation site not all were applicable. Below, the recommendations are listed and commented separately.

Crippa et al. (2014) report the following methodology:

1. Unconstrained run (PMF).

This was our first step, which did not result in stable and unambiguously interpretable solutions.

2. Constrain the HOA mass spectrum (MS) with a low a value (e.g., a =0.05–0.1) and test various number of factors.

The HOA was constrained and the mean result of solutions within the HOA a range given in TabS1 is reported.

3. Look for BBOA (if not identified yet): constrain the BBOA MS if f60 (i.e., the fraction of m/z 60 to the total organic mass) is above background level and check temporal structures like diurnal increases in the evening during the cold season due to domestic wood burning (suggested a value = 0.3–0.5).

f60 was investigated and elevated contributions, especially in winter, lead to the introduction of BBOA in the source apportionment but only the seasons winter 2012/2013 and summer 2013 led to contributions above 1% which is why BBOA was not considered during the other seasons. The mean results of solutions within the BBOA a range given in TabS1 are reported.

4. Look for COA (if cooking not found yet): check the f55–f57 plot for cooking evidence (where f55 and f57 are the fraction of m/z 55 and m/z 57 to the total organic mass respectively; see Mohr et al., 2012). Fix it in any case and check its diurnal pattern (the presence of the meal hour peaks is necessary to support it at least in urban areas).

The vertical transport pattern makes it very difficult to separate HOA and COA arriving from the valley due to the absence of usable diurnal cycles which usually present a strong argument for COA. A note that it cannot be excluded that part of the advected HOA actually is COA was added to the text.

5. Residual analysis: a structure in the residual diurnals might indicate possible sources not separated yet by the model (refer to Section 3.2.3). For each step the residual plots should always be consulted in order to evaluate whether the constrained profile(s) has(have) caused structures in the residuals. If so, the constrained profile should be tested with a higher scalar a value.

Residual analysis is a very important step and was conducted throughout the analysis. Diurnal average residual plots for all seasons have been added to the supplement.

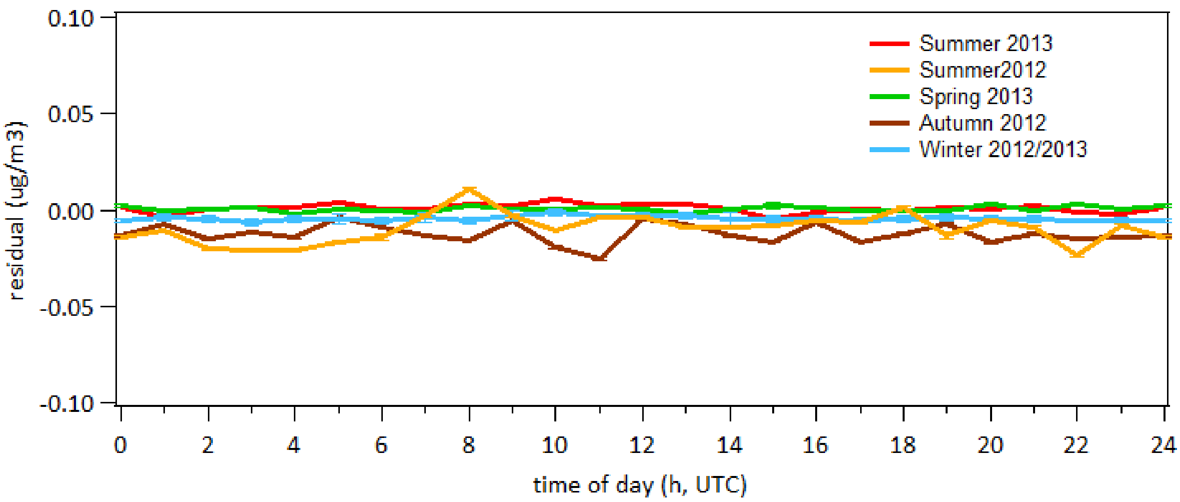

Figure 1: Average diurnal residuals in ug/m3. The mean of all ME-2 runs included in the presented solutions is shown. The error bars indicate the first standard deviation.

Residuals are close to zero during all seasons. No significant structure remained in the residuals. During some of the seasons (winter, autumn and summer 2012) slightly negative residuals are observed indicating a slight overestimation of the OA factors.

6. In general the OOA components are not fixed, but are left as 1 to 3 additional unconstrained factors.

1-2 unconstrained OOAs are reported depending on season.

Fröhlich et al. (2015) give the following recommendations

Profile constraints on the m/z 44 signal should be avoided or kept as loose as possible (high a value for m/z 44).

As mentioned in a comment below the extracted POAloc exhibits f44 of zero and for HOA (f44 < 0.02) and BBOA (f44 > 0.03) large ranges of a values were explored and taken into account in the reported solution.

If constraints are applied to the m/z 44 signal, a sensitivity analysis, e.g. by manual modification of the relative amount of the m/z 44 signal is recommended.

The absence of usable external tracers at the JFJ to help optimise solutions makes it impossible to ascertain the correct f44 value. However, considering the CE = 1 at the JFJ makes it unlikely that f44 is increased a lot in the ToF-ACSM data from the JFJ, see reply concerning the f44 in POAloc.

Anchor profiles constructed from the studied data set are preferable to database profiles. These profiles can often be extracted from solutions with additional factors (e.g. this study) or from separate PMF on parts of the data set with high fractional contributions of a factor (e.g. period with nearby forest fires or high primary traffic emissions).

The POAloc was extracted directly from the dataset. For HOA and BBOA this was not possible.

The PMF results of short-term, high-resolution AMS measurements overlapping with long-term ACSM measurements can provide useful constraints on the source apportionment of the ACSM data set (e.g. number of factors, special features in a profile).

Not applicable here.

If no profiles can be extracted with the methods described above, it is advised to try and compare different database anchor profiles (e.g. by comparing SA results to external data or comparing changes in diurnal cycles). This is more crucial for factors for which the profiles typically show larger variations between sites (e.g. BBOA, see Ng et al., 2011b) as opposed to factors with more similar profiles (e.g. HOA, see Ng et al., 2011b).

The absence of usable external tracers to optimise solutions makes it impossible to judge which profile gives the more exact solutions. Therefore the averaged reference spectra from Ng. et al. (2011) were used. The reporting of the mean of many solutions spanning a wide range of a values reduces the bias towards a reference.

Also, Q values doesn’t seem to be used here, but it is an essential mathematical parameter of PMF analysis; is there a reason for that?

Q values are more important for pure PMF source apportionments, by applying constraints with ME-2 the Q-value is modified (increased) and does not give much additional information compared to a close look at the residuals. Already Ulbrich et al. (2009) point out in their conclusions that the change in the Q values does not lead to strong conclusions for the real world data case they investigated. For this reason Q values are not discussed.

The profile variability also theoretically applies for air mass origins (clusters) and FT/PBL, where different kind of profiles can reasonably be expected.

Yes, but since we are not able to make a definitive selection (no optimisation of a values like e.g. in Fröhlich et al. (2015) possible) we report the mean of a range of solutions with different a values which covers small profile variations. Larger profile variations would show up in the residual plot (e.g. increased residual at m/z 44 if the air masses from one region were significantly more aged. No such increased residuals were observed. The difference FT/PBL is inherent in the separation between the two OOAs. The contribution of the OOA with the lower oxidation is increased during periods with increased PBL air injection (see FigS13). This is also discussed in the text, e.g. on P18249 (top) or P18254 (middle) or in Fig. S8.

From Fig10, the f44 & f43 are mostly influenced by seasons, and not much by the air mass origins or FT/PBL (which is somehow surprising, but is a very important result that is not really discussed).

We indeed think the f44 vs f43 is affected by the vertical transport pattern, i.e. FT/PBL. The change in the strength of the vertical transport causes most of the seasonal differences. In the warmer season more of the less oxidised OOA fraction is transported to the JFJ. This is discussed in Sect. 3.2.2. Also we think that the difference FT/PBL in Fig 10 is only little smaller compared to the difference between the seasons, indicating that not all of the seasonal difference can be explained by the increased vertical transport but also by different OOAs (see squares in Fig 10d). Air masses transported from the PBL to the JFJ can already be well aged due to the increased photochemistry on days with fair weather favouring thermally induced vertical transport.

This means that doing PMF differentiated by clusters or FT/PBL (which would have been appreciated in this study) would not help much; but in Fig10, POA factors were subtracted, which leads me to another major concern : - While I don’t disagree on the method used to extract POA profile, I have serious doubts on the outcome. How do the authors justify the fact that no m/z44 is present in the profile, as opposed to the CSOA profile from Faber et al. (2013)?

We observed frequent short-term OA peaks at the JFJ which are also evident in the particle number and only appear during the daytime and only during hours when tourists are present. These short-term spikes can only originate from a local primary source. Inclusion of the profile of these short-term peaks (resembling very much primary OA profiles containing high fractions of aliphatic compounds) into the ME2 analysis enabled a clear separation of all short-term peaks from the rest of the data. This fact represents a very strong additional evidence for a local source. Because of the mentioned reasons the factor is termed local POA. The only potential sources for local primary emissions are limited to activities related to tourism. The options are: fossil fuel combustion, cooking and cigarette smoking. By weighting the evidence we concluded that cigarette smoke was the most likely source (but still refrain from calling it cigarette smoke OA). Due to the frequency and regularity of the spikes fossil fuel combustion can be excluded (compare Fig. 1 below and Fig. S10 in the supplement) because these emissions would either be caused by scheduled construction activities, irregular helicopter flights or snowcat emissions (maximum once or twice a day). See also discussion in the text on P18250.

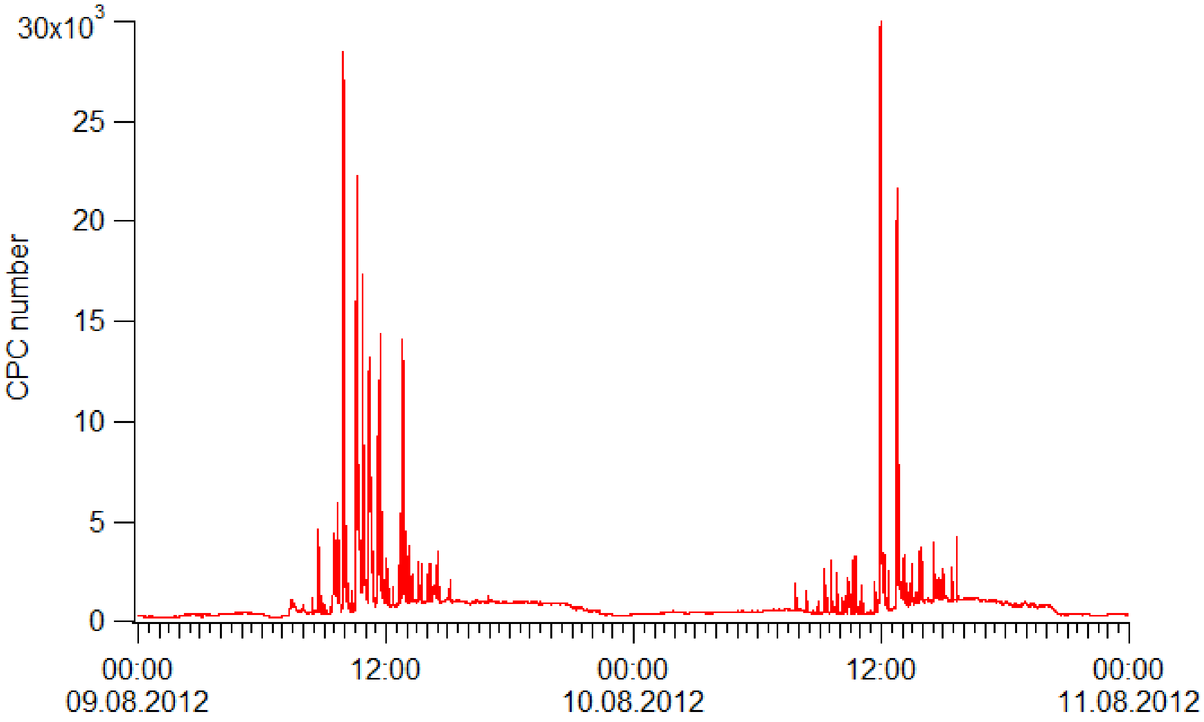

Figure 2: CPC number concentration with high time resolution. The time with peaks correlates with the timetable of the Jungfraujoch trains.

Correlations of POAloc with COA and cigarette smoke OA showed larger similarities with the cigarette smoke OA profile provided by Faber et al. (2013) Additionally, environmental tobacco smoke markers were measured at the same site before by Morrical and Zenobi (2002)and nicotine is one of the major ions seen by colleagues on site with an API-TOF (personal communication with Carla Frege, Paul Scherrer Institute). Further evidence for tobacco as the source of POAloc is given by the increased frequency of signal spikes on days with agreeable weather (see Fig. S9), no night-time events and the increased response of the near-ultraviolet wavelength signal of the Aethalometer (370nm, see Fig. 3 below) during POAloc spikes. On many occasions (prerequisite is that the ToF-ACSM is not in filter mode and the Aethalometer is measuring at the correct wavelength), the POAloc spikes appear concurrently with an increased Aethalometer signal at the 370 nm channel. Tobacco smoke is known to have increased optical absorption at the near-ultraviolet wavelength of 370 nm (see Aethalometer manual: Hansen (2005)). Fig. 3 was added to the Supplement and a paragraph was added to the text. However, as mentioned in the text, the application of the cigarette smoke OA profile of Faber et al. (2013) or other COA profiles both did not result in good separation of the short-term peaks, i.e. in increased mixing with the HOA factor. For comments concerning the absence of f44 in the POAloc, see the replies below.

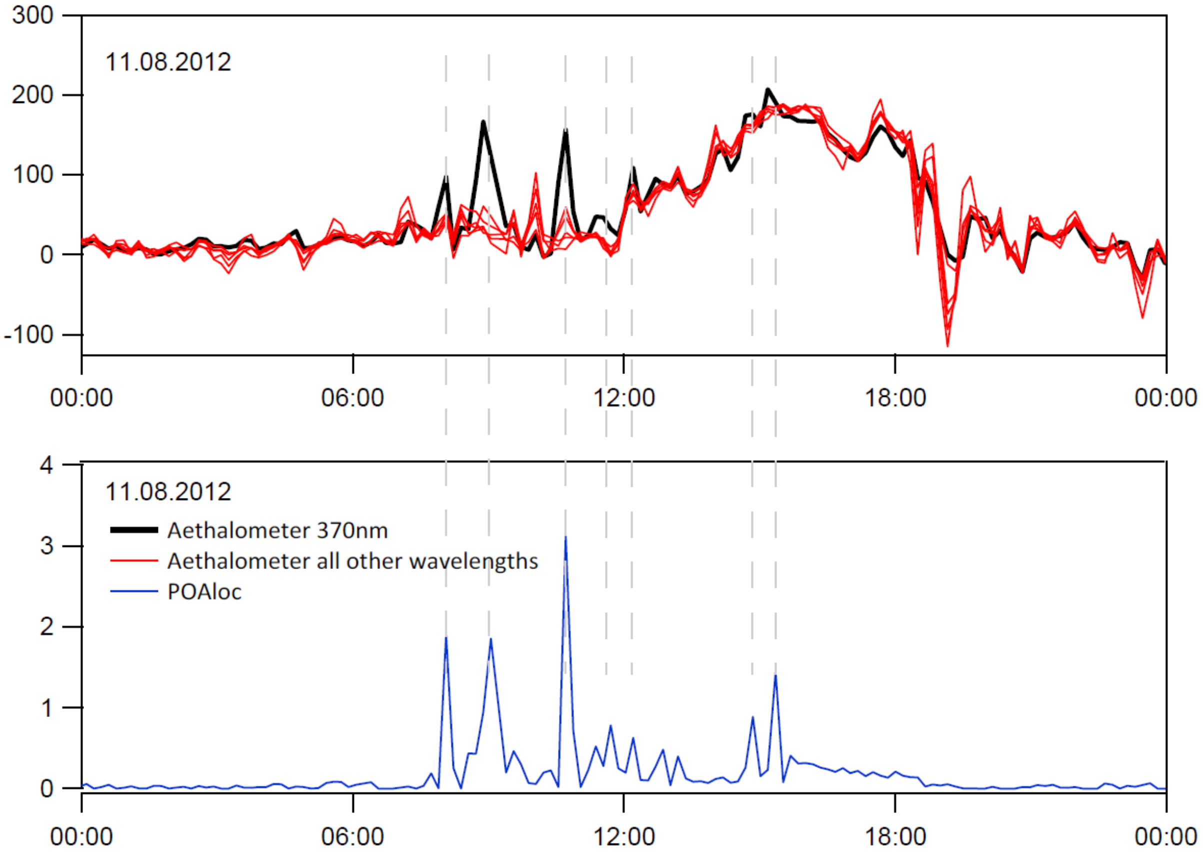

Figure 3: Top: example time series of the Aethalometer Aug 11, 2012, black: 370nm signal, red: signal of all other wavelengths. Bottom: time series of POAloc during the same day. Dashed grey lines are added manually to guide the eye. Cigarette smoke is known to have increased optical absorption at the near-ultraviolet wavelength of 370nm.

From the ACSM intercomparison, the TOF ACSM has the highest f44. It wouldn't thus have been illogical to find higher f44 in POAloc than CSOA; but the total absence of m/z44 cannot be justified by the f44 instrument-to-instrument variability.

Indeed, the ToF-ACSM exhibited the highest f44 during the ACSM intercomparison. But this does not necessarily imply that the f44 measured with the ToF-ACSM at the JFJ would have been relatively elevated. Firstly, the extent of the elevated f44 in the ACSMs compared to the AMS depends on instrument history and increases after exposure to high mass concentrations. The ToF-ACSM was brand new at the JFJ and measured only low concentrations; in contrast, before Paris the instrument was exposed to large loadings during laboratory testing and then experienced high loadings during the study. Secondly, the additional f44 in the ACSMs is believed to originate from delayed further oxidation of other organics in the vaporiser region (this is still under investigation and several publications are in preparation) but at the JFJ we already see collection efficiencies close to one also with the AMS, leaving only very few material to be further oxidised and increase f44.

Could it be that the high S/N of 44 and a non-optimized downweighting can cause the quasi exclusive apportionment of 44 into OOA profiles?

It is possible that the separate PMF on only the spikes is prone to larger uncertainties because of the limited number of points and underlying variability. The big competition of the f44 by the OOA may lead to the underestimation of the f44 in POAloc but also in Faber et al. (2013) f44 is only a minor fraction of the laboratory measured CSOA (~3-4% in Fig. 1 of Faber et al. (2013)). There are other published cigarette smoke OA spectra showing lower f44 than Faber et al. (2013) (e.g. Fig. 4 in

Northway et al. (2007), DOI: 10.1080/02786820701496587 where m/z 44 is about 1/12th of m/z 43, or the sidestream smoke case of Fig. 4 in Tang et al. (2012), DOI:10.1080/02786826.2012.663949 where m/z 44 is about 1/5th of m/z 43). A paragraph was added to the text of Sect. 3.2.1 and 3.2.2 discussing the discrepancies and a possible underestimation of f44. However, a possibly slightly incorrect apportionment of f44 does not significantly alter the results (absolute and relative concentrations) and does not change the conclusions of the section. If one assumes that the "real" f44 was about 3.5% as in the Faber et al spectrum, this would change the total contributions of POAloc to the total OA by less than 1%.

One simple test would be (if some of the authors are smokers) to smoke just below the ACSM inlet to have a clear instrument specific signal of cigarette smoke; have the authors tried that?

No, unfortunately we never tried that because at the time of measurement we were not expecting to find cigarette smoke OA to such an extent at the JFJ. The prototype ToF-ACSM used in that campaign however does not exist anymore in the same state. In the meantime many components were upgraded and exchanged and the vaporiser was exposed to different aerosols potentially affecting the additional f44. It has to be noted that also the mode of operation has changed with faster valve switching cycles more closely resembling the AMS chopper timescales in an effort to diminish discrepancies in observed f44 between the different instruments.

In its current form, I don't believe the POA profile to be real. If the authors think it is, then they need to better prove it.

We are very much convinced that the POA is real because of the above mentioned points. The spikes are very effectively separated from the rest of the data. We agree that the MS profile may not accurately represent the MS of the source (in particular for CO_2^+) as a consequence of the limited number of spikes available to extract the profile. But the effect on absolute and relative factor concentrations is small and within the expected errors (see Fröhlich et al. (2015)). Furthermore we believe that also considering the newly added Figures in the Supplement (Fig. 3 above showing the 370nm Aethalometer signal) we presented convincing evidence for our interpretation that the POAloc is connected with cigarette smoke.

Thus, I am not convinced with Fig10 (although the idea is excellent) and its interpretation.

The results of Fig. 10 would not be affected significantly by an inappropriate f44 in the POAloc factor because the f44 contribution of that factor to the total f44 would remain small in any case. If one assumes that the correct f44 was similar to cigarette smoke OA of Faber et al. (2013) then the f44 that came from POAloc was about 3-4% (f44 in CSOA) times 7-12% (POAloc in OA) = 0.2-0.5% of total OA while the f44 contributed by OOA is 30% (f44 in OOA) times 71-88% (OOA in OA) = 21-26% of total OA. The relative change of the vertical position of the (f44) in Fig. 10 therefore would be on the order of 1-2% (i.e. about 5 times smaller than the width of a marker in Fig. 10a) with even smaller additional variation between seasons since (not considering f44 in HOA and BBOA which are still included in Fig. 10, which would reduce the effect even more). Thus we conclude that also in the case of a possible underestimation of f44 in POAloc the overall picture of Fig. 10 would remain within the order of the shown accuracy and the interpretation remains valid.

I also have concerns with BBOA factor. From Fig7, f60 has a nice seasonal variability with highest values in winter 2012/2013 (and also widest distribution, so we except significant temporal variations).

With f60 Fig. 7 shows the relative contribution of m/z 60 to the total OA in the different seasons. Because in winter the concentrations are very low (median about 0.1 $\mu g/m^3$), the influence of the noise is much bigger, i.e., the wider distribution is caused by the noise. All fractions show a wider distribution in winter although the real amplitude of the temporal variations is typically bigger in summer due to the frequent injections of PBL air with different OA mixtures. A note was added to the figure caption explaining the width of the distribution.

However, from Fig.S6, BBOA during this period looks like noise, has no significant temporal variation, and overall level is very near the LOQ (if LOQ=10*LOD/3) of OA.

Yes, in winter the time series are much more affected by noise (also visible for all the other factors) because of the very low concentrations. If the time series is averaged to a longer time step (see below for 3h) then clear temporal variations and significant non-zero values are better visible. BBOA constitutes 7% of total OA in winter which is above the 5% of the guidelines from Ulbrich et al. (2009)

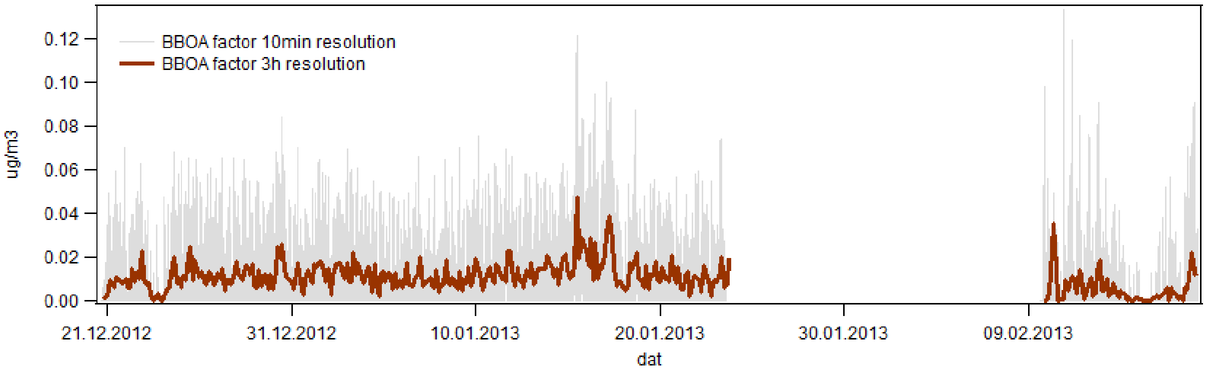

Figure 4: Fig. 4. BBOA factor of the ME2 analisis at 3h time resolution.

More importantly, still in Fig.S6, it is in summer 2013 that highest BBOA are measured. But from Fig.7, summer 2013 does not exhibit high f60 values. These two figures thus provide contradictory information. Can the authors provide an explanation for that?

We do not think that these plots display contradictory information. In the whole summer we see three events with elevated BBOA concentrations (27.06, 05.07 & 06.07) which we attribute to air masses advected from the valley carrying aerosol from agricultural waste burning which does happen occasionally in summer. However, these events only cover a very short period of the total summer, meaning elevated f60 values would not show up in Fig. 7 whose whiskers are showing the 10th to 90th percentile only. Additionally, in the same air masses also a lot of other OA not carrying molecules that show up at m/z 60 was measured (LVOOA I: 4ug/m3, LVOOA II: 1.5ug/m3, HOA: 0.25ug/m3 vs BBOA only 0.25ug/m3,). This overlies the amount of m/z 60 in the BBOA when the fractions are calculated from the total OA.

Minor comments.

P18227, l1: While I don't see how history can be combined with future, this first sentence is way too navel-gazing. Peace around the world, starvation, poverty, are also some great challenges for humankind. Yes, our work is important, but please moderate.

Revised. New text: "Many environmental topics which are becoming increasingly important in the future are closely linked to aerosols…"

P18227, l24: what is a "good" time resolution?

Revised. Text changed to: "…with time resolutions on the order of minutes to hours on a long-term basis…"

P18228, l10: please provide an approximative number of measuring locations for the observation of free tropospheric aerosols. Give some examples.

We removed that statement since we are unable to provide an exact number here and in theory there are many locations (almost every mountaintop) that would allow the probing of FT air but only at a few of them the facilities exist. If one queries the data base of the Global Atmosphere Watch (http://gaw.empa.ch/gawsis/find.asp) only 16 operating observatories above 3000m are listed worldwide. In Europe the list is limited to only three: Jungfraujoch (CH), Sonnblick (A) and Plateau Rosa (I).

P18229, l21: talking about representativity is important. How representative is the presented dataset compared to several-decade trends? This would be a very interesting input to the paper, as it helps interpreting the results

The results in this paper are in good agreement with previous measurements of chemical composition making the findings representative. A note about representativity and a reference to the review article of Bukowiecki et al. (2015) which compiles aerosol measurement results at the JFJ of the last 20 years was added to the text.

P18229, l25: please clearly state how seasons were differentiated

Revised. See also P18237 L3 and Fig. 1b.

P18231, l14-15: how did the calibration values (IENO3, RIENH4 & RIESO4) vary over time? As monthly/bimonthly calibrations were performed, please provide a standard deviation.

Revised. Calibrated RIE values were 3.2+/- 0.4 for NH4 and 0.6 +/- 0.1 for SO4. More detail about IE can be found in the answers to referee #3.

P18231, l20: the CE=1 is expected at JFJ, but is unexpected some lines later (p18232, l2). Please revise

Revised.

P18231, l20: a good correlation (r or r2) will still be obtained with other CE values. Only the slope of the correlation will change. Please be more specific

Revised. This was caused by a language misconception. The word correlation should only refer to "plotted against each other".

P18231, l25-26: please clearly state how SDE were identify, or add a link to section 2.6.

Revised.

P18231, l29: SO4 and OM are not always > 80% of total PM1 (see p18238, l8). Please revise

Revised.

P18232, l25: saying that eBC concentrations are subject to uncertainties is way too vague. Please provide an estimate of the uncertainties associated with this measurement. If not possible, please discuss it a bit more in details. By the way, why eBC data haven't been corrected?

The Aethalometer data used in this study was treated according to the recommendations of the World Data Centre for Aerosols: "For all instruments manufactured by Magee, please use the corresponding level 0 template only for all types of data reporting, since there are no accepted Standard Operating Procedures for producing higher data levels available for these instruments." (http://www.gaw-wdca.org/SubmitData/RegularAnnualDataReporting/FilterAbsorptionPhotometerregular.aspx). Furthermore, for very low attenuation values the loading correction does not always improve the results (see Weingartner et al., 2003). At the JFJ the attenuation remains low for a considerable time after a filter change even if the highest possible flow rate is applied. Thus the application of the loading correction is subject to bias in this case. An estimation of the site specific uncertainties of MACabs (used to calculate eBC from the raw attenuations) is still under investigation and a publication is in preparation by Zanatta et al. (2015). The text was changed accordingly.

P18235, l19: the recommendations from Griffiths et al. (2014) is 0.75 – 2 Bq.m-3. So why did the authors choose 1.5? Is it an empirical determination?

Yes, this value was determined empirically and it agrees with the value found by Herrmann et al. (2015) in a long-term (6 years) investigation of the aerosol size distributions at the JFJ.

P18236, l6-8: so what is the take-home message of section 2.5? How does the choice of the methodology change the interpretation? Why didn't the authors perform a "careful exploration" as in Herrmann et al. (2015)?

In this subsection of the methods description the three methods are merely described. Hence, the take home message is that several approaches exist and were applied to the dataset. The results are then discussed in detail in Sect. 3.1.3 (Basically all three methods deliver similar results for the median FT aerosol composition and concentration). The more detailed exploration was not performed because it was deemed to be out of the scope of this publication. On the one hand Herrmann et al. (2015) published this in a separate paper and on the other hand the back dispersion raw data necessary for a deeper investigation was not available to us at the time when the work was performed.

P18237, l3-4: please revise Fig1b. There is supposed to be a continuity of seasons throughout the year.

Due to the measurement interruptions visible in Fig. 1b no continuous data was collected. The regions in Fig. 1b show the periods that were used to calculate seasonal concentrations etc. Gaps do not mean that data was omitted, just that no data was available before and after. The figure caption was revised to avoid misunderstandings

P18237, l5: “in the summer months”. Months have not been used to differentiate the seasons. Please revise

Revised. Here and elsewhere.

P18248, l8: m/z60 is not the principal fragment of BBOA. It is rather the most specific fragment of its profile.

Revised.

P18248, l19: what is the influence of small variations of a value for POAloc (+ or – 0.05)?

See table S2 showing the variability of the averaged results for all factors due to the applied a value range. Table S2 contained an incorrect table caption which was revised.

P18251, l20-21: the summer 2013 eBC concentrations is similar to summer 2012. Diesel engine generators don’t emit OA? This explanation is too vague, and in case these engines occur to be a significant eBC source, why didn’t these periods deleted from the PMF analysis?

Yes, absolute eBC concentrations are similar (see Table 1) but relative eBC contributions to the total aerosol are higher in summer 2013 (4% vs 6%, see Fig. 2 or sum in Table 1), i.e. the ratio OA to BC is different. The HOA to BC ratio of on-site diesel generators potentially differs for the HOA to BC ratio of aged fossil fuel combustion emissions transported to the JFJ from the surrounding valleys. The mentioned construction activities were taking place over a longer period and no significant BC spikes can be seen in the eBC data. But since this cannot be excluded as a potential contamination it is mentioned here together with a second possibility. An underestimation of HOA in the source apportionment would be a third possibility and was added to the paper.

P18251, l26-27: this explanation is very subjective and is not illustrated. From what I can see in Fig. S6, the temporal variations of BBOA in winter 2012/2013 looks like noise and doesn’t really follow OOA general trend. Then, BBOA is much higher in summer, but is not discussed. (see major concern)

See replies and BBOA time series in major concern section. The missing BBOA winter diurnal variation plot was added to the supplement.

In the beginning of section 3.2, the authors wrote that “Figures 7a-e show the fractions of total OA). But in the caption of the figure, it is stated that local primary OA have been subtracted. If it is the case, then see my concern for POA above; if not, then delete this from the caption.

The POAloc was subtracted, i.e. the caption is correct. The text in section 3.2 was changed accordingly. For comments about the concerns dealing with POAloc and the OA fractions see above.

Table S2 : this table has nothing to do with HOA – eBC ratios. Please revise

Revised. A wrong table caption was displayed for Table S2.

Technical comments.

While the general language is correct (and appreciated), many typos are present in the text. Some obvious ones are listed, but I suggest the authors to thoroughly proofread the manuscript.

P18226, l5: please replace a.s.l. by above sea level

Revised.

P18227, l13: please replace real time by near real time

Revised.

P18227, l14: near real time and high time resolution is equivalent. Please choose one or the other

Revised.

P18228 ,l17: please remove one “and”

Revised.

P18228, l17: please insert a “–“ in “gasphase”

Revised. Here and elsewhere.

P18238, l15: please remove one “which”

Revised.

P18238, l22: “In autumn, winter and spring”

Revised.

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Reply to:

Anonymous Referee #2

Referee comments in black, author replies in blue

Overall Comment and Recommendation: This manuscript presents 14 months of near-continuous, real-time measurements of non-refractory submicron aerosol (NR-PM1) by using a time-of-flight aerosol chemical speciation monitor (ToF-ACSM) at the Jungfraujoch mountain site in Switzerland. This is an important study as it provides in depth insights into the sources of organic aerosol as well as seasonal trends at a high elevation site in Europe. Long-term mass and chemical measurements of NR-PM1 are starting to really take off around the world, including sites in Europe, the United States, and southeast Asia. This is an exciting time and this study certainly adds to this growing body of data that will likely be useful to the modeling community that estimate impacts of PM on air quality and climate. The authors find that NR-PM1 concentrations peak in summer due to increased planetary boundary layer (PBL) air influences and lower concentrations in winter. The largest fraction is from organic compounds and in transient months sulfate can be rather high at this site. Interestingly, from backward air trajectory analyses, the authors find that sulfate is elevated from the south but organics are dominant from all cardinal directions. The major source of organic aerosol at this site is low-volatility oxidized organic aerosol (LV-OOA), where LV-OOA 1 is assigned to a background type and LV-OOA 2 is assigned to vertically transported type mostly seen in summer. BBOA was only seen during a rare regional event in summer 2013 and during winter. The authors will likely be interested in papers coming from the Surratt Group at the Look Rock, Tennessee USA mountain site using the quadrupole ACSM. One of these papers was just published in ACP (Budisulistiorini et al., 2015) and the other one that presents yearlong data will appear soon in ACPD (Budisulistiorini et al., 2015). It seems many of the findings, such as aged OOA and some infrequent BBOA events, are shared by both mountain sites. Overall, the data presented in this study will be of interest to the atmospheric chemistry community and should be published in ACP.

However, I kindly ask that the authors address the specific and minor comments below before publication.

Specific and Minor Comments:

1.) Page 18227, Line 11: delete ".e.g.," as this is not necessary.

Revised.

2.) Page 18227, Line 14: insert hyphen between "high" and "time"

No change was made because several native English speakers were asked and all of them preferred either “high time resolution” or “high time-resolution”

3.) Page 18227, Line 19: delete "of"

Revised.

4.) Page 18227, Line 19: insert "of sampling" after the word "weeks"

Revised.

5.) Page 18227-18228: The authors may want to include in their citation here for 1 year studies a 1 year study in both Atlanta, GA, USA and Look Rock, TN, USA by Budisulistiorini et al., 2015 (ACPD). This paper is in press for ACPD. Here are the details - S. H. Budisulistiorini, K. Baumann, E. S. Edgerton, S. T. Bairai, S. Mueller, S. L. Shaw, E. M. Knipping, Avram Gold and J. D. Surratt (2015). Seasonal Characterization of Submicron Aerosol Chemical Composition and Organic Aerosol Sources in the Southeastern United States: Atlanta, Georgia and Look Rock, Tennessee. Atmos. Chem. Phys. Discuss., in press.

The suggested reference was added to the list.

6.) Page 18228, Line 18: Change "gasphase" to "gas-phase"

Revised.

7.) Page 18229, Line 3: comma needed after "Furthermore"

Revised.

8.) Page 18230, Line 1: UTC or local time?

Local time. Revised.

9.) Experimental: The authors are confident a naifion dryer is not needed for sampling???

Yes, the always large temperature differences between outside and laboratory (usually >25°C) make additional drying superfluous. This is standard procedure at the JFJ site and is confirmed in long-standing measurements. The RH of the inlet line is continuously monitored (< 40% required by GAW) and always lies below 25%. An RH of 20% corresponds to a dew point of 0°C at indoor temperatures of 25°C. Typical dew point values at the JFJ are below 0°C.

10.) Backward air trajectories: I ’m curious, how accurate are the backward trajectories if 10 days is used? Why not a shorter time scale? I would think the meteorology is highly dynamic at this site, so 10 days of backward trajectory analysis seems quite ambitious to me. The authors need to justify this selection.

This question is similar to the one asked by referee #3 and additional arguments are given there. We would like to point out again that we are not using a single trajectory model in our analysis but simulations of a Lagrangian particle dispersion model. The difference being that the latter simulates the transport of thousands of air parcels for a given release time and describes their movement with the mean flow, but also turbulent and convective transport. We are not sure what the referee refers to when saying that the “meteorology is highly dynamic”. Our model simulations are based on 3-hourly input fields and not on any steady state fields. Hence, the flow calculation accounts for as much variability as is possible. Selecting 10 days is somewhat arbitrary. However, it is based on the fact that the total accumulated source sensitivity does not increase strongly after this time scale anymore (e.g. Folini et al., 2008). Others have even used longer backward simulation times with the same model for similar transport categorisations (e.g. Hirdman et al., 2010).

11.) Page 18237, Line 4: You mean "Following sections?" Sounds like this came directly from a PhD thesis.

Revised.

12.) Page 18239, Line 4: Delete "also"

Revised.

13.) Aerosol Acidity: Based on recent studies from GA Tech groups (Hennigan et al., 2015, ACP; Guo et al., 2015, ACP), using neutralization degree is no longer a good proxy to estimate aerosol acidity. It is better to use thermodynamic models, such as ISOROPPIA, to do this using ACSM inorganic data and meteorological data as inputs. I would revise this.

A note of caution referencing to the two mentioned articles was added to the text (“Furthermore, it is noted that recent studies have shown that the molecular ratio, i.e. degree of neutralisation is not a good proxy for the determination of aerosol pH aside from giving a very rough information if an aerosol is alkaline or acidic (Hennigan et al., 2015; Guo et al., 2015).)

14.) Page 18242, Line 4: It is not clear to me what does "non-FT" mean. Is it concentrations during injection layer (IL) or else?

The acronym was clarified in the text.

15.) Page 18242, Line 17: Delete "suggesting that"

Revised.

References:

Hirdman, D., Sodemann, H., Eckhardt, S., Burkhart, J.F., Jefferson, A., Mefford, T., Quinn, P.K., Sharma, S., Ström, J. and Stohl, A.: Source identification of short-lived air pollutants in the Arctic using statistical analysis of measurement data and particle dispersion model output, Atmos. Chem. Phys., 10, 669-693, 2010.

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Reply to:

Anonymous referee #3

Referee comments in black, author replies in blue

This manuscript reports results obtained with a time-of-flight aerosol chemical speciation monitor (ToF-ACSM) during a long-term measurement period (14 months) at the Jungfraujoch research station, Switzerland. The authors described the seasonal and diurnal variations of non-refractory submicron particles (NR-PM1), and discussed the properties of NR-PM1 as a function of the air mass origin. The exceptional situation of the Jungfraujoch (a high elevation site in the heart of Europe) allowed the authors to compare on one hand free tropospheric air masses with periods influenced by the planetary boundary layer (PBL), and on the other hand air masses from different regions of Europe. They also performed a source apportionment of organics by PMF analysis, and discussed in detail the sources and processes of organics based on mass spectra (also f44 vs f43), diurnal and seasonal variations.

This manuscript is very interesting, and fits totally the scope of the journal. I recommend its publication in ACP after the authors address the following comments.

Specific comments:

1) Page 18229, line 25 to page 18230, line 2: if the authors used UTC for the entire dataset, it means that they did not take into account the daylight saving time in summer. This introduces a bias in the diurnal patterns of anthropogenic species, given that human activities are shifted by 1-hour between summer and winter.

Yes, UTC was used throughout the document. Diurnal plots however are always shown separate for all seasons. The return to standard time in 2012 was made on October 28 and the switch to daylight saving time in 2013 on March 31. Therefore no significant bias is expected in the diurnals of winter and summer. Also spring 2013 is unaffected due to the interruption of the measurements during most of March 2013 (see Fig. 1). The time shift in October took place after about half of our “autumn 2012” period has passed, i.e. the autumn diurnals might be affected. However, the emission times of the local pollution are limited by the train timetables which are also changing with season. The first train arrives at 08:52 LT (07:52 UTC in winter, 06:52 UTC in summer) year-round while in winter (October 29 – March31) the last train is leaving JFJ earlier at 16:50 LT (15:40 UTC) than in summer, when the last train is leaving at 17:45 LT (15:45 UTC). Consequently, the application of UTC prevents a bias at the end of the day but might cause one in the beginning of the day in autumn. No changes were made since we do not think a shift to LT would improve the manuscript.

2) Page 18231, lines 12-16: it would be very useful for ToF-ACSM users to include in the supplementary material a table with the details of the different calibrations for each month with the statistics (average, standard deviation, etc.). This information is important to assess the stability of these instruments, and to determine at which frequency they need to be calibrated.

We agree with the referee that such information is useful for ToF-ACSM users and added the standard deviations of the RIE values to the text. However, the mIE value does depend on the instrument hardware and TOF voltages ; changes in these may result in significant changes in the ions/pg measured. This was the first field deployment and the instrument underwent several hardware upgrades and consequent tunings of the TOF voltages. Therefore no statistics on the mIE value are reported in the paper. With the different instrument voltage profiles, mIE values between 26 and 103 ions/pg were recorded over the measurement period. After each bigger intervention (e.g. opening of the vacuum chamber, exchanging of components, transport) the mIE value was re-calibrated and adjusted in the subsequent data analysis.

3) Page 18234, line 5: I am surprised that the authors performed a back trajectory analysis over 10 days. This is too much, given that beyond 3 days, the uncertainty on the back trajectory calculation is already high. Indeed, according to Rolph and Draxler (1990), the horizontal deviations are between 200 and 700 km at 4 days, depending on the spatial and temporal resolution of the meteorological data.

We are not using single trajectory analysis in this work (as in Rolph and Draxler, 1990) but simulations of a Lagrangian particle dispersion model (LPDM). The difference being that the latter simulates the transport of thousands of air parcels for a given release time and describes their movement with the mean flow, but also turbulent and convective transport. One of the sources of uncertainties in single trajectory models is the assumption of a not dispersing air parcel. Hence, divergence in the flow field will lead to large uncertainties in the trajectory calculation. In an LPDM, divergence just adds to the overall dispersion of the particle plume through turbulence. In this context we strongly believe that running our model 10 days back in time is not using it beyond its abilities. Also others have used similar or longer backward integration times to categorise transport to measurement sites (e.g. Hirdman et al., 2010).

4) Page 18248, line 6: in the absence of a thermodenuder and information on the volatility of the particles, I think it is not appropriate to use the “LV-OOA” terminology in this study. Even “more oxidized OOA” (MO-OOA), which is found in papers with HR-ToF-AMS datasets, cannot be used, given that we do not have the O/C ratios. I would suggest to use “OOA I” and “OOA II” throughout the manuscript, which is recommended by Zhang et al. (2011) in this case.

We agree with the referee’s position that without a thermodenuder we do not have direct evidence of the volatility of our OOA. However we are convinced that we are dealing with LV-OOA. We made our decision to attribute the OOAs to the LV-OOA family on the basis of spectral similarities to the ones shown in Ng et al. (2010). There LV-OOA profiles show high f44 (0.17±0.04) while SV-OOA shows an f44 range of 0.07±0.04. Furthermore, according to Jimenez et al. (2009) LV-OOA has O:C ratios higher than 0.58 in rural areas, using the formula of Aiken et al. (2008) this corresponds to f44 higher than 0.13. Our OOA profiles show always f44 ratios above 0.20 (see Fig. 10d). Even taking into account a potential positive bias of f44 in the ACSM compared to the AMS as reported in Fröhlich et al. (2015) and Crenn et al. (2015) this indicates rather an LV-OOA than an SV-OOA. We clarified our selection in the text by an additional sentence following the introduction of OOA on P18248 L7. Also the paragraph on P18249 L6 contains a note that the decision was not made on the basis of direct volatility observations.

Technical corrections:

All mentioned technical corrections were taken into account in a revised document.

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Hirdman, D., Sodemann, H., Eckhardt, S., Burkhart, J.F., Jefferson, A., Mefford, T., Quinn, P.K., Sharma, S., Ström, J. and Stohl, A.: Source identification of short-lived air pollutants in the Arctic using statistical analysis of measurement data and particle dispersion model output, Atmos. Chem. Phys., 10, 669-693, 2010.

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Date: 7 September 2015

Fourteen months of on-line measurements of the non-refractory submicron aerosol at the Jungfraujoch (3580 m a.s.l.) – chemical composition, origins and organic aerosol sources

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Abstract

Chemically resolved (organic, nitrate, sulphate, ammonium) data of non-refractory submicron (NR-PM$_1$) aerosol from the first long-term deployment (27 July 2012 to 02 October 2013) of a time-of-flight aerosol chemical speciation monitor (ToF-ACSM) at the Swiss high altitude site Jungfraujoch (3580 m above sea level) are presented. Besides total mass loadings, diurnal variations and relative species contributions during the different meteorological seasons, geographical origin and sources of organic aerosol (OA) are discussed. Backward transport simulations ~~shows~~ show that the highest (especially sulphate) concentrations of NR-PM$_1$ were measured in air masses advected to the station from regions south of the JFJ while lowest concentrations were seen from western regions. OA source apportionment for each season was performed using the Source Finder (SoFi) interface for the multilinear engine (ME-2). OA was dominated in all seasons by oxygenated OA (OOA, 71–88 %), with lesser contributions from local tourism-related activities (7–12 %) and hydrocarbon-like OA related to regional vertical transport (3–9 %). In summer the OOA can be separated into a background low-volatility OA (LV-OOA I, possibly associated with long range transport) and a slightly less oxidised low-volatility OA (LV-OOA II) associated with regional vertical transport. Wood burning-related OA associated with regional transport was detected during the whole winter 2012/2013 and during rare events in summer 2013, in the latter case attributed to small scale transport for the surrounding valleys. Additionally, the data were divided into periods with free tropospheric (FT) conditions and periods with planetary boundary layer (PBL) influence enabling the assessment of the composition for each. Most nitrate and part of the OA is injected from the regional PBL while sulphate is mainly produced in the FT. The south/north gradient of sulphate is also pronounced in FT air masses (sulphate mass fraction from the south: 45 %, from the north: 29 %). Furthermore, a detailed investigation of specific marker fragments of the OA spectra (f_{43}, f_{44}, f_{55}, f_{57}, f_{60}) showed different degrees of ageing depending on season.

1 Introduction

Many ~~vital topics determining the future history of humankind~~ environmental topics which are becoming increasingly important in the future are closely linked to aerosols, e.g. climate change on global (Charlson et al., 1992; Lohmann and Feichter, 2005; Boucher et al., 2013) and regional scales (Ramanathan et al., 2001; Stott, 2003; Shindell and Faluvegi, 2009), or impacts on human health (Seaton et al., 1995; Laden et al., 2000; Cohen et al., 2005; Pope and Dockery, 2006) and Earth's ecosystem (Mahowald, 2011). Therefore a good knowledge of aerosol chemical and physical properties in the atmosphere is an essential scientific task. In situ measurements of these properties provide the basis for a deeper understanding of the aerosols influence on the topics mentioned above.

Knowledge of the aerosol concentrations and properties in the lower FT is important due to its impact on cloud formation and to validate model results from the FT. The high altitude research station on the Jungfraujoch (JFJ) at 3580 m a.s.l. in the Swiss Alps allows the investigation of free tropospheric aerosol year round due to its elevated location. Nevertheless, vertical transport of polluted air masses from the planetary boundary layer (PBL) is observed occasionally especially in summer (see Lugauer et al., 1998; Henne et al., 2004, 2010) . However, suitable approaches have been applied in the past to discriminate between PBL-influenced conditions and free tropospheric air masses (see Sect. 2.5). Due to its well-developed infrastructure and unique location many decades of scientific measurements of gas-phase constituents (Zander et al., 2008; Pandey Deolal et al., 2012) , meteorology (Appenzeller et al., 2008) and atmospheric aerosols (Baltensperger et al., 1997; Collaud Coen et al., 2007; Cozic et al., 2008; Bukowiecki et al., 2015 been performed there. Given the absence of local vegetation and small scale of local emissions, the JFJ is an ideal location for the measurement of pollution arriving from all over Europe (Reimann et al., 2008; Uglietti et al., 2011) .

An important property of atmospheric aerosol particles is their chemical composition providing insight ~~e.g.~~ into their origin and chemical evolution pathways. Aerosol mass spectrometry provides a tool for measuring the chemical composition ~~in real time and with high time~~ with high-time resolution as opposed to the collection of filter samples, which are often prone to sampling artefacts. The application of the aerosol mass spectrometer (Jayne et al., 2000, AMS, Aerodyne Research Inc., Billerica, MA, USA) has produced a large database of aerosol chemical composition around the planet (see e.g., Zhang et al., 2007; Jimenez et al., 2009; Crippa et al., 2014). However, because of the complexity and cost of the instrument, most AMS measurements cover only ~~of~~ a few days to weeks of sampling. Exceptions are a 1 year continuous AMS measurements in London by Young et al. (2014) and a 3 year data set from Mace Head by Ovadnevaite et al. (2014).

To facilitate long-term mass spectrometric measurements, the aerosol chemical speciation monitor (Ng et al., 2011c, ACSM) was developed. ~~It~~ Long-term measurements are essential to capture long-term trends, inter-season variations or other effects taking place on longer time scales. Furthermore, increasing data coverage allows for a more reliable determination of the typical aerosol conditions at a specific site. The ACSM provides a valuable and robust tool for measuring chemical composition of submicron aerosol with ~~good time resolution on~~ time resolutions on the order of minutes to hours on a long-term basis. Several long-term and medium-term ACSM datasets have been presented in the literature: 2 years near Paris (France) (Petit et al., 2015), 1.5 years in central Oklahoma (Parworth et al., 2015), 1 year in Zurich (Switzerland) (Canonaco et al., 2013, 2015), near Johannesburg (South Africa) (Tiitta et al., 2014; Vakkari et al., 2014), ~~and~~ near Barcelona (Spain) (Ripoll et al., 2015; Minguillón et al., 2015), and in the Southeastern United States (Budisulistiorini et al., 2015) , between 1.5 and 3.5 months in Tijuana (Mexico) (Takahama et al., 2013), on Crete (Greece) (Bougiatioti et al., 2014), in Atlanta (USA) (Budisulistiorini et al., 2013), in Beijing (China) (Sun et al., 2012) and in Santiago de Chile (Chile) (Carbone et al., 2013). In addition, a large database of long-term ACSM datasets (including the data set presented in this manuscript) will be made available in the framework of the European ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure) project (see stations overview at http://www.psi.ch/acsm-stations) via the EBAS database hosted by the Norwegian Institute for Air Research (NILU, http://ebas.nilu.no/).

~~Only a small number of measurement locations allow the investigation of free tropospheric aerosol year round. The high altitude research station on the Jungfraujoch (JFJ) at 3580in the Swiss Alps is one of them. Nevertheless, vertical transport of polluted air masses from the planetary boundary layer (PBL) is observed occasionally especially in summer (see Lugauer et al., 1998; Henne et al., 2004, 2010) . However, suitable approaches have been applied in the past to discriminate between PBL-influenced conditions and free tropospheric air masses (see Sect. 2.5). Due to its well-developed infrastructure and and unique location many decades of scientific measurements of e.g. gasphase constituents (Zander et al., 2008; Pandey Deolal et al., 2012) , meteorology (Appenzeller et al., 2008) and atmospheric aerosols (Baltensperger et al., 1997; Collaud Coen et al., 2007; Cozic et al., 2008; Bukowiecki et al., 2015 been performed there. Given the absence of local vegetation and small scale of local emissions, the JFJ is a suitable location for the measurement of pollution from all over Europe (Reimann et al., 2008; Uglietti et al., 2011) .~~

In the present manuscript 14 months of data from the first long-term deployment of a time-of-flight aerosol chemical speciation monitor (ToF-ACSM, Fröhlich et al., 2013) are presented. The ToF-ACSM provides the advantage of increased sensitivity compared to the ACSM version using a quadrupole mass spectrometer making it more suitable for remote locations with low expected mass concentrations like JFJ. The high time resolution of 10 min allows for a year-round detailed analysis of chemical composition of aerosol which to our knowledge to date is unique for the high alpine environment and was made possible only by the development of the ToF-ACSM. Diurnal as well as seasonal cycles are discussed together with the influence of injected air from the PBL and the influence of different source regions on the chemical composition. Furthermore, a closer look at the chemical evolution of the organic aerosol fraction and its sources is presented.

2 Methods

2.1 Measurement site

The Sphinx observatory is part of the High Alpine Research Station Jungfraujoch, which is integrated into several measurement networks: amongst others there are the international Global Atmosphere Watch (GAW) program of the World Meteorological Organisation (WMO), the Swiss National Monitoring Network for Air Pollutants (NABEL) and the European ACTRIS infrastructure project. It is located at an elevation of 3580 m a.s.l. (07°59′02″ E, 46°32′53″ N) on an exposed rock formation on the saddle between the two mountains Jungfrau (4158 m a.s.l.) and Mönch (4107 m a.s.l.). The surrounding topography leads to a channelling of local winds in north-westerly or south-easterly directions (see e.g. Hammer et al., 2014). In the north-west the terrain descends steeply towards the Bernese Oberland with Lake Thun and Lake Brienz while in the opposite (SE) direction the descent is less steep over the Valaisian Great Aletsch glacier and the Rhône valley. While the upper two floors of the Sphinx observatory are reserved solely for scientific purposes the lower levels are accessible to tourists who are the only small but ever growing (866 000 visitors in 2014) source of local pollution. Monthly average outside temperatures are below freezing year round. Appenzeller et al. (2008) reported about 10–20 annual days with minimum daytime temperatures above 0 °C, with an increasing trend (50 % increase for the investigated period between 1961 and 2005).

Measurements took place between 27 July 2012 and 02 October 2013, spanning all seasons ~~and~~ (see Fig. 1a and b) and totalling more than one year. Recorded concentrations are in agreement with previous studies investigating chemical composition at the JFJ, making the findings representative of the JFJ aerosol. A recent review compiling the results of 20 years of aerosol measurements at the JFJ was published by Bukowiecki et al. (2015) . All data are reported in UTC, which is local time minus 1 h in winter and ~~UTC~~ local time minus 2 h in summer (daylight saving time), respectively.

2.2 Instrumentation

The ToF-ACSM (Aerodyne Inc., Billerica, MA, USA and Tofwerk AG, Thun, BE, Switzerland) which is described in detail in ~~(Fröhlich et al., 2013)~~ Fröhlich et al. (2013) , is applied for the chemical composition measurements. Like the quadrupole ACSM (Q-ACSM, Ng et al., 2011c), the ToF-ACSM is based on Aerodyne AMS technology but is smaller, less costly, and optimised for long-term deployment with minimal maintenance. In comparison to the Q-ACSM, the ToF-ACSM features improved mass-to-charge resolution ($\frac{M}{\Delta M} = 500$, enabling separation of some isobaric components in the mass spectrum using peak fitting if desired) and, more importantly for deployments at remote sites, improved sensitivity. Additionally, the ToF-ACSM provides the possibility to span a larger m/z range (up to $m/z \approx 300$ Th) than the Q-ACSM where the technical limitation lies around m/z 150. At the JFJ data was averaged to 10 min (corresponding to an organic aerosol detection limit of 63 ng m^{-3} according to Fröhlich et al., 2013).

The deployment at the JFJ represented the first field test of the ToF-ACSM instrument. Optimisation and upgrading of the instrument and software continued throughout the deployment, especially during the first half of the year, resulting in occasional breaks in operation (cf. Fig. 1a). Even including these planned downtimes, the ToF-ACSM measured for 73 % of the entire deployment and 97 % during the last five months (after the final configuration was reached).

The ToF-ACSM provides quantitative mass spectra of non-refractory (NR) submicron (PM$_1$) aerosol. The operational principles are described in detail elsewhere (Fröhlich et al., 2013) and summarised here in four key steps: separation of particles from ~~gasphase~~ gas-phase molecules, flash vaporisation, ionisation of the resulting vapour molecules, and sorting of the consequent ions by time-of-flight mass spectrometry. Separation, focusing and PM$_1$ size cut of the particles is achieved by combination of an aerodynamic lens and a skimmer cone. Because of the low ambient atmospheric pressures at the JFJ (average 655 hPa) the instrument inlet was modified by replacing the standard critical orifice ($d = 100$ µm) with an orifice that has a diameter of $d = 130$ µm. This keeps the inlet mass flow rates comparable to those obtained during standard operation at lower elevations. Flash vaporisation of non-refractory species takes place at $T = 600\,^{\circ}$C on a heated porous tungsten plate and ionisation is performed by electron ionisation at $E_{\mathrm{kin}} = 70\,\mathrm{eV}$.

Ion fragments are attributed to the main constituents of aerosol particles, organics, nitrate (NO_3^-), sulphate (SO_4^{2-}), ammonium (NH_4^+) and chloride (Cl^-) according to the fragmentation table-based analysis developed by Allan et al. (2004). At the JFJ, chloride concentrations were always below the 10 min detection limit of the ToF-ACSM (4 ng m^{-3}) and hence chloride is omitted in the following discussion.

All necessary calibrations as detailed in Fröhlich et al. (2013) (signal-to-mass (mIE), NO_3^- relative ionisation efficiency (RIE) of sulphate and ammonium, flow rate) were performed on a monthly to bimonthly schedule. ~~Mean calibrated RIE values of~~ Calibrated RIE values were 3.2 ± 0.4 for NH_4^+ and 0.6 ± 0.1 for SO_4^{2-}. The mean values were applied throughout the dataset. For organic molecules, the standard RIE of 1.4 was applied (Alfarra et al., 2004; Canagaratna et al., 2007).

Previous short-term measurements with ACSM and AMS at the JFJ showed a particle collection efficiency (CE) close to unity (Lanz et al., 2010; Jurányi et al., 2010; Fröhlich et al., 2013). The same CE = 1 was applied to the data of this study. This expectation was confirmed by ~~a correlation of the~~ plotting total mass concentration measured with the ToF-ACSM plus equivalent black carbon (~~EBC~~eBC) from optical absorption measurements ~~with~~ versus the total mass estimated from a scanning mobility particle sizer (SMPS, for a detailed setup description see Jurányi et al., 2011; Herrmann et al., 2015), which resulted in distributions around the 1 : 1 line during all seasons (see Fig. S1 in the Supplement). For that analysis, periods with high concentrations of refractory particles (e.g. Saharan dust events - see Sect. 2.6 for method of separation - or construction work) were excluded from the correlation. To convert SMPS number size distributions into mass, a density ρ_{part} was estimated according to the relative densities of the main species measured by the ToF-ACSM at the JFJ: SO_4^{2-} and organics (together almost always > 80 % of total PM_1). Densities of 1.8 g cm^{-3} for sulphate and 1.3 g cm^{-3} for organics (experimentally determined by Cross et al., 2007) were applied. The high CE close to unity is ~~unexpected~~ uncommon as typically a CE around 0.5 is reported for AMS/ACSM instruments because a fraction of NR particles is lost due to bounce off the vaporiser before flash vaporisation. According to Matthew et al. (2008) this bounce depends on particle phase and is reduced if particles are either wet, acidic or containing high fractions of nitrate. All three conditions are not fulfilled at the JFJ. The reason for the discrepancy is still unknown but it is noted that compared to other atmospheric measurement sites the JFJ exhibits extreme ambient conditions (pressure, temperature).

The ToF-ACSM was connected to the total inlet (see e.g. Weingartner et al., 1999; Henning et al., 2003) which is also used for the aerosol monitoring instrumentation of the GAW programme on site. Heating of the inlet to indoor temperatures ($T = 25\,^{\circ}\mathrm{C}$) avoids build-up of ice and ensures dry aerosol without the use of additional drying equipment due to the always low outside temperatures at the JFJ (annual mean temperature: $T_{\text{mean}} = -7\,^{\circ}\mathrm{C}$, highest monthly mean temperature in July: $T_{\text{mean, July}} = -1.2\,^{\circ}\mathrm{C}$). A bypass flow of $50\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ in addition to the $2.4\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ flow of the ToF-ACSM makes particle losses in the inlet line ($d = 5\,\mathrm{mm}$; $l \approx 2\,\mathrm{m}$) negligible.

Furthermore, data from a nephelometer (Model 3563, TSI inc., Shoreview, MN, USA), a condensation particle counter (CPC, Model 3772, TSI inc., Shoreview, MN, USA), and an aethalometer (AE31, Magee Scientific, Berkeley, CA, USA) operated at the JFJ in the framework of the GAW activities were used in the context of this study. The ~~recommended mass absorption~~ default mass attenuation cross section for aerosol on the filter matrix (MAC$_{\text{atn}}$ value) from the AE31 manual of $16.6\,\mathrm{m}^2\,\mathrm{g}^{-1}$ at 880 nm (no loading correction) was applied to determine ~~EBC~~eBC. MAC$_{\text{atn}}$ ~~values can vary~~ accounts for instrumental error and optical properties of the aerosol. The latter varies between sites and aerosol ~~types and therefore EBC loadings are subject to uncertainties (Weingartner et al., 2003)~~ type (for details see Weingartner et al. (2003) and Zanatta et al. (2015)). For the determination of the boundary layer influence on the air masses at the JFJ, data from a ^{222}Rn analyser built by the Australian Nuclear Science and Technology Organisation (ANSTO) and operated by the University of Basel (for more details see Griffiths et al., 2014), NO$_y$ data measured by chemiluminescence (CraNO$_x$, Eco Physics, Dürnten, Switzerland, Pandey Deolal et al.,

2012) and CO data from a cavity ring-down spectrometer (model G2401, Picarro Inc, Santa Clara, CA, USA, Zellweger et al., 2012) of the NABEL network were used.

2.3 Bilinear factor analysis with the multilinear engine (ME-2)

Positive matrix factorisation (PMF, Paatero and Tapper, 1994; Paatero, 1997) facilitates disentanglement of bulk mass spectral time series into several contributing factors by minimisation of the quantity Q, consisting of the sum of the squares of the error-weighted residuals of the model. Especially for the organic part of the aerosol mass spectra recorded with AMS/ACSM instruments this method is very successful (Lanz et al., 2007) and has been applied to a great number of studies around the world (Zhang et al., 2011). In conventional PMF analyses, rotational ambiguity coupled with limited rotational controls can impede clean factor resolution. In contrast, the multilinear engine implementation (ME-2, Paatero, 1999; Paatero and Hopke, 2009) enables efficient exploration of the entire solution space by the application of specifically designed penalties or restrictions to mathematically viable but physically unrealistic or ambiguous solutions. A simple approach utilises the so-called a value (Lanz et al., 2008; Brown et al., 2012; Canonaco et al., 2013; Crippa et al., 2014). Here a priori information is introduced by fixing one or more anchor spectra from previous campaigns/analyses with varying degree of freedom. The freedom is regulated with the a value which can vary between 0 and 1 and stands for the percentage each m/z signal of the final solution spectra may differ from the anchor. 0 means no deviation allowed, 1 means 100 % deviation allowed.

The source finder (SoFi, Canonaco et al., 2013) tool version 4.9 for Igor Pro (WaveMetrics Inc., Lake Oswego, OR) was used for ME-2 input preparation and result analysis.

2.4 Back dispersion (BD) clustering

For the full measurement period, the history of air masses arriving at the JFJ was calculated using backward simulations of the Lagrangian particle dispersion model FLEXPART (v9.01, Stohl et al., 2005). Taking into account mean flow, deep convection, and turbulence the model calculated the backward trajectories (10 days) of 50 000 particles released every three hours at the location of JFJ. The model was driven off-line with meteorological data from the European Centre for Medium Range Weather Forecast (ECMWF) at a vertical resolution of 91 levels (138 levels after 25 June 2013) and a horizontal resolution of $0.2^\circ \times 0.2^\circ$ for the Alpine area (rest: $1^\circ \times 1^\circ$) between 4° W–16° E and 39–51° N. Since in the Alps many terrain features are not well resolved by a $0.2^\circ \times 0.2^\circ$ resolution, a starting height for the released particles of 3000 m a.s.l. was used, which lies between the real elevation of the JFJ station (3580 m a.s.l.) and the model ground at ~ 2500 m a.s.l. Previous studies (Keller et al., 2011; Brunner et al., 2012) reported best model performance with this selection.

FLEXPART provided emission sensitivities (footprints) with a horizontal resolution of $0.1^\circ \times 0.1^\circ$, covering the European region shown in Fig. 5). The surface footprints were then categorised according to the clustering technique detailed in Sturm et al. (2013) and Pandey Deolal et al. (2014). Here, seven categories were distinguished and can be identified by their main source region, i.e. the region with largest intensity of surface influence (see caption of Fig. 5).

2.5 Characterising air masses: influence of the planetary boundary layer

Although JFJ's elevation above the surrounding low lands is well above typical PBL heights (see e.g. Seidel et al., 2010; Chan and Wood, 2013) frequent transport of polluted air masses from the PBL can be observed, as it is the case for many mountainous sites (Rotach and Zardi, 2007). This transport is mainly driven by three processes (Zellweger et al., 2003; Forrer et al., 2000): dynamically by deflection of synoptic winds over mountainous terrains (e.g. Foehn winds), vertical turbulent mixing over flat terrain and advection to the JFJ (e.g. thunderstorms) or thermally by anabatic mountain winds. Especially during the warm season the thermal vertical transport drawing in PBL air from a radius up to ~ 80 km (Weissmann et al., 2005) leads to frequent increases of aerosol concentrations during the afternoon hours (Henne et al., 2005). This thermal transport results in the creation of a dynamically decoupled injection layer (IL) (Nyeki et al., 2000).

In the literature, several methods for the separation of FT air from IL air have been described. In the context of this study three methods were selected and applied~~(cf. Sect. 2.5)~~: ^{222}Rn concentrations as tracer (Griffiths et al., 2014), the ratio of the sum of oxidised nitrogen species (NO_y) to carbon monoxide (CO), i.e. NO_y/CO as tracer (Zellweger et al., 2003; Pandey Deolal et al., 2013) and back trajectory analysis using footprint clustering (more details in Sect. 2.4). Figure S2 shows an example time series of both ^{222}Rn and NO_y/CO. Both methods assume different signatures in the FT and the IL. ^{222}Rn is naturally emitted from ice-free land surfaces (Yamazawa et al., 2005; Griffiths et al., 2014) and has a half-life of less than 4 days. Hence, elevated ^{222}Rn concentrations at the JFJ are a good indicator for influence of air masses with boundary layer origin. A threshold of 1.5 $\mathrm{Bq\,m^{-3}}$ was chosen with periods with ^{222}Rn concentrations below the threshold categorised as FT conditions. This choice of threshold is in accordance with the recommendations from Griffiths et al. (2014) (0.75–2 $\mathrm{Bq\,m^{-3}}$). The NO_y/CO ratio is a suitable proxy for the "age" of an air mass with ratios of 0.1 to 0.16 close to anthropogenic sources and ratios of < 0.01 after a few days of transport (Jaeglé et al., 1998; Stohl et al., 2002). Zellweger et al. (2003) reported NO_y/CO ratios of 0.002 to 0.005 for free tropospheric conditions at JFJ depending on the season. In this study, a threshold ratio of 0.004 was selected. Both thresholds are in accordance with the thresholds found by Herrmann et al. (2015) at the same site. A comparison of the ^{222}Rn and NO_y/CO time traces in Fig. S2 shows similar behaviour with radon being the slightly stricter criterion – ^{222}Rn: free tropospheric conditions during 41.1 % of the overlapping measurement period, NO_y/CO: free tropospheric conditions during 47.7 % of the overlapping measurement period. These fractions are higher than the annual fracitons reported by Herrmann et al. (2015) (25.7 and 39.1 %, respectively), which is due to the inclusion of two summers (injection of PBL air is more frequent in summer) and a longer period without measurement in winter 2012/2013 (see Fig. 1a). In contrast, cluster #1 of the backward dispersion (BD) analysis identified as FT was only active during 11.2 % of the overlapping measurement period due to selection of BD only with maximal time (10 days) passed since last PBL contact (t_{PBL}). A more careful exploration of this parameter as it is performed by Herrmann et al. (2015) may allow for a lower t_{PBL} threshold.

2.6 Saharan dust events

Transport of dust plumes from the Saharan desert (SDE for Saharan dust event) up to the latitudes of the JFJ happens several times a year (Schwikowski et al., 1995; Collaud Coen et al., 2004; Bukowiecki et al., 2015). These plumes sometimes carry sufficient material with them that the dust can be seen by bare eye as a brown-reddish layer on the Great Aletsch glacier and all other snow-covered surfaces. According to Collaud Coen et al. (2004) the distinctively different size, index of refraction and chemical composition of the SDE particles compared to the usual aerosol at the JFJ make SDEs easily detectable by their optical properties: while typically the exponent of the single scattering albedo (SSA) increases with wavelength, it decreases if mineral dust is present. The SSA is routinely measured by a nephelometer and an aethalometer at the JFJ. During the study period, eight extended SDEs (longer than 12 h) were detected. These periods are highlighted in light brown in Fig. 1b.

3 Results

3.1 Time series and concentrations

The top and middle panel of Fig. 1 show the full time series of organics (green), sulphate (red), nitrate (blue), and ammonium (orange) in the aerosol measured by the ToF-ACSM and the equivalent black carbon (black) concentration time series measured by the aethalometer from 27 July 2012 to 2 October 2013 in relative (top) and absolute (middle) terms. On top of Fig. 1b the periods used for the separation of seasons in the seasonal analyses of the following ~~chapters~~ sections are identified. Saharan Dust Events are highlighted in light brown in the middle panel. In the summer ~~months~~ periods average concentrations of all species were significantly enhanced compared to winter. The two bottom panels of Fig. 1 show expanded views of typical periods during summer (left) and winter (right). In summer the concentrations exhibit a strong variability between night/morning and afternoon/evening. While ~~total NR-~~tota PM$_1$ concentrations in the night and morning usually were below 1 µg m^{-3} they increased to several µg m^{-3} in the evening hours (maximum 9.6 µg m^{-3} on 1 August 2012 20:50 UTC). This pattern is caused mainly by thermally induced vertical transport and injection of PBL air up to the altitudes of the JFJ as detailed in Sect. 3.1.3. Usually concentrations decrease again during the night. Night-time elevated levels, e.g. 12 to 13 August 2012 (Fig. 1c left), were caused by larger scale meteorology. In the example above, a likely reason is a thunderstorm (several instances of remote lightening detected in the evening of the 12th) causing large scale turbulences, i.e. vertical mixing of air masses which then were subsequently transported to the JFJ site. Additionally several short-term spike-like increases of the organic fraction can be observed during daytime (also before the vertical mixing sets in). These spikes are attributed to local pollution by tourism or construction related activities (cf. Sect 3.2.1). It is noted that the resolution of Fig. 1b which shows the whole 14 month measurement period does not allow discrimination of spikes and therefore average concentrations given in Fig. 2 cannot be estimated by eye from Fig. 1b. There are no afternoon increases in winter and concentrations are typically below 0.3 µg m^{-3} (less than during night and morning in summer). The daytime spikes are likewise visible, however smaller than in summer due to decreased tourism activity in the cold season.

3.1.1 Seasonal variations

In Fig. 2 the statistics for each season of the species mass concentrations, measured by the ACSM are shown in absolute and relative terms (including ~~EBC~~eBC). Corresponding concentration values for each species and season are given in Table 1. It is evident that the mean concentrations in every case lie well above the median concentrations due to the strong increases during injection of air masses from the PBL, which results in a skewed distribution of the observations (note the logarithmic scale of the y ~~-scale -~~-axes). Generally SO_4^{2-} and organics were the dominant species, together comprising 73 to 81 % of the total ~~NR-~~PM$_1$ mass over all seasons. NO_3^-, NH_4^+ and ~~EBC~~ eBC contributed lower amounts, with none of these species accounting for more than 10 % of the mass in any season. Average contributions as well as absolute mass concentrations agree well with previous short-term AMS studies which reported average NR-PM_1 concentrations of 1.7 µg m^{-3} in March 2004, 2.5 µg m^{-3} in July/August 2005 (Cozic et al., 2008) and 1.6 µg m^{-3} in May 2008 (Lanz et al., 2010). A winter period from February/March 2005 reported in Cozic et al. (2008), which ~~which~~ had atypical, spring-like meteorological conditions, featured much higher absolute concentrations (2.5 µg m^{-3}) than recorded during winter in the present work (0.4 µg m^{-3}).

Organic species dominated the total ~~NR-~~PM_1 mass, especially during the warm months (summer 2012 and 2013) when transport from the PBL was most abundant. In summer, the contribution of organics to total PM_1 was between 50 and 57 % while during the rest of the year it remained between 37 and 42 %. Average absolute concentrations of organics were around 1 µg m^{-3} during summer. In autumn~~and~~, winter and spring they only amounted to 0.18, 0.16 and 0.20 µg m^{-3}, respectively. This seasonal pattern of organic mass concentrations indicates that the organics in the FT mainly originate from organics that are emitted or formed in the PBL and mixed into the FT, while SOA production within the FT gives a minor contribution.

Sulphate was the dominant ~~NR-~~PM_1 species in autumn (44 %) while in winter sulphate and organics were equally abundant (39 %). Absolute concentrations of sulphate did not vary as much between winter and summer as other species. This can be explained as follows: the atmospheric lifetime of SO_2 is, due to the low oxidation rate, similar or longer than the time scale for mixing of PBL air into the FT air (Lee et al., 2011). This results in moderate vertical gradients of SO_2 and thus ~~also~~ formation of sulphate within the FT. Consequently, the difference between the sulphate concentration in the PBL and the FT is moderate (cf. Sect. 3.1.3) and the seasonal pattern of the sulphate concentration in the FT is weaker than that of particulate species which are exclusively emitted/formed in the PBL.

The nitrate to sulphate ratio observed in this study at JFJ is low, in accordance with previous results from the JFJ (Henning et al., 2003; Herich et al., 2008) and other high-elevation sites around the world (e.g. Hidden Valley, Nepal 5050 m a.s.l., Shrestha et al., 1997; Vallot Observatory, France 4361 m a.s.l., Preunkert et al., 2002; Mauna Loa, USA 3397 m a.s.l., Galasyn et al., 1987). This can be explained with the faster production of nitrate from NO_x

compared to sulphate from SO_2. Therefore, NO_x is rapidly depleted with increasing age of air masses such that most nitrate formation occurs within the PBL, whereas nitrate formation within the FT is of minor importance. Accordingly, the ratio between nitrate concentration in the PBL and nitrate concentration in the FT is larger than the ratio for sulphate (cf. Sect. 3.1.3), and nitrate at JFJ shows a distinct seasonal pattern linked to vertical transport.

Indeed, nitrate was generally low (highest average concentrations of 0.12 $\mu g\,m^{-3}$ in the summers of 2012 and 2013) with exceptionally low median values in autumn and winter when transport from the PBL was less frequent. However, the large 90th percentile and a closer look at the full time trace of nitrate in Fig. 1b in winter reveal occasional strong increases of NO_3^- possibly attributed to special synoptic conditions that favour orographically driven vertical transport that can also occur in the colder seasons.

The ammonium mass fraction approximately corresponds to the amount required to neutralise the inorganic cations (sulphate and nitrate). Accordingly, the ammonium shows a small seasonal variability (7–10 % mass fraction) as the inorganic mass fraction varies between 28–48 % mass fraction. It is important to note that neutralised aerosol does not imply excess ammonia, as nitric acid only partitions into the particle phase in significant amounts together with ammonia. Therefore, the amount of particulate phase ammonium nitrate may be limited by the availability of either ~~gas phase ammonia or gas phase~~ gas-phase ammonia or gas-phase nitric acid. Furthermore, it is noted that recent studies have shown that the molecular ratio, i.e. degree of neutralisation is not a good proxy for the determination of aerosol pH aside from giving a very rough information if an aerosol is alkaline or acidic (Hennigan et al., 2015; Guo et al., 2015) .

Equivalent black carbon concentrations were between 4 and 6 % year-round except in winter (8 %). During winter the concentrations were lower in general, leading to an increased influence on total mass of occasional PBL contributions. The correlation of the ~~EBC~~ eBC concentrations with the overall yearly cycle (i.e. higher total ~~NR-~~PM$_1$ concentrations with higher outside temperatures, see Fig. S3) presumably is mostly related to increased vertical pollution transport which is implied by good covariance with nitrate mass. The higher ~~EBC~~ eBC fraction in summer 2013 compared to summer 2012 may in parts be related to increased local construction work activity in 2013 including the operation of diesel engine generators but also to higher organic concentrations in 2012.

In summary the seasonal variations of concentration and chemical contribution showed the importance of the injection layer and hence aerosol transport from the PBL in the vicinity of JFJ for the total measured concentrations at the JFJ.

3.1.2 Diurnal variations

Median and mean diurnal cycles (in µg m^{-3}) of organic, ammonium, nitrate, and sulphate for each season are shown in Fig. 3. Thermally induced transport caused increased nitrate and to a lesser extent also organic mass concentrations in the afternoon starting around 11:00 to 12:00 UTC and peaking between 16:00 and 18:00 UTC. This behaviour was strongest during the summer ~~months~~ periods (orange: 2012, red: 2013) and also evident in spring (green) but mostly absent in autumn (brown) and winter (blue).

The diurnal pattern shows that injections from the PBL result in substantially increased nitrate and organic particulate mass concentrations. This can be attributed to the fact that they are mainly emitted and formed within the PBL, as already argued in Sect. 3.1.1. In contrast, sulphate only exhibits a very weak diurnal pattern. This indicates that the sulphate concentrations in the upper PBL are similar to those in the FT, as it is also produced in the FT (cf. Sect. 3.1.1). The relative magnitude of the diurnal cycle of ammonium lies in between those of nitrate and sulphate~~, because the aerosol is neutralised in most cases within experimental uncertainty~~.

Generally, the concentrations observed during summer 2012 and 2013 were comparable for all species except SO_4^{2-}. A partitioning of both summers by ~~airmass~~ air mass origin showed an increased frequency of southerly origins (51 % in summer 2012 vs. 39 % in summer 2013, cf. Fig. S4) at the expense of ~~airmass~~ air mass transport from the north. In Sect. 3.1.4 it is shown that air masses arriving from the south on average were carrying more sulphate which leads to higher SO_4^{2-} concentrations in summer 2012. Mean and median show the same trends except in autumn 2012 where the mean diurnal cycles of organics and nitrate showed a strong increase during daytime, while no such increase is seen in the median. This increase stems only from one day (14 October 2012) when especially high nitrate concentrations (the highest values of the whole campaign, up to 4 µg m^{-3}) and increased concentrations of all other species were measured. This was attributed to non-thermally induced transport of air masses from the valley floor (frontal lifting). Mean concentrations of NH_4^+ and SO_4^{2-} were not or only little affected because elevated concentrations of both are measured more frequently in autumn 2012 while NO_3^- is close to 0 during most of autumn 2012.

3.1.3 Free tropospheric concentrations

Three methods to distinguish periods with free tropospheric air masses at the JFJ from periods with recent influence of the PBL were compared, using the ToF-ACSM dataset to explore the chemical composition of FT air. Figure 4a shows the median concentrations during periods independently classified as free tropospheric conditions by the three criteria introduced in Sect. 2.5: ^{222}Rn, NO_y/CO and BD clustering. All three methods yielded similar median concentrations comparable to the mean concentrations in winter: 0.10–0.12 µg m^{-3} of organics, 0.02–0.03 µg m^{-3} of NH_4^+, 0.16–0.18 µg m^{-3} of SO_4^{2-}, 0.01 µg m^{-3} of NO_3^- and 0.02 µg m^{-3} of ~~EBC~~eBC.

The boxplots of Fig. 4b–d show both, concentrations during FT conditions (left boxes, highlighted in light blue) and ~~non-FT (~~times when PBL aerosol reached the JFJ (non-FT, right boxes, highlighted in light yellow) ~~conditions~~ with mean (star) and median (horizontal line) indicated in the plots and given as numbers above each boxplot. The boxes indicate the interquartile range (IQR) and the whiskers the 10th and 90th percentile. Again, a comparison of (b), (c) and (d) shows good agreement of all three methods with slightly lower FT concentrations for the BD method. This difference may arise from a more strict FT definition used by the BD method: only BD without significant PBL contact during the last ten days were assigned to the FT cluster. Each method uses specific cut-off parameters, i.e. FT thresholds which are all subject to uncertainties. A more strict cut-off will lead to lower mean concentrations during both FT and non-FT conditions.

A comparison of the median concentration values (^{222}Rn or NO_y/CO criterion) during non-FT and FT conditions yielded ratios of 1.8 for organics and 1.7 for NH_4^+, a higher ratio of 2 to 3 for NO_3^- and a lower ratio close to $1:1$ for SO_4^{2-}. This is consistent with the interpretation of the diurnal patterns (Sect. 3.1.2) suggesting that ~~suggesting that~~ the aerosol from PBL injections has higher mass concentrations and mass fractions of organics and nitrate compared to the FT aerosol. A more detailed look at the mass spectra (local primary organic aerosol contributions were subtracted from the spectra in advance, cf. Sect. 3.2.1) showed a non-FT$/$FT ratio of the signal at m/z 44 of 1.9, which is comparable to the non-FT$/$FT ratio for total organic mass. However, m/z 55, 57 and 60, which are mainly related to primary sources, showed larger ratios of around 3 (m/z 55: 2.9, m/z 57: 3.6, m/z 60: 3.3) similar to NO_3^-. These values are similar to m/z 43 (3.0), which is present in primary OA but also in less oxidised SOA. These results indicate an increased importance of primary OA (POA) sources during periods when PBL aerosol was injected into the JFJ region.

Similar conclusions could be drawn from the differences of the (seasonal) relative species fractions between FT (Fig. 4e) and non-FT conditions (Fig. 4f). During autumn and winter the fraction of SO_4^{2-} was increased by about 60 % during FT conditions while the organic fraction was decreased by about 30 %. The NO_3^- fraction showed by far the largest difference with a decrease of about a factor 3 during FT conditions (autumn and winter). The NH_4^+ contributions, however, stayed more or less the same. The difference between FT and non-FT conditions was much smaller in both summers, also showing decreased NO_3^- during FT conditions but largely similar contributions of the other species. These observations lead to several conclusions: (1) most nitrate measured at the JFJ was injected from the PBL, (2) significant amounts of organics were injected from the PBL, (3) sulphate loadings in the FT and upper PBL are similar such that PBL influence does not cause distinct diurnal or seasonal patterns, (4) the constant NH_4^+ fraction through all seasons is due to the compensating effects of NO_3^- and SO_4^{2-} with which NH_4^+ is associated, and (5) in summer aerosol levels remained elevated and retained a similar chemical composition also during FT conditions, indicating an overall larger PBL influence on the regional scale lower free troposphere. Long-term ACSM measurements at a site in the Magadino plain (Switzerland, 204 m a.s.l., latitude: 46°9′37″ N, longitude: 8°56′2″ E) showed comparable species contributions in summer 2014 (see Fig. S5). Similar findings of decreased nitrate and enhanced sulphate and organic concentrations during FT conditions were reported from the French elevated site puy-de-Dôme (1465 m a.s.l.) by Freney et al. (2011).

3.1.4 Geographical aerosol origins

Its central European location makes the JFJ a good receptor site for pollutants from different source regions within Europe (and beyond, e.g. SDE). A clustering of air mass origin into seven footprint regions is shown in Fig. 5 together with the corresponding NR-PM$_1$ aerosol composition and equivalent black carbon. Mean and median concentrations of each cluster are given below the pie charts. For all clusters good statistics with total measuring times between 765 h and 1527 h were achieved. The clusters are numbered from #1 to #7 and can be characterised by the prevailing cardinal directions/origins (cf. Table 2 including frequencies of each cluster.)

It should be noted again that footprints were calculated using meteorological input data with a horizontal resolution of $0.2° \times 0.2°$. While these simulations are able to capture the large scale synoptic flow, local meso-scale flow patterns in the complex mountain topography are not represented well in the model and are only estimated by the inclusion of enhanced turbulent transport over terrain with large sub-grid scale topography variations (Stohl et al., 2005). Hence, some locally driven transport events may be missed by the model and could be misclassified by the BD clustering.

Highest mean and median total concentrations were recorded from clusters #3–#5 (south-west to south-east directions) with average concentrations between 1.59 and 1.63 µg m^{-3} (median: 0.63–1.03 µg m^{-3}). Clusters #6 and #7 (north-west to north-east directions) showed about 20 % lower mean concentrations between 1.25 and 1.37 µg m^{-3} (median: 0.55–0.69 µg m^{-3}) and cluster #2 (west) showed ~ 50 % lower mean concentrations of 0.85 µg m^{-3} (median: 0.43 µg m^{-3}). The free tropospheric cluster #1 showed an equally low median (0.40 µg m^{-3}) but higher mean, indicating stronger influence of regional transport phenomena that was not captured by the transport model. A possible explanation is a frequent connection between subsidence (i.e. FT air masses) and anticyclonic conditions leading to fair weather with higher temperatures (i.e. increased thermally-induced regional vertical transport).

A comparison of the different aerosol chemical species showed dominant organic aerosol from all regions, with highest OA concentrations from north-west (63 %) and for the FT cluster (66 %) and lowest OA concentrations from the south (43 %). Sulphate was most abundant in air masses from southern (#3: 27 %, #4: 33 %, #5: 27 %) and western regions (#2: 28 %). The lowest sulphate fraction was detected from the north-west (17 %). Nitrate fractions were relatively constant (8–10 %) from all regions with slightly lower contributions in clusters #1 and #2 (6 %). The same was true for ~~EBC~~ eBC which ranged between 3 and 5 %. Large fractions of the total NO_3^- and ~~EBC~~ eBC are expected to be imported from the regional boundary layer (cf. Sect. 3.1.3). The level of ammonium depended on the sum of NO_3^- and SO_4^{2-}, suggesting mainly ammonium nitrate and ammonium sulphate aerosol in all clusters.

Summarised, ~~NR-~~PM_1 concentrations in air masses advected from south of the Alps (where regions with known high aerosol loadings like the Po valley are located, cf. van Donkelaar et al., 2010) were about 20 % higher (BeNeLux, UK, Germany) to 50 % higher (France, Atlantic) than the ~~NR-~~PM_1 in air masses from north of the Alps (Germany, Scandinavia). These air masses also carried higher fractions of sulphate aerosol while in the northern air masses larger fractions of organic aerosol were measured. This higher sulphate mass fraction was also observed if only FT air masses in clusters #2 to #7 using the NO_y/CO criterion for additional air mass separation were considered. 45 % of the mass was sulphate in FT air masses from clusters #3, #4 and #5 while the mass fraction of sulphate from the northern clusters #6 and #7 is at 29 % (cf. pie charts in Fig. 6). The apparent discrepancy between organics dominance in the cluster #1 and the above analysis where for FT conditions sulphate was most abundant is due to the fact that the footprint analysis is mostly restricted to northern air masses in cluster #1, while sulphate is higher with southern air masses. Air masses advected from the west over France and the Atlantic ocean carried the lowest mean aerosol loading but a sulphate fraction comparable to aerosols from the south. This could be a hint towards influence of shipping emissions off the Atlantic coast.

3.2 Organic mass spectra

A large fraction of all m/z channels in the aerosol mass spectra is attributed to organic compounds. However, fragmentation, thermal decomposition and partly also insufficient mass resolution (although the possibility of limited high resolution peak fitting of ToF-ACSM data has been demonstrated by Fröhlich et al., 2013) cause the loss of information about the parent compounds. Nevertheless, techniques like ME-2 or PMF allow for a further separation according to emission/production sources. Furthermore, a closer look at m/z channels known to be dominated by well-understood ions can shed more light on the evolution and sources of the organic fraction.

Figures 7a–e show the fractions of total OA ~~of~~ (the contributions of a minor local primary OA factor - see Sect. 3.2.1 - were subtracted for total OA beforehand) of the UMR m/z 43, 44, 55, 57 and 60 (f_{43}, f_{44}, f_{55}, f_{57} and f_{60}). A clear maximum during ~~summer months~~ the summer periods and the minimum in winter of f_{43} can be recognised while f_{44} stayed more or less constant throughout the year. Both of those m/z are typically found in secondary organic aerosols (SOA) with f_{43} being more abundant in more recently formed SOA (Chhabra et al., 2010; Pfaffenberger et al., 2013) while f_{44} increases with age and oxidation state (Ng et al., 2010, 2011a). Additionally f_{43} is an important fragment in many POAs (e.g. cooking, traffic). A constant f_{44} points towards similarly aged background aerosols in summer and winter and the increase of f_{43} during the summer is attributed to vertical transport of: (1) less oxidised SOA (possibly associated with increased emission of biogenic SOA precursors by plants) and (2) f_{43} containing POA. An investigation of the POA and SOA factors found in the OA source apportionment of Sect. 3.2.1 showed POA contributions to f_{43} between 17.8 and 65.9 % depending on the season (summer 2012: 17.8 %, autumn 2012: 40.1 %, winter 2012/2013: 65.9 %, spring 2013: 35.7 %, summer 2013: 18.7 %)

The major part of f_{57} is usually attributed to hydrocarbon-like emissions e.g. by combustion engines (Zhang et al., 2005). No clear trend is visible for f_{57}. It contributed around 0.5 %

year-round which suggests a generally low, but constant influence of HOA at the JFJ. Part of the OA fraction at m/z 55 is as well attributed to HOA emissions but f_{55} does also have other important sources like cooking (Mohr et al., 2012) or SOA at lower oxidation stages. The f_{55} followed the same trend as f_{43} and was elevated during the summer ~~months~~period, which was likewise due to increased up-slope transport. The effect of varying local pollution was accounted for by subtracting the local POA identified by ME-2 from the organic mass spectra (for details see Sect. 3.2.1). The winter/summer difference was a little more pronounced for f_{43} but overall the seasonal behaviour of f_{55} was comparable. The mean and median fraction of m/z 60 exceeded the 0.3 % threshold reported to be characteristic of biomass burning only in winter (Cubison et al., 2011).

The IQR of all fractions was increased during the colder months which is mainly due to the increased influence of noise resulting from low concentrations. In general the analysis of these markers supported the conclusion of increased vertical transport from the PBL during summer and indicated biomass burning influence in winter which could be either from longer range transport or local (or regional) vertical mixing.

3.2.1 ME-2 results

ME-2 organic source apportionment was performed separately for all seasons ~~.~~ to account for seasonal changes of factor profiles, especially OOA. Seasonal PMF for long-term datasets was also performed before by Minguillón et al. (2015) and Tiitta et al. (2014) . Parworth et al. (2015) went one step further and were performing separate PMF analyses on shifting two week windows (which they call “rolling window technique”) over a full period of 19 months to capture changes in the OOA and BBOA factors.

ME-2 input matrices with an m/z range of 12–120 were prepared. Higher m/z channels were omitted due to low signal to noise at the low mean concentrations prevalent at the JFJ. Errors were calculated accounting for Poisson counting statistics and electronic noise in accordance with Allan et al. (2003). Peaks calculated from m/z 44 were considered in the ME-2 analysis but their uncertainties were adjusted according to the recommendations of Ulbrich et al. (2009) to avoid overweighting.

The daily vertical mixing (during appropriate seasons) poses a challenge to the ME-2 analysis since PMF relies on unique source variabilities for a good separation of sources. Simultaneous advection of aerosols from different sources hence cannot be separated autonomously. The approach applied to deal with this issue can be described as an extended chemical mass balance (CMB, Watson et al., 1997; Ng et al., 2011b). A priori information of organic aerosol source spectra is introduced into the model using the a value technique available in ME-2. In the absence of distinct criteria for the determination of ideal a values due to contemporaneous advection of typical tracers a large range of a values was taken into account for the final result which ultimately constitutes the arithmetic mean of all reasonable solutions using the range of a values indicated in Table S1 in the Supplement. This table also contains reasons for the respective choice of a ranges. Variability (1σ) of the result as percent of the total source contribution is given in Table S2. There, in addition to the variability due to different a values, also the variability due to different random starting points of the ME-2 (seeds) is taken into account by averaging five seeds for each set of a values. It is noted that although large a value ranges were considered the variability usually is below $\pm 10\,\%$.

Three to five factors could be identified depending on season. During all seasons, a primary hydrocarbon-like OA (HOA), a locally emitted primary OA (POA_{loc}) and secondary oxygenated OA (OOA), which in summer was split up into LV-OOA I and LV-OOA II, could be identified. Due to the absence of direct volatility measurements the attribution of the OOAs to the LV-OOA family was made indirectly on the basis of spectral similarities to the range shown in Ng et al. (2010) . A biomass-burning related OA (BBOA) was identified when the signal of its ~~principal~~ most specific fragment peak at m/z 60 was above the background level. This occurred in winter as well as in summer 2013, when three distinct biomass-burning events were identified (presumably due to forestry related fires, see Fig. S6). Mean HOA and BBOA reference spectra taken from Ng et al. (2011b) were used in the ME-2. The anchor spectrum of POA_{loc} was extracted directly from the dataset by a separate unconstrained PMF only on all short-term peaks visible in the organic time series (cf. Fig. 1c). This separate PMF resolved (next to the always present background OOA) only one local primary OA factor, suggesting that the local emissions mainly came from a single local source. Also an additional k-means clustering analysis of all mass spectra of the short-term peaks (with subtraction of the background by interpolation of the spectrum before and after each peak) only resulted in a single cluster.

In the following analysis $\mathrm{POA_{loc}}$ always remained tightly constrained ($a = 0.05$), while for HOA (and if applicable, BBOA) many solutions with different a values (varied in steps of $\Delta a = 0.1$) were averaged. The OOAs were always completely unconstrained (no a priori mass spectrum).

As an example, the solution (time series and profiles) from summer 2012 is shown in Fig. 8a–c. All other solutions discussed here behave similarly and their time series and profiles can be found in the Supplement (Figs. S6 and S7). The profiles of Fig. 8a show a similarity between HOA and $\mathrm{POA_{loc}}$ while the time series of these two factors are completely independent. HOA follows the general diurnal pattern influenced by vertical transport, similar to ~~EBC~~ eBC (cf. Fig. S10) and $\mathrm{POA_{loc}}$ mainly consists of sharp short-term peaks only appearing during daytime (see zoom in Fig. 8c). It is noted that due to the large similarity of HOA and cooking-related (COA) profiles it cannot be excluded that a fraction of the presented HOA may be influenced by COA.

The two OOAs generally followed the same diurnal pattern as HOA with LV-OOA I showing less temporal variability and a higher relative signal at m/z 44 than LV-OOA II. This points towards a more aged oxidised OA. Although LV-OOA I presumably does have the lower volatility since it is more oxidised, the separation in this case was rather driven by origin or formation processes than by volatility since temperatures are always low at the JFJ. The vertical transport pattern was pronounced in the less oxidised LV-OOA II and it showed the same diurnal trends as nitrate (cf. Fig. S8) while the other (LV-OOA I) represents the background OOA and correlated better with sulphate (cf. Fig. S8). This indicates that further oxidation of the OA takes place in the FT.

The seasonal diurnal cycles of HOA, $\mathrm{POA_{loc}}$ and OOA are shown in the bottom panels of Fig. 8. HOA in (d) and LV-OOA II in (f) showed afternoon increases which were less pronounced in winter and autumn. LV-OOA I however exhibited a much less pronounced diurnal trend then LV-OOA II confirming its background nature. $\mathrm{POA_{loc}}$ (Fig. 8e) was mainly observed between 09:00 and 15:00 LT coinciding with the opening hours of the tourist facilities and the train to the JFJ. Autumn to spring, the concentrations of $\mathrm{POA_{loc}}$ outside the opening hours went down almost to zero while in the peak tourist season in summer low concentrations of $\mathrm{POA_{loc}}$ were also found in the non-spiky background during the night which indicates a not perfect separation of $\mathrm{POA_{loc}}$, i.e. a small overestimation during the summers. The autumn diurnals were dominated by two large non-thermally induced vertical transport events on the 14 and 26 October causing the peak between 06:00 and 14:00 UTC in HOA and OOA (see Figs. S6 and S7), similar to Sect. 3.1.2.

Relative source contributions for all five seasons between summer 2012 and summer 2013 are depicted in Fig. 9 as pie charts. Secondary OOA dominated the OA all over the year constituting between 71 % (winter 2012/2013) to 88 % (summer 2013).

$\mathrm{POA_{loc}}$ contributed 7–8 % in both summers and spring and 12 % in autumn and winter. This means that relative contributions of $\mathrm{POA_{loc}}$ were higher in winter when non-local OA was generally low while the absolute concentrations of $\mathrm{POA_{loc}}$ were higher in summer when there were more visitors at the station, i.e. a higher tourist activity. The time series of $\mathrm{POA_{loc}}$ overlayed with a shaded background in either blue (days when global radiation is below average) or red (days when global radiation is above average) is shown in the top panel of Fig. S9 for a period of two months in summer 2013. The bottom panel shows number concentrations measured with a CPC (time resolution 10 s) for the same period. A strong evidence for a connection of $\mathrm{POA_{loc}}$ to tourist activities is the generally lower occurrence of spikes during the (less sunny) “blue” days than the “red” days. This was confirmed by the CPC number concentrations, which also showed fewer spikes on the same days.

Possible sources of local pollution by tourism related activities are: cigarette smoke, fuel combustion by helicopters or snowcats and emissions of the three on-site restaurants. Previous studies have shown that significant differences between source profiles of these three sources exist (see e.g. Mohr et al., 2009; Faber et al., 2013). The results of PMF and the cluster analysis on the spikes described above suggested a single source for the majority of the peaks. Figure S10 shows a one-week time series (7 to 13 August 2012) of

HOA, POA$_{\mathrm{loc}}$, ~~EBC~~ eBC and CPC with high time resolution (for values cf. legend). The fact that ~~EBC~~ eBC did not show any short-term spikes at all while POA$_{\mathrm{loc}}$ and CPC number showed many spikes during daytime allowed for the exclusion of combustion engines as likely POA$_{\mathrm{loc}}$ source since they are expected to emit significant amounts of black carbon as opposed to cigarettes or restaurants (Hildemann et al., 1991; Kleeman et al., 1999). Furthermore, the spikes are too frequent (> 100), too regular and distributed over the whole day with time scales of one to a few minutes to have been emitted by occasional helicopter flybys (less frequent), irregular construction work (more constant emissions) or snowcat activities (typically only in the morning and evening). A correlation of the POA$_{\mathrm{loc}}$ profile (see Fig. S11) with known reference profiles of traffic and cooking (COA) resulted in R^2 of 0.74 for HOA from Ng et al. (2011b), $R^2 = 0.77$ for COA from Crippa et al. (2013) and $R^2 = 0.94$ for cigarette smoke OA ~~(CSOA)~~ from Faber et al. (2013). Only the m/z range between 45 and 120 was considered for the correlations to avoid uncertainties related to f_{44} (for details see Fröhlich et al., 2015). The ~~CSOA~~ cigarette smoke OA from Faber et al. (2013) is also shown in Fig. S11. The striking similarity of POA$_{\mathrm{loc}}$ and ~~CSOA~~ cigarette smoke OA above m/z 44 points towards smoking of cigarettes as the most likely source for the local pollution spikes. This assumption is supported by a concurrent increase of the near-ultraviolet (370 nm) absorption signal of the Aethalometer (see Fig. S18). Tobacco smoke is known to have increased optical absorption at the near-ultraviolet wavelength compared to longer wavelengths (Hansen, 2005) . Some of the f_{44} difference between POA$_{\mathrm{loc}}$ and cigarette smoke OA is expected due to the mentioned f_{44} uncertainties in the ACSM systems but the POA$_{\mathrm{loc}}$ exhibits a particularly low f_{44} close to zero. This may indicate that a small fraction of the POA$_{\mathrm{loc}}$ is misallocated to one of the other factors, most likely the OOA, partly offsetting the potential overestimation during night-time. In the literature, several cigarette smoke OA spectra were reported showing different amounts of f_{44}. The cigarette smoke OA of Northway et al. (2007) shows low f_{44} ($f_{44}/f_{43} \approx 0.08$) while Tang et al. (2012) show a f_{44}/f_{43} ratio of about 0.25 in sidestream environmental tobacco smoke and $f_{44}/f_{43} \approx 0.5$ in mainstream smoke similar to Faber et al. (2013) . However, ME-2 including a ~~CSOA~~ cigarette smoke OA anchor profile (or COA anchor profile) did not result in a similarly good separation of the local spikes from the HOA. It is noted, that also under the assumption that the "real" f_{44} was similar to Faber et al. (2013) , the difference in the total $\mathrm{POA_{loc}}$ concentration was smaller than 10%, which lies within the estimated uncertainties of the method reported by Fröhlich et al. (2015) . Morrical and Zenobi (2002) have previously identified environmental tobacco smoke markers in the particulate phase at the JFJ in a non-quantitative way.

HOA contributions varied between 3 % (summer 2013) and 9 % (winter 2012/2013). The higher relative HOA fractions in the colder months can be explained by the large contribution to the total OA mass of a few vertical transport events containing higher amounts of HOA as opposed to the FT air masses (cf. HOA time series in Fig. S7). In addition, the restriction of the PMF output to positive values can cause a small positive bias at low concentrations. Absolute concentrations, however, were higher in summer due to increased overall influence of vertical transport. Previous PMF studies of a short-term AMS dataset from May 2008 found HOA contributions of 6 % (Crippa et al., 2014) and 7 % (Lanz et al., 2010) similar to the 8 % found in this study for spring 2013.

Table 3 shows the HOA-to-BC ratios as a function of season. Values around 0.5 were observed, with the exception of summer 2013 when a significantly lower ratio of 0.27 was measured. A likely reason is a faster oxidation of the semi-volatile fraction of HOA reducing the remaining HOA/BC (Hildebrandt et al., 2010). Another possible influence on the changed ratio is increased construction work activity in summer 2013 (e.g. renovation of a restaurant roof) entailing the use of diesel engine generators possibly emitting higher amounts of ~~EBC~~ eBC on site. A third possibility is an underestimation of HOA in the source apportionment during summer 2013. The reported ratios are in agreement with measurements in a Swiss highway tunnel (Gubrist tunnel) by Chirico et al. (2011) and smog chamber studies of a EURO 3 diesel passenger car (0.43 ± 0.17, Chirico et al., 2010).

BBOA was only identified in winter 2012/2013 when it comprised 7 % of OA and summer 2013 with about 1 %. The flat diurnal of BBOA (see Fig. S16) and its correlation with the overall trend of OOA in winter suggest long-range transport of BBOA rather than regional vertical transport. A possible source region for BBOA could be alpine valleys or the surrounding regions of the Alps where wood burning is very important in winter (Lanz et al., 2010; Herich et al., 2014; Zotter et al., 2014). During all other seasons BBOA could not be identified reliably. Even forcing a BBOA factor profile with strict constraints ($a \leq 0.05$) into the ME-2 solution always resulted in BBOA mass fractions of 1 % or less.

3.2.2 f_{44} vs. f_{43} triangle plots

Evolution of OA particles is often represented in the f_{44} vs. f_{43} space introduced by Ng et al. (2010). There, the relative contribution to total OA by the two major fragments at m/z 44 (mainly CO_2^+) and m/z 43 (mainly $C_2H_3O^+$ and $C_3H_7^+$) of ambient AMS data typically fall into a triangular space indicated with red lines in Fig. 10 and temporal changes of the position up and down along the edges of the triangle can be interpreted as ageing while changes in the horizontal direction indicate anthropogenic (biomass burning: left, traffic: left to middle) or biogenic (right) influence. The frequent injection of OA from the PBL which often experienced a different amount of ageing than the OA in the FT poses an additional important factor governing the f_{43}/f_{44} differences at the JFJ. Absolute values of f_{44} in the ACSM have to be treated with caution due to large instrument dependent variations of f_{44} found in an intercomparison of ACSM instruments by Fröhlich et al. (2015). However, the interpretations of the f_{44} vs. f_{43} triangle still hold for variations within an ACSM instrument.

In panel (a) of Fig. 10 mean f_{44} and f_{43} are shown for the full OA mass (circles) and after a subtraction of the locally emitted OA (POA_{loc}, squares), again separated by seasons. The subtraction of the fresh POA_{loc} which contains no f_{44} and about 6 % f_{43} (see Fig. S11) ~~lead~~ leads to an increase of f_{44} and a small decrease of f_{43} during all seasons, i.e. a movement in the f_{44} vs. f_{43} space towards the upper left. It is noted that a potential underestimation of f_{44} in POA_{loc} as discussed in Sect. 3.2.1 would change the shown f_{44} by less than 1%. The overall picture, however, ~~remained~~ remains similar: in both summers a larger f_{43} was measured compared to the rest of the year indicating a mix including less aged OA with a possible predominant biogenic origin (Canonaco et al., 2015). Of the two summers, the point of summer 2012 lies more to the bottom right in the diagram than summer 2013. This is caused by a stronger contribution of vertical transport in summer 2012 compared to summer 2013 as already shown by the SA (higher LV-OOA II fraction; cf. Fig. 9) and the higher f43 (cf. Fig. 7). The points of autumn 2012 and spring 2013 almost lie on top of each other in the diagram, indicating similar ageing and sources. Before subtraction of $\mathrm{POA_{loc}}$ the autumn point showed a lower f_{44} caused by the larger amount of $\mathrm{POA_{loc}}$ detected compared to spring (12 vs. 7 %, cf. Fig. 9). The winter point is the only one lying on the left side of the triangle, meaning larger influence of the remaining primary sources (anthropogenic wood burning OA Heringa et al., 2011, 2012 or HOA) also after subtraction of $\mathrm{POA_{loc}}$. This is justified by the increased fraction of HOA detected at the JFJ in winter compared to other seasons, which mainly originated from rare vertical transport events in winter dominating the mean values. Additionally, different importance of sources for OOA in winter (more anthropogenic) and in summer (more biogenic) may play a role (see e.g. Andreani-Aksoyoğlu et al., 2008; Hoyle et al., 2011).

Panel (b) of Fig. 10 shows the mean f_{44} and f_{43} in the presence of mainly free tropospheric air masses (white square) and during times with influence from the PBL (black square) after the subtraction of $\mathrm{POA_{loc}}$. The separation was made with the method using $\mathrm{NO}_y/\mathrm{CO}$ which was described in Sect. 2.5. FT OA shows smaller f_{43} and larger f_{44}. This difference is mainly due to a higher degree of oxidation of the OOA in free tropospheric air masses consistent with the absence of sources emitting fresh OA and the longer life time of particles in the FT. Figure S13 shows a 30 % higher mass fraction of LV-OOA II to total OOA when PBL injection is happening compared to FT conditions in summer 2013.

A separation according to air mass origin (using the source area clusters described in Sect. 2.4 and displayed in Fig. 5) is shown in Fig. 10c ($\mathrm{POA_{loc}}$ subtracted). The very similar position of all points indicated a similar mix of OA sources from all cardinal directions. If the vertical position in Fig. 10c is interpreted as indicator for ageing, the highest degree of ageing was found in air masses from the north and south-east and the lowest degree of ageing in air masses from the west and south-west. However, the differences were small and may lie within the range of uncertainties of the methods applied. The same plot is shown in Fig. S14 after additional subtraction of the non-local POA sources identified in the ME-2 source apportionment (HOA and BBOA). The points moved up even more along the right edge of the triangle and form two clusters: a lower one containing only air masses from the west and south-west and a higher one containing the rest indicating a small difference (less oxidation) in SOA arriving from the Atlantic ocean.

The position of only the OOA factors determined in the ME-2 analysis are shown in Fig. 10d (full OOA spectra are shown in Fig. S12 of the Supplement). For both summers LV-OOA I, LV-OOA II and the combination of both are plotted separately. Systematic variability of the degree of oxidation of OOA was observed over the course of the year. The combined OOA in summer 2012 showed the lowest f_{44} and the highest f_{43}. The fraction of 44 increased in the colder seasons while f_{43} decreased at the same time (Canonaco et al., 2015). The points move along the right edge of the triangle indicating different degrees of oxidation. The OOAs of autumn and spring were very similar as already shown in panel (a) and the combined OOA of summer 2013 lies between summer 2012 and spring/autumn consistent with less vertical transport contribution in summer 2013 compared to summer 2012. The differences of the OOAs are mainly attributed to a difference in OA age. Vertical transport of less oxygenated OOA increases in frequency with temperature and at the JFJ transported OOA mixes with the background OOA. LV-OOA I and LV-OOA II in summer 2013 span a larger region in the f_{44} vs. f_{43} space than in summer 2012. A reason is the imperfect overlap of both summer periods. During summer 2013 the ToF-ACSM measured during the full summer of 2013 (beginning of June to mid September) while in summer 2012 it was only measuring between end of July and mid September, i.e. only the late summer aerosol. A restriction of the ME-2 only to late summer 2013 resulted in a smaller range albeit the combined OOA was still more aged (see Fig. S14).

4 Conclusions

A ToF-ACSM was operated at the Swiss site Jungfraujoch at 3580 $\mathrm{m\,a.s.l.}$ for a 14 month period spanning all meteorological seasons. A general trend of elevated ~~NR-~~PM_1 concentrations in summer, connected with increased PBL air influence due to thermally induced vertical transport and lower concentrations in winter was observed. The largest fraction

(37–57 %) was comprised of organic compounds, especially in summer while in winter and during the transient months comparably high fractions of SO_4^{2-} were measured. NO_3^- and NH_4^+ contributed lower amounts. All over the year the ~~aerosol was~~ inorganic anions were neutralised by NH_4^+ within the measurement accuracy. The major fraction of NO_3^- all over the year and significant fractions of organics mainly in summer at the JFJ were imported from the PBL by regional vertical transport. In contrast, SO_4^{2-} concentrations in the FT were higher and comparable to the concentrations of the PBL injections. Similar transport effects are expected to be taking place all over the alpine region contributing to the exchange of air masses between PBL and FT. For the separation of PBL air from FT air three methods (^{222}Rn, NO_y/CO and back trajectory clustering) were applied and compared, yielding similar results. This way seasonal averages of chemically speciated free tropospheric aerosol concentrations could be determined, representing the FT aerosol background over central Europe. The highly time resolved chemical composition data provides the opportunity to explore important aerosol parameters like CCN (cloud condensation nuclei) activity which represents an important variable for the estimation of aerosol climate effects.

In addition, air masses transported to the JFJ were divided into seven origin regions by backward dispersion cluster analysis. Highest total concentrations were measured in southerly air masses (south-west to south-east) and lowest concentrations in westerly air masses from the Atlantic ocean. Organics were dominant from all cardinal directions but the fraction of SO_4^{2-} was significantly elevated from the south.

A closer investigation of spectral markers revealed summer maxima of f_{43} and f_{55} confirming the influence of vertical transport while constant f_{44} during all seasons indicated highly aged background aerosol. f_{60} was increased only in winter indicating the presence of wood burning-related OA at the elevation of the JFJ.

A more detailed seasonal source apportionment using ME-2 (SoFi interface) allowed for a separation of the locally emitted OA fraction due to tourist activities (7–12 %). Comparison with highly time resolved aethalometer and CPC measurements together with a comparison of source profiles suggested cigarette smoke as main source of the local pollution. This observation indicates that increasing numbers of visitors may pose an issue for the validity of atmospheric observations at the JFJ during daytime (no local pollution was detected during the night hours when visitors are absent). Generally, the observed local pollution represents only a minor fraction of the total aerosol mass ($\lesssim 5\,\%$ of NR-PM$_1$) and only the organic fraction is affected, i.e. it does not play a dominant role for most long-term observations performed at the JFJ. Nevertheless, if a separation is desired, the high frequency of the local pollution spikes makes it difficult to exclude all events manually. Since cigarette smoke was identified as likely source of the local pollution a smoking ban on the visitors terrace of the Sphinx research station (see sketch of Fig. S15) should be considered.

Furthermore a small HOA fraction (3–9 %) advected to the JFJ by vertical transport with HOA/BC ratios around $1:2$ was found. The prevailing OA source year-round however was the aged, oxygenated OOA (71–88 %) splitting up in a background LV-OOA I and a vertically transported LV-OOA II during summer. f_{44} in OOA spectra decreased in the warmer seasons while f_{43} increased at the same time. OOA profiles of autumn and spring showed a close similarity. BBOA was only detected in a few rare regional vertical transport events in summer 2013 and continuously during winter 2012/2013 pointing to longer-range regional transport.

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Table 1. Mean and median concentrations in µg m^{-3} during each season.

geometric mean	summer 2012	autumn 2012	winter 2012/13	spring 2013	summer 2013	annual mean*
organic	0.64	0.13	0.09	0.12	0.47	0.13
sulphate	0.38	0.13	0.06	0.09	0.18	0.09
nitrate	0.06	0.02	0.01	0.02	0.07	0.02
ammonium	0.16	0.07	0.04	0.04	0.11	0.05
~~EBC~~ eBC	0.05	0.01	0.02	0.03	0.06	0.02
sum NR-PM_1 and ~~EBC~~ eBC	1.29	0.36	0.22	0.30	0.89	0.31
arithmetic mean						
organic	1.01	0.18	0.12	0.20	0.81	0.25
sulphate	0.63	0.21	0.12	0.15	0.28	0.17
nitrate	0.12	0.02	0.02	0.05	0.12	0.04
ammonium	0.16	0.05	0.02	0.05	0.13	0.05
~~EBC~~ eBC	0.10	0.02	0.04	0.05	0.10	0.05
sum NR-PM_1 and ~~EBC~~ eBC	2.02	0.48	0.32	0.50	1.35	0.55
median						
organic	0.64	0.11	0.08	0.11	0.54	
sulphate	0.37	0.16	0.06	0.09	0.20	
nitrate	0.05	0.01	0.01	0.01	0.06	
ammonium	0.10	0.04	0.01	0.04	0.10	
~~EBC~~ eBC	0.07	0.01	0.01	0.03	0.07	
sum NR-PM_1 and ~~EBC~~ eBC	1.23	0.33	0.17	0.28	0.97	

* Annual geometric/arithmetic mean weighted by seasonal data cover fot the period 01 October 2012 to 01 October 2013.

Table 2. Transport footprint clusters and main origins.

cluster	main origin in PBL	frequency
#1	no recent PBL contact/free tropospheric	11.3 %
#2	west	14.9 %
#3	east/south-east	14.1 %
#4	south	22.5 %
#5	south-west	13.4 %
#6	north-west	16.3 %
#7	north/north-east	22.2 %

Table 3. Ratios of HOA to ~~EBC~~ eBC for all seasons.

season	HOA : BC
summer 2012	0.56
autumn 2012	0.54
winter 2012/2013	0.43
spring 2013	0.53
summer 2013	0.27

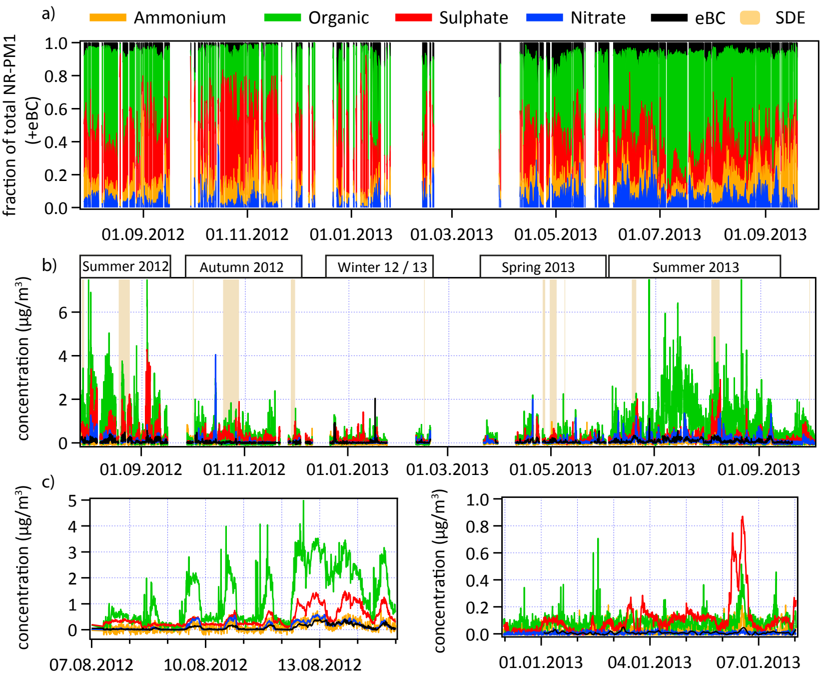

Figure 1. (a) Time series of relative organic (green), sulphate (red), nitrate (blue), and ammonium (orange) contributions to the total PM_1 aerosol measured by the ToF-ACSM and the ~~EBC~~ eBC (black) concentration time series measured by the aethalometer from 27 July 2012 to 02 October 2013. **(b)** Same as **(a)** in absolute concentrations ($\mu g\,m^{-3}$). Saharan dust events (SDE) are highlighted in light brown. On top of **(b)** the ~~seasons~~ periods used in the following seasonal analyses are identified. Gaps between seasons are caused by gaps in the data. **(c)** Left: mass concentrations in $\mu g\,m^{-3}$ during a typical summer period (7 August 2012 00:00 to 15 August 2012 00:00); right: mass concentrations in $\mu g\,m^{-3}$ during a typical winter period (01 January 2013, 00:00 to 08 January 2013, 00:00). Note the different y scales of the two plots in **(c)**. Times are given in UTC.

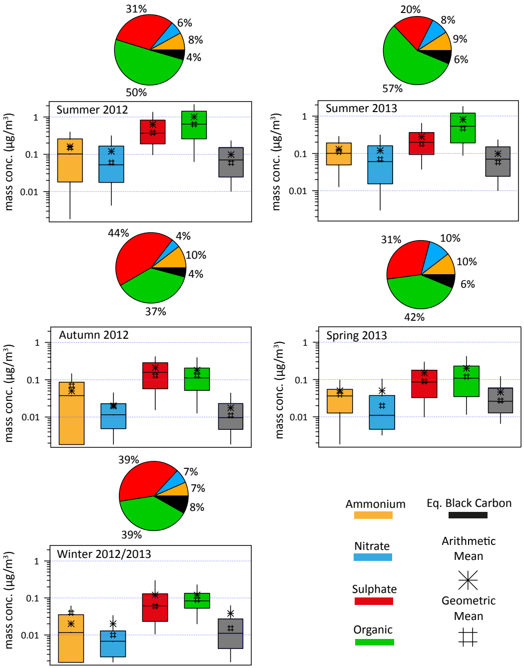

Figure 2. Pie charts of the relative average concentration and boxplots (in $\mu g\,m^{-3}$, line: median, box: interquartile range, whiskers: 10–90th percentile range) separated by seasons (summer 2012, autumn 2012, winter 2012/2013, spring 2013 and summer 2013) for species measured with the ACSM (organic: green, sulphate: red, nitrate: blue and ammonium: orange)~~. Pie charts also show the EBC concentration~~ and eBC derived from optical absorption measurements. The arithmetic mean of each species is indicated by a star and the geometric mean by a hash in the respective boxplot. Mean and median concentrations values for each species and season can be found in Table 1. Relative concentrations are given in percent in the pie charts.

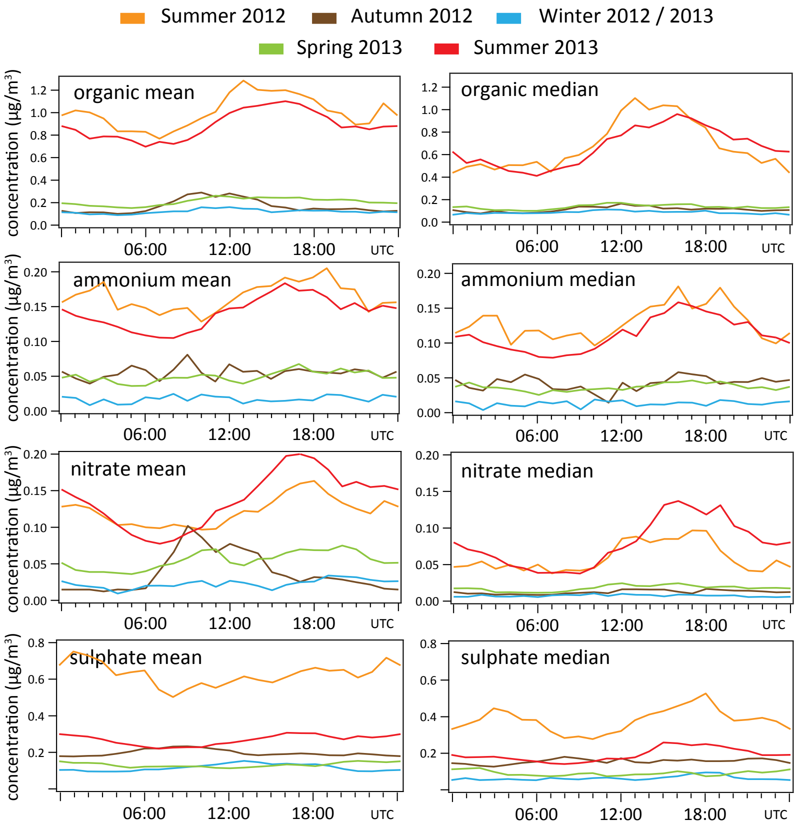

Figure 3. Seasonal diurnal plots for organics, ammonium, nitrate and sulphate (from top to bottom) in $\mu g\,m^{-3}$. On the left: mean diurnal concentrations, on the right: median diurnal concentrations. The different traces show the seasons: summer 2012 in orange, autumn 2012 in brown, winter 2012/2013 in blue, spring 2013 in green and summer 2013 in red. Times are shown in UTC.

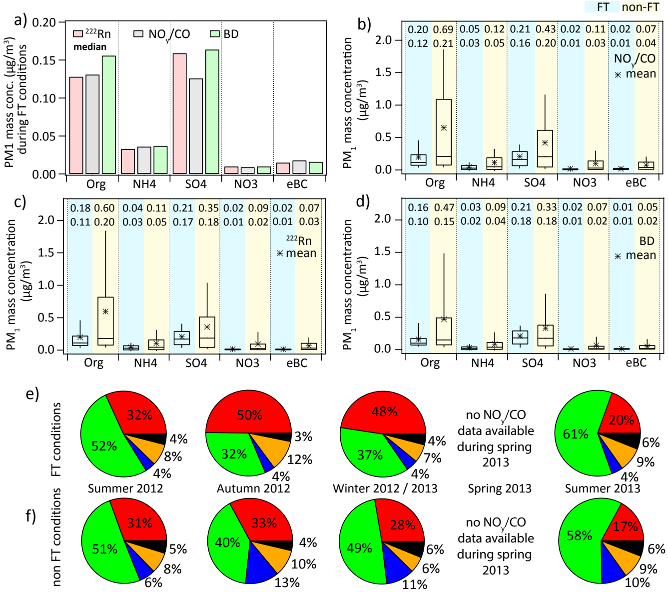

Figure 4. **(a)** Median NR-PM$_1$ species concentrations during free tropospheric conditions for three different criteria of FT separation: ^{222}Rn, NO$_y$/CO and backward dispersion clustering. **(b, d)** Show mean (star) and median (horizontal bar) concentrations for each species measured by the ToF-ACSM during the periods with data for all three different criteria – **(b)**: NO$_y$/CO, **(c)** ^{222}Rn, **(d)** BD clustering. Blue background: FT condition, yellow background non-FT condition. Absolute mean (top) and median (bottom) values in µg m^{-3} are given above each plot. The boxes represent the IQR and the whiskers the 10th to 90th percentile range. The pie charts show the relative species concentration of SO_4^{2-} (red), NH_4^+ (orange), NO_3^- (blue) and organics (green) for FT conditions **(e)** and for non-FT conditions **(f)** separated by seasons using NO$_y$/CO for FT discrimination. No NO$_y$ / CO ratios were available in spring 2013. ^{222}Rn data were not available after February 2013.

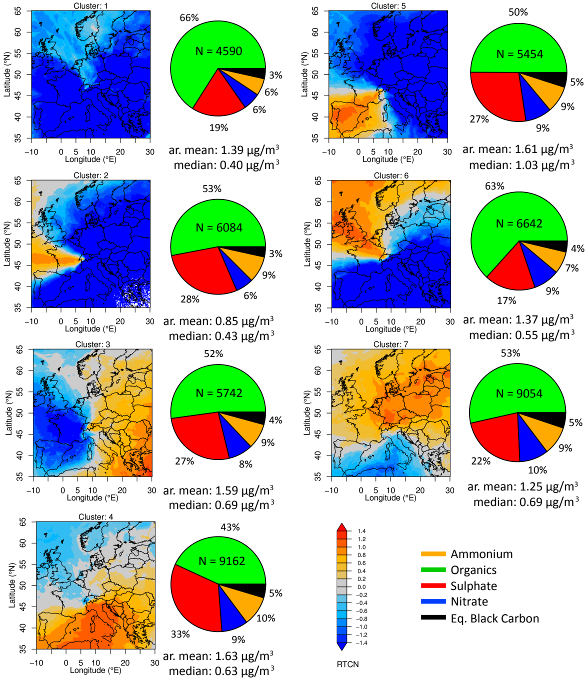

Figure 5. Aerosol footprint clusters with corresponding relative contribution of PM_1 organics (green), sulphate (red), nitrate (blue), ammonium (orange) and equivalent black carbon (black). Arithmetic mean as well as median total concentrations are given below each pie chart. The number N in each pie chart indicates the number of 10 min averages included in the calculation of mean and median. The unitless RTCN (residence times by cluster normalised) shows the normalised difference between cluster average and total average residence times. Positive (negative) values indicate increased (decreased) surface sensitivity compared to the overall footprint. The scale extends from -2 to 2 with values larger than 1 (smaller than -1) indicating regions with at least three times longer (shorter) residence times, for details see Sturm et al. (2013).

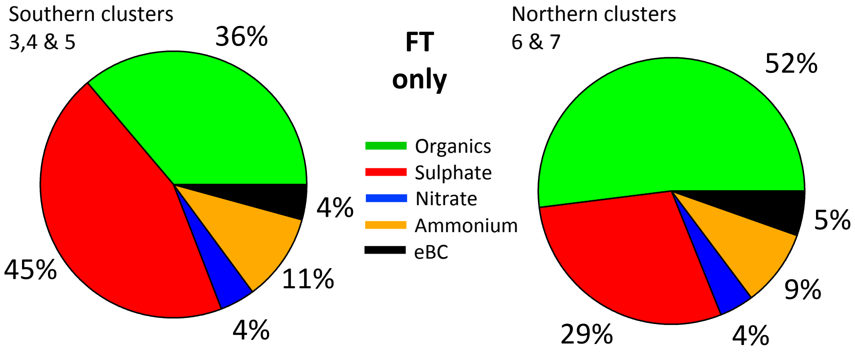

Figure 6. Relative species contributions only during FT conditions separated by air mass origin. Left: southern air masses (clusters #3, #4 and #5 of Fig. 5), right: northern air masses (clusters #6 and #7 of Fig. 5). Note that contributions of cluster #1 were not considered.

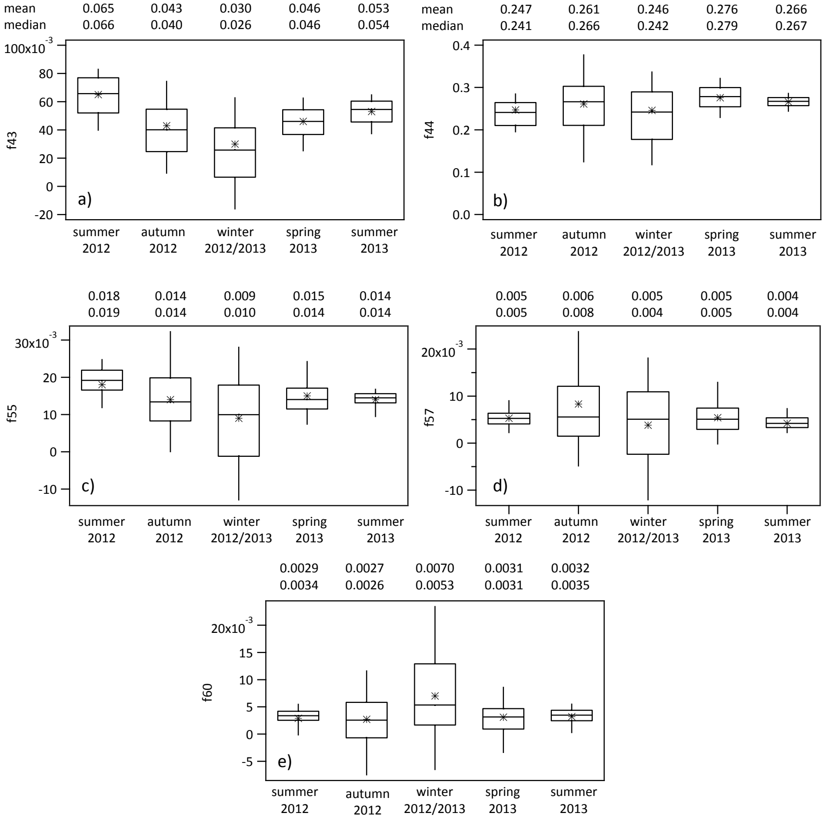
mean 0.065 0.043 0.030 0.046 0.053
median 0.066 0.040 0.026 0.046 0.054
f43
100x10^-3
80
60
40
20
0
-20
a)
summer 2012
autumn 2012
winter 2012/2013
spring 2013
summer 2013
mean 0.247 0.261 0.246 0.276 0.266
median 0.241 0.266 0.242 0.279 0.267
f44
0.4
0.3
0.2
0.1
0.0
b)
summer 2012
autumn 2012
winter 2012/2013
spring 2013
summer 2013
0.018 0.014 0.009 0.015 0.014
0.019 0.014 0.010 0.014 0.014
f55
30x10^-3
20
10
0
-10
c)
summer 2012
autumn 2012
winter 2012/2013
spring 2013
summer 2013
0.005 0.006 0.005 0.005 0.004
0.005 0.008 0.004 0.005 0.004
f57
20x10^-3
10
0
-10
d)
summer 2012
autumn 2012
winter 2012/2013
spring 2013
summer 2013
0.0029 0.0027 0.0070 0.0031 0.0032
0.0034 0.0026 0.0053 0.0031 0.0035
f60
20x10^-3
15
10
5
0
-5
e)
summer 2012
autumn 2012
winter 2012/2013
spring 2013
summer 2013

Figure 7. Seasonal variation of fractions of total OA for different mass-to-charge ratios: **(a)** f_{43}, **(b)** f_{44}, **(c)** f_{55}, **(d)** f_{60}. Mean (star) and median (horizontal bar) values are given above each boxplot. The IQR is shown as a box and the 10th to 90th percentile range as whiskers. The contribution of local primary organic aerosols was subtracted from the mass spectra before calculation of the fractions. It is noted, that the increased width of the distribution in winter and autumn is due to smaller signal-to-noise ratio during these seasons.

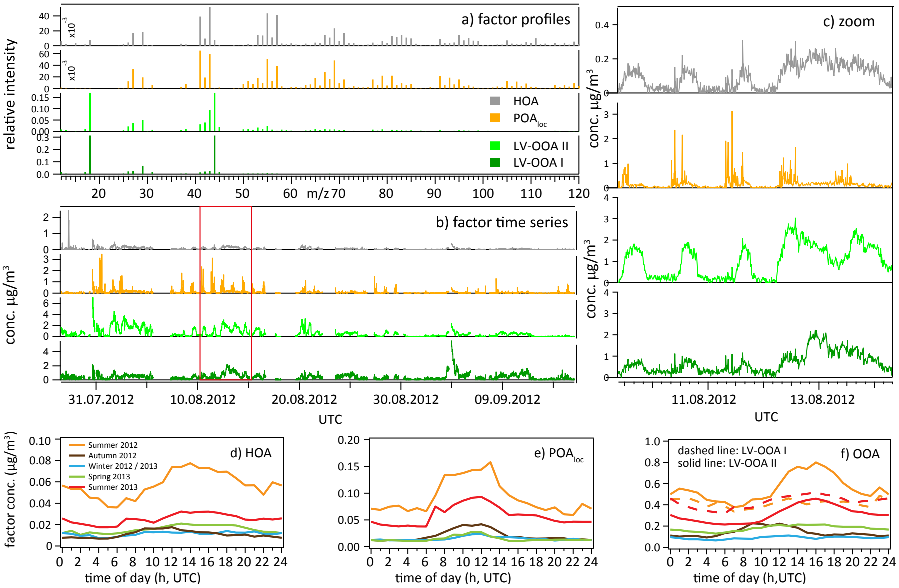

Figure 8. ME-2 example solution for summer 2012 and diurnal plots. **(a)** Factor profiles of HOA (grey), POA$_{loc}$ (orange), LV-OOA I (dark green) and LV-OOA II (light green). **(b)** Factor time series of HOA, POA$_{loc}$, LV-OOA II and LV-OOA I. **(c)** Zoom of the region indicated in red (about five days) in the time series plot. **(d)** HOA diurnal cycles for all seasons. orange: summer 2012, brown: autumn 2012, blue: winter 2012/2013, green: spring 2013, red: summer 2013. **(e)** POA$_{loc}$ diurnal cycles for all seasons. **(f)** OOA diurnal cycles for all seasons, dashed line: LV-OOA I, solid line: LV-OOA II. All times are in UTC.

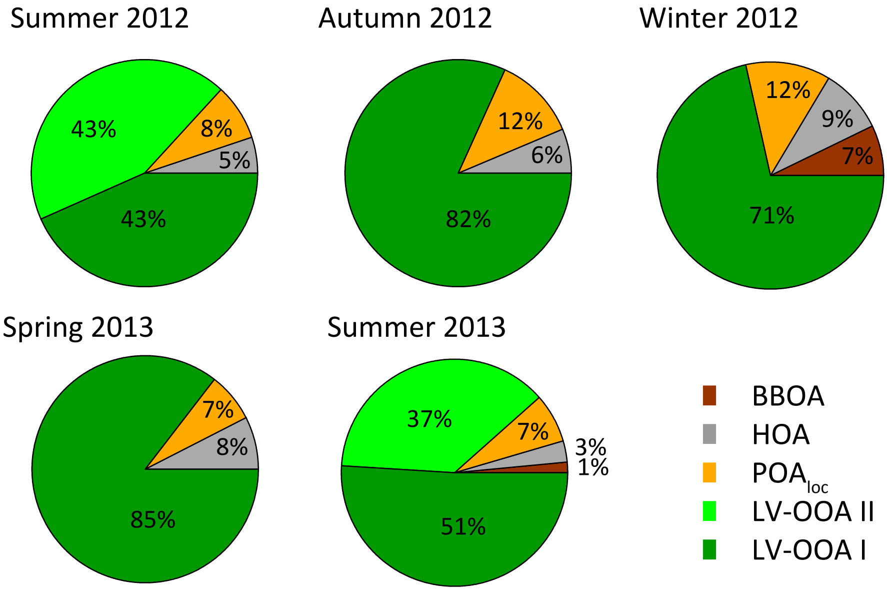

Figure 9. OA source contributions for all seasons. Orange: POA$_{loc}$, grey: HOA, brown: BBOA, dark green: LV-OOA I, light green: LV-OOA II.

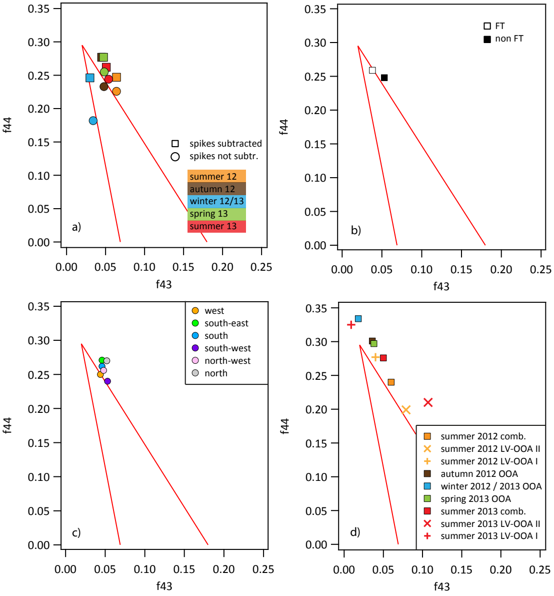

Figure 10. f_{44} vs. f_{43} plots for different boundary conditions. The triangular space in between the red lines is the region in the f_{44}/f_{43} space described by Ng et al. (2010), where atmospheric AMS data typically show up. **(a)** Separation by seasons: summer 2012 (orange), autumn 2012 (brown), winter 2012/2013 (blue), spring 2013 (green), summer 2013 (red). Circles show f_{44} and f_{43} calculated from the full dataset and squares show f_{44} and f_{43} after subtraction of local OA (POA$_{\mathrm{loc}}$, see Sect. 3.2.1. **(b)** Separation by air masses (using NO$_y$/CO, see Sect. 2.5): free tropospheric air masses (white square), boundary layer influenced air masses (black square). **(c)** Separation by air mass origin (using the clusters described in Sect. 2.4 and shown in Fig. 5): west (orange), south-east (light green), south (blue), south-west (violet), north-west(pink), north (grey). **(d)** Location of OOA factors from Sect. 3.2.1 in f_{44} vs. f_{43} triangle. In summer two OOAs were found, both and the combination are shown in the plot.

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Date: 7 September 2015

Supplement

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Table S1. Applied a value ranges with reasoning.

season	a range HOA	reason for a range	a range BBOA	reason for a range
summer 2012	0.1–0.7	$a < 0.1$: no good separation OOAs $a > 0.7$: mixing HOA & OOA	–	
autumn 2012	0.0–0.4	$a > 0.4$: mixing HOA & OOA	–	
winter 2012 / 2013	0.0–0.5	$a > 0.5$: mixing HOA & BBOA	0.0–0.1	$a > 0.1$: decrease of m/z 60 & mixing OOA & BBOA
spring 2013	0.3–0.5	$a < 0.3$: large background in $\mathrm{POA_{loc}}$ $a > 0.5$: mixing HOA & OOA	–	
summer 2013	0.0–0.4	$a < 0.3$: worse separation OOAs	0.0–0.4	$a > 0.4$: mixing HOA & BBOA

Table S2. Variability (1-σ) ~~Ratios~~ of ~~HOA to EBC for all seasons~~the ME-2 results.

season	BBOA	HOA	$\mathrm{POA_{loc}}$	OOA (I/II)
summer 2012	–	2.6 %	1.2 %	8.1 % / 8.1 %
autumn 2012	–	6.5 %	2.3 %	0.3 %
winter 2012 / 2013	4.9 %	6.0 %	2.5 %	0.8 %
spring 2013	–	11.1 %	5.9 %	1.1 %
summer 2013	8.9 %	2.4 %	1.1 %	1.5 % / 2.1 %

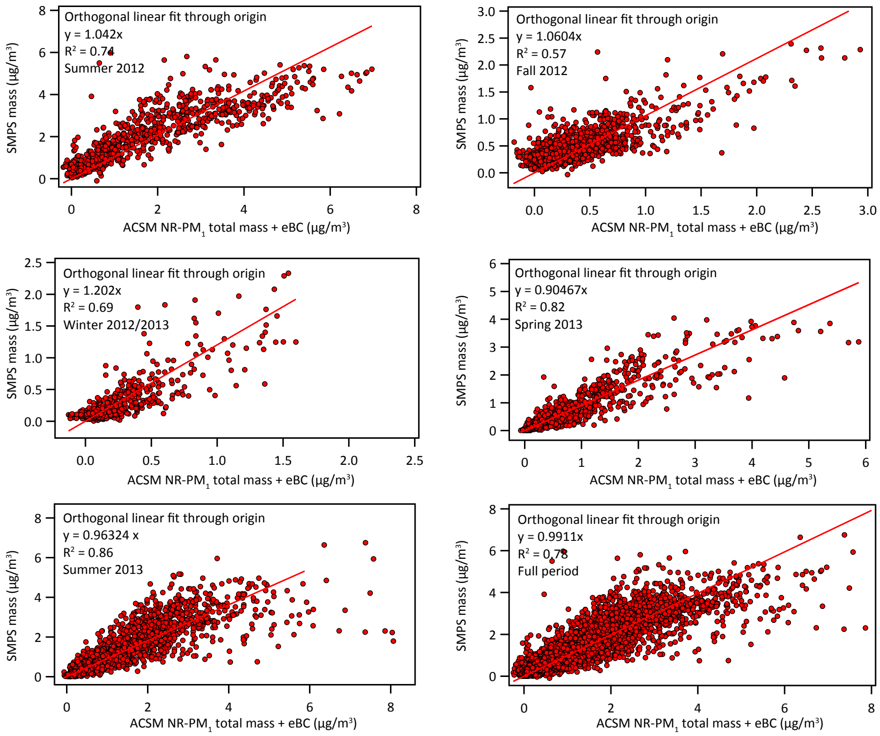

Fig. S1. Correlation plots of mass estimated from the SMPS measurements versus mass measured by the ToF-ACSM plus equivalent black carbon in µg/m^3 for all seasons. The bottom right panel shows the correlation for the full period. Slopes close to 1 all over the year lead to a constant collection efficiency of 1.

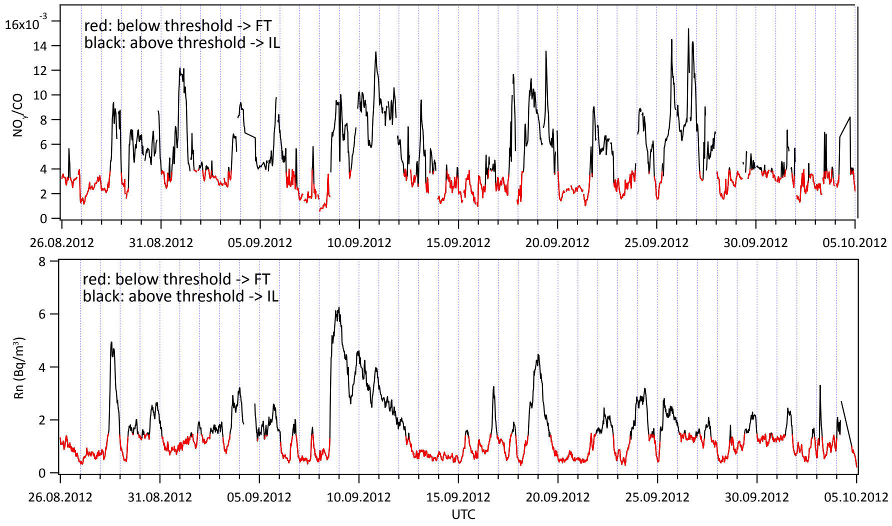

Fig. S2. NO$_y$/CO (upper panel) and ^{222}Rn concentrations during the same >1-month example period. Applied thresholds are indicated in red. Concentrations above the threshold are considered influenced by PBL air masses. A comparison shows largely the same result for both criteria with ^{222}Rn showing slightly more PBL influence.

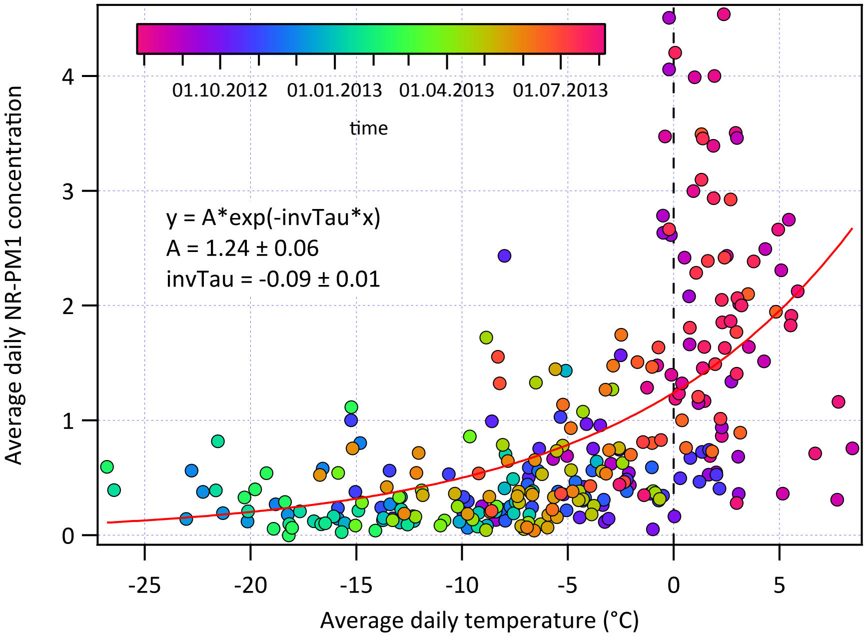

Fig. S3. Daily average PM_1 in µg/m^3 plotted against daily average temperature T in °C. Data is coloured by date. A strong exponential increase at above zero temperatures is observed. It is noted that obviously the exponential function must level off when full vertical mixing with PBL air is reached.

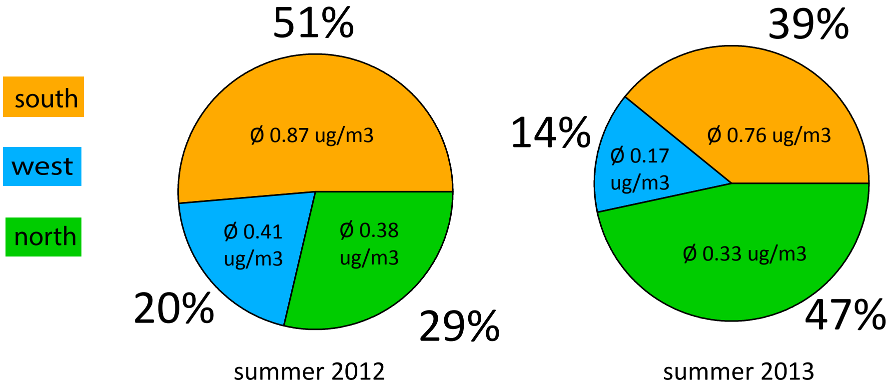

Fig. S4. Frequency of air mass origin during summer 2012 (left) and 2013 (right) including average mass concentrations. Air mass origin was calculated according to the description in Sect. 2.5. North includes clusters # 6 & # 7, south includes clusters # 3, # 4 & # 5 and west includes cluster # 2 as shown in Fig. 5.

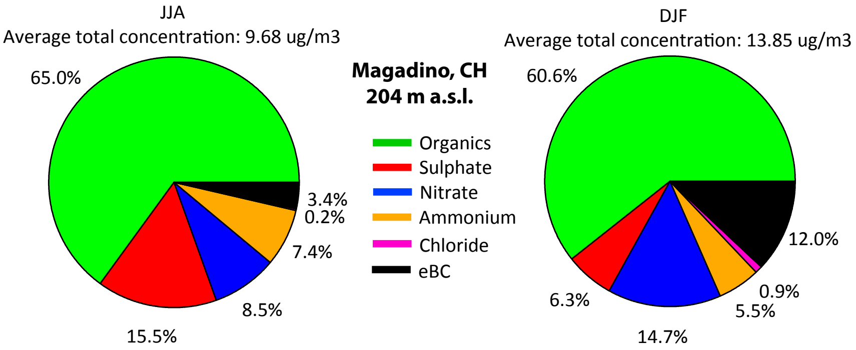

Fig. S5. Relative mass contributions measured with a Q-ACSM (NR-PM_1) and an aethalometer (~~EBC~~eBC) in the Swiss Magadino plain. Left: summer 2014 (June, July & August), right: winter 2013 / 2014 (December, January & February).

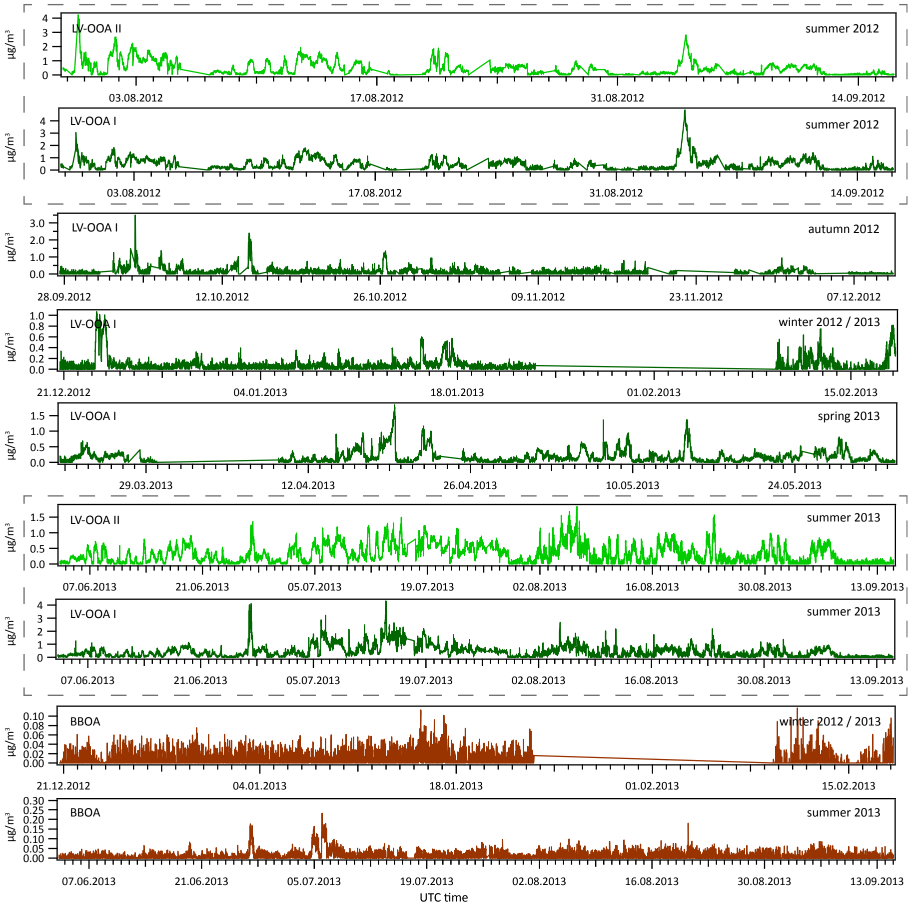

Fig. S6. Time series of ME-2 factors OOA I (dark green), OOA II (light green) and BBOA (brown) for all seasons investigated. BBOA was only identified in winter 2012/2013 and summer 2013.

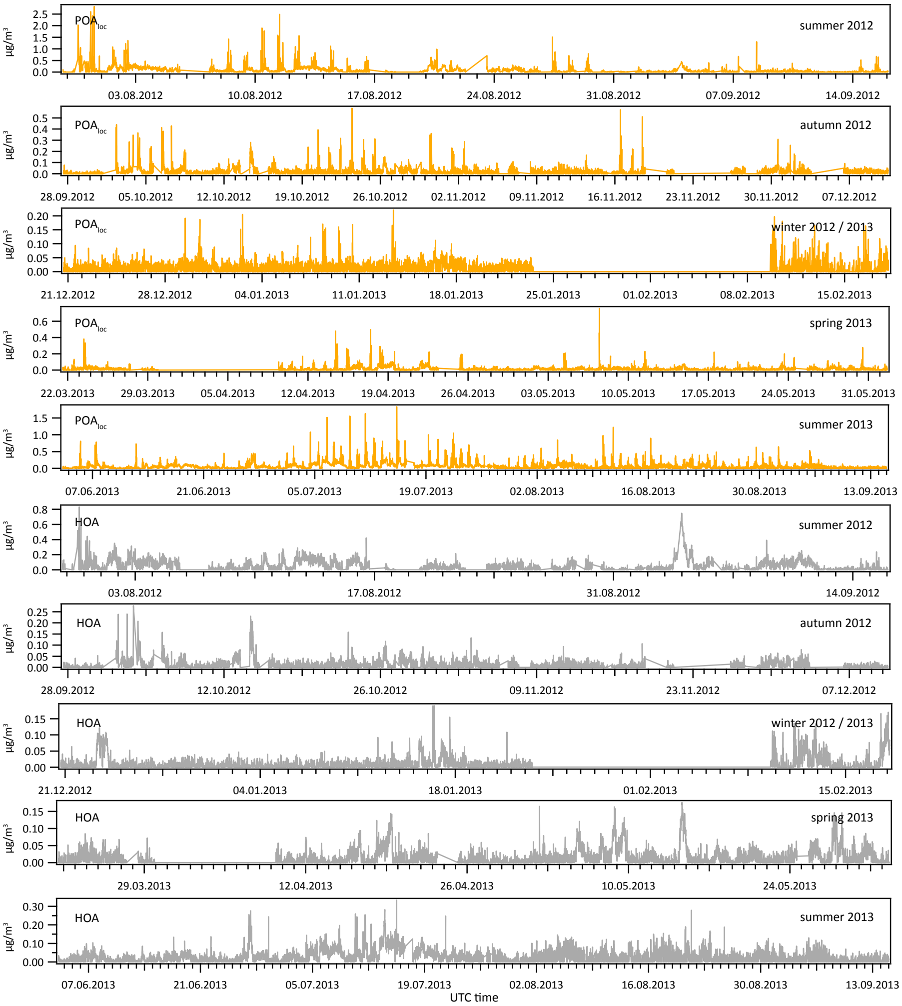

Fig. S7. Time series of ME-2 factors POA$_{loc}$ (orange) and HOA (grey) for all seasons investigated.

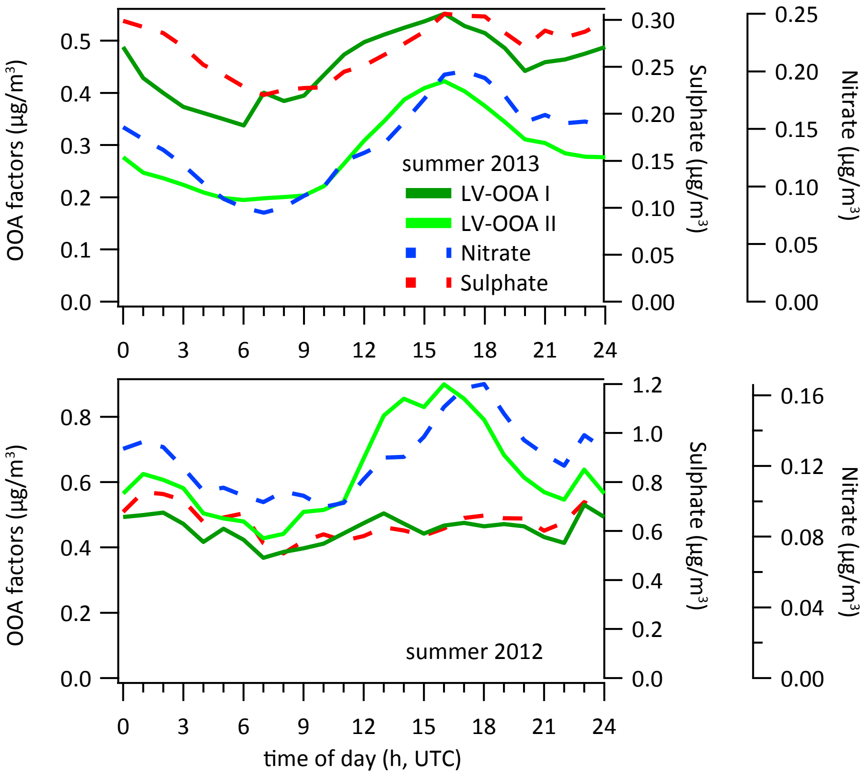

Fig. S8. Diurnal trends of OOA I (dark green), OOA II (light green), SO_4 (red) and NO_3 for summer 2013 (top panel) and summer 2012 (bottom panel).

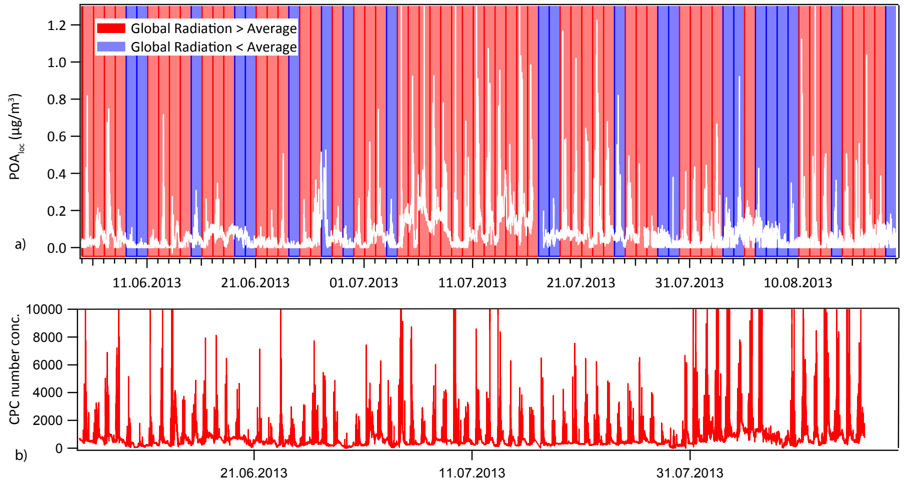

Fig. S9. (a) POA_{loc} (white trace) in summer 2013 with background shaded by average global radiation. Blue (red) means global radiation was below (above) average during that day. (b) CPC number concentrations for the same period.

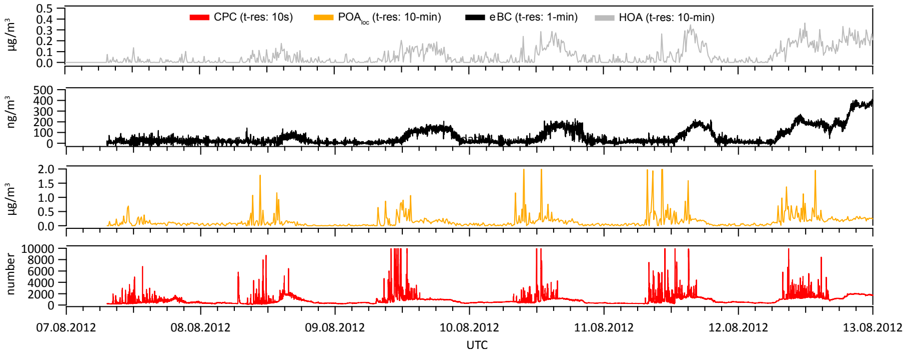

Fig. S10. One-week time series of HOA (grey, time resolution: 10-min), ~~EBC~~ eBC (black, time resolution: 1-min), POA$_{\mathrm{loc}}$ (orange, time resolution: 10-min) and CPC number concentration (red, time resolution: 10-s) in August 2012.

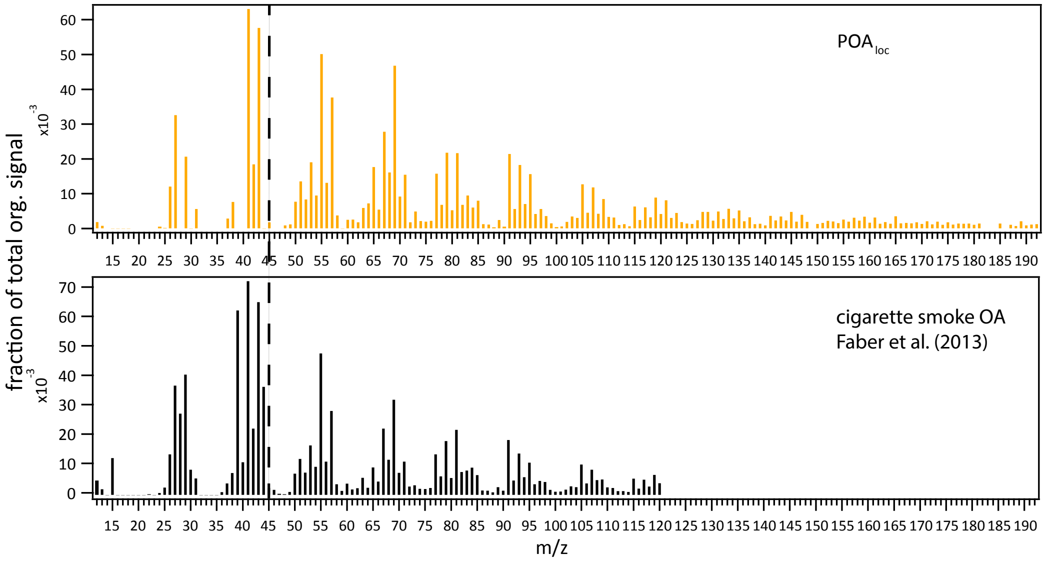

Fig. S11. Top: Mass spectral profile of POA$_{\mathrm{loc}}$, extracted by unconstrained PMF from only short-term peak data. Bottom: Mass spectral profile of cigarette smoke measured with an HR-ToF-AMS under laboratory conditions (adapted and recalculated to UMR from Faber et al., 2013). The ~~CSOA~~ cigarette smoke OA is only shown up to m/z 120. Correlations given in the text are calculated for $m/z > 44$ (dashed line).

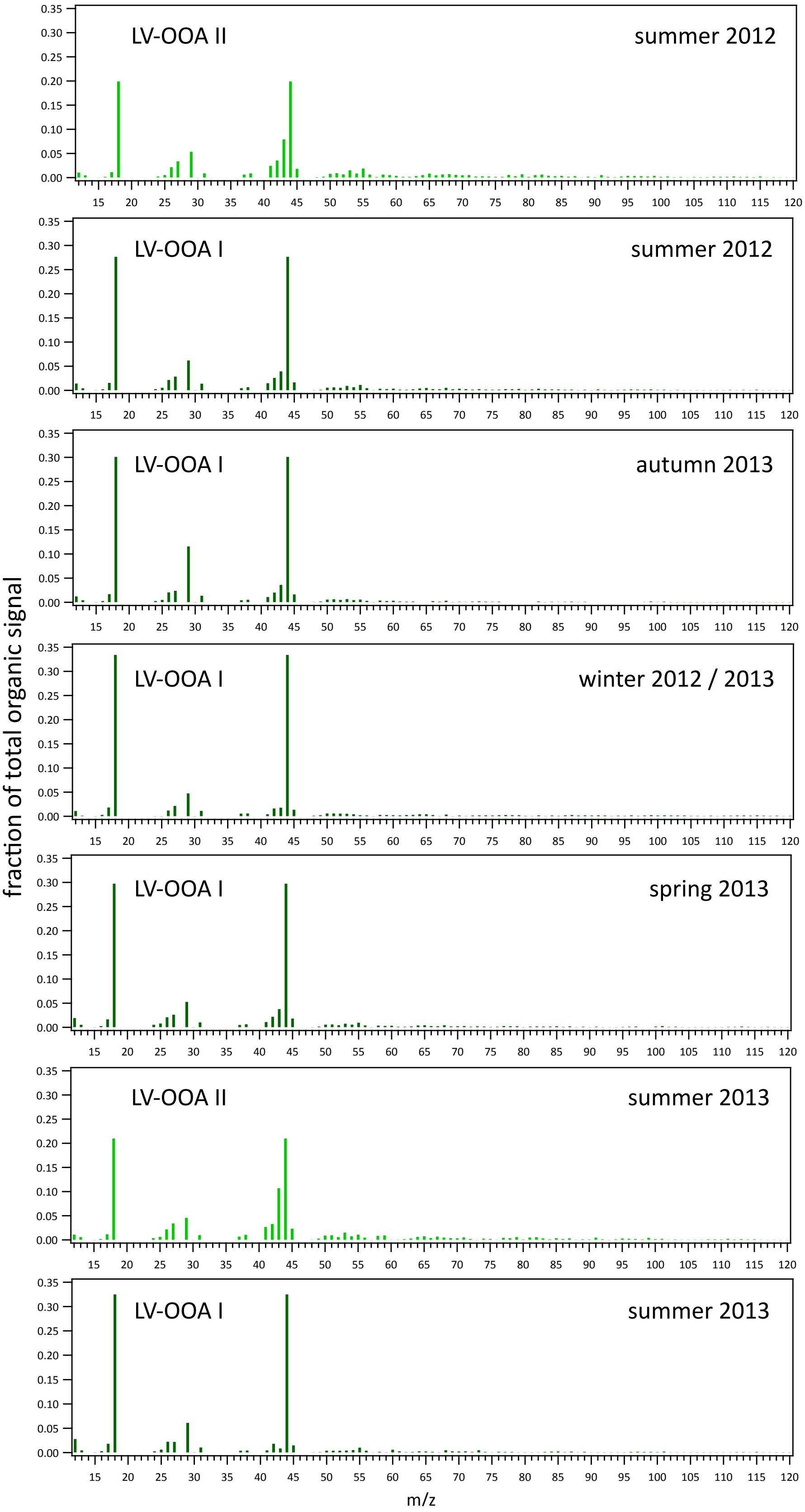

Fig. S12. Mass spectral profile of OOAs for all seasons extracted by ME-2. In both summers OOAs could be split into OOA I (dark green) and OOA II (light green).

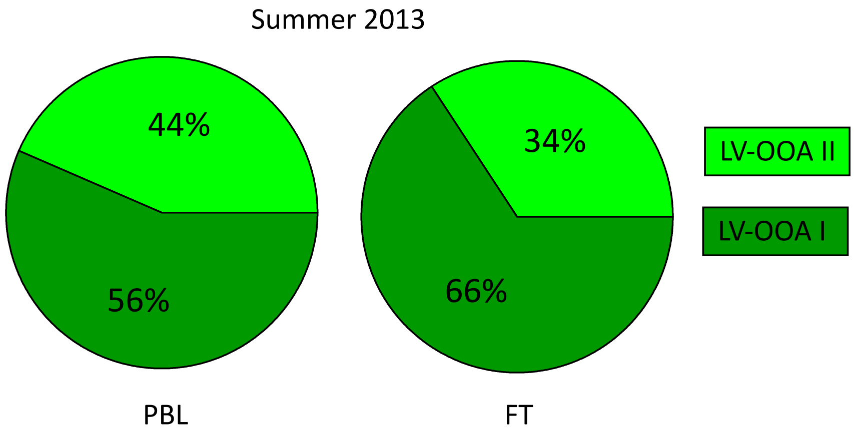

Fig. S13. Relative contributions of LV-OOA I (dark green) and LV-OOA II (light green) in summer 2013 in the FT and with PBL injection.

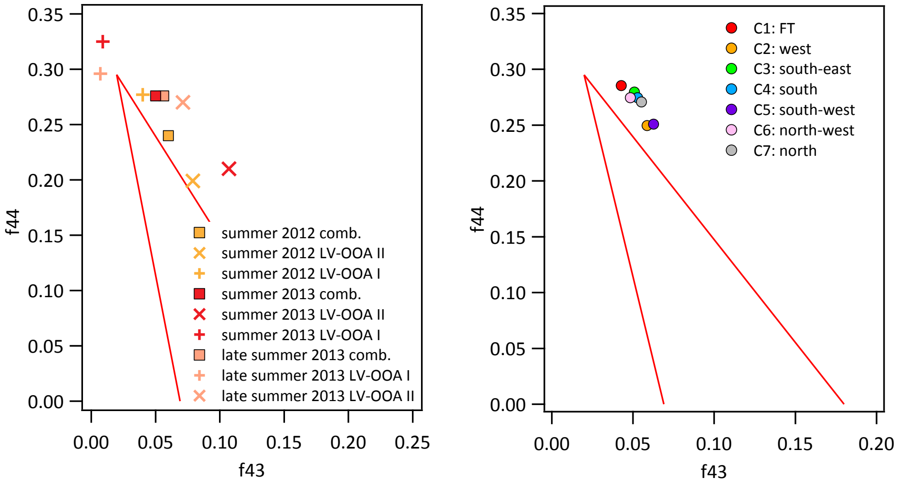

Fig. S14. Triangle plots. Left: Similar to Fig. 9d including data points from a separate ME-2 analysis of only the late summer 2013 overlapping with the summer 2012 period. Right: Triangle plot separated by air mass origin after the subtraction of all POA sources identified in the ME-2 source apportionment. The clusters are the same as in Fig. 5.

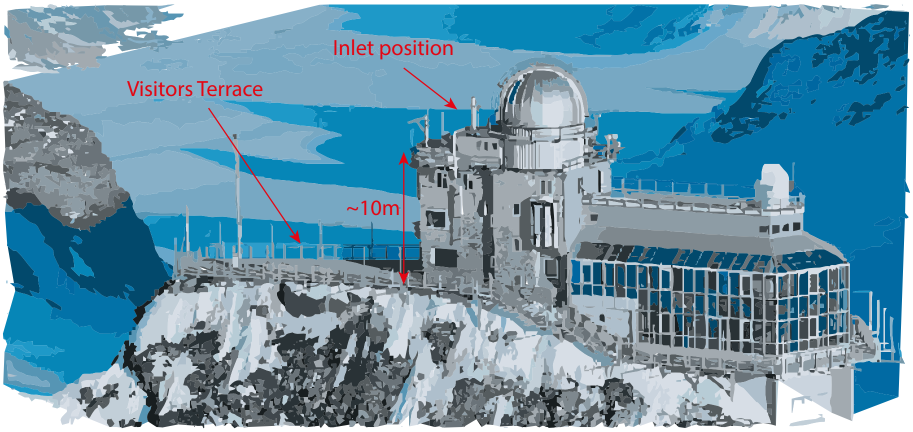

Fig. S15. Sketch of the Sphinx research station at the JFJ showing inlet location and visitors terrace (original image: courtesy of jungfraubahn.ch).

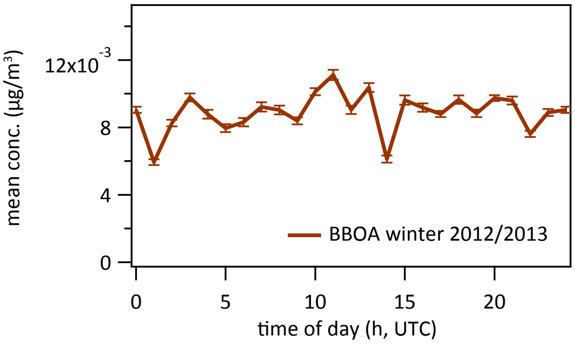

Fig. S16. Mean diurnal variation of the BBOA factor retrieved for winter 2012 / 2013. The error bars show the variation of the different a values applied.

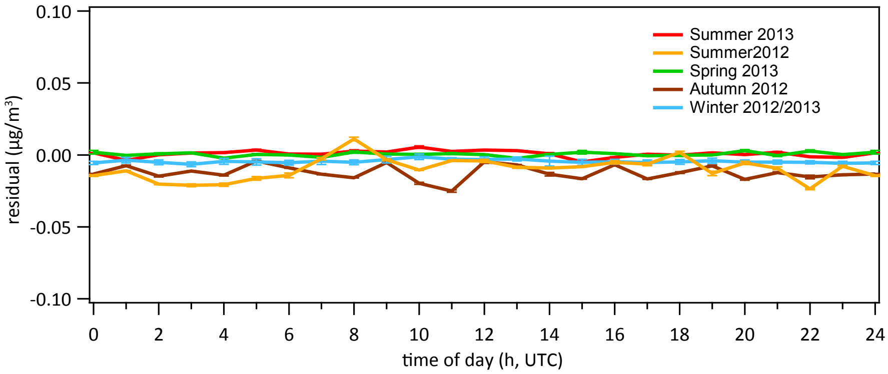

Fig. S17. Diurnal variation of the sum of the absolute residuals from the PMF analysis for each season. Residuals are close to zero and show no remaining significant variations.

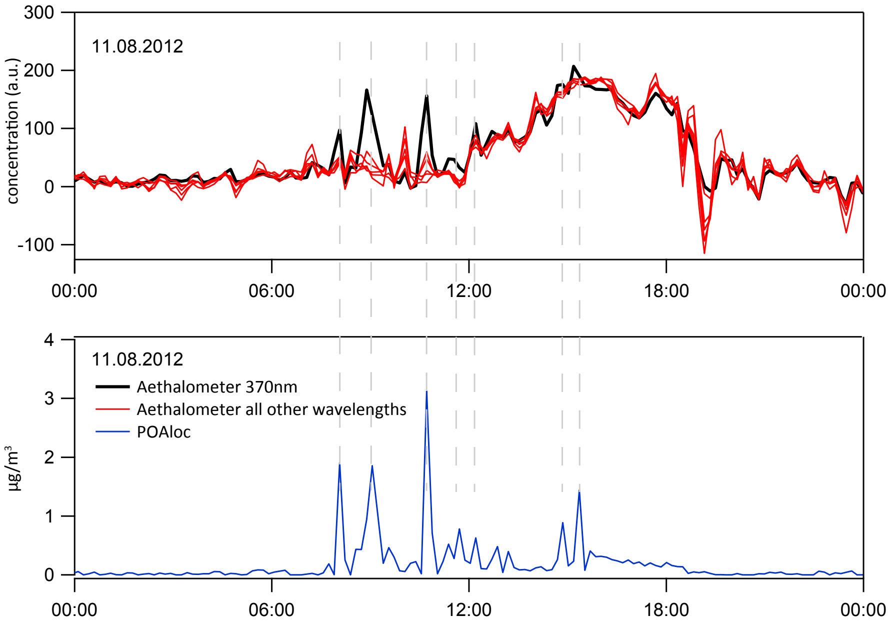

Fig. S18. Top: Aethalometer example timeseries Aug 11, 2012, black: 370 nm signal, red: signal of all other wavelengths. Bottom: POA_{loc} timeseries during the same day. Dashed grey lines are added manually to guide the eye. Cigarette smoke is known to have increased optical absorption at the near-ultraviolet wavelength of 370 nm.

References

Faber, P., Drewnick, F., Veres, P. R., Williams, J., and Borrmann, S.: Anthropogenic sources of aerosol particles in a football stadium: Real-time characterization of emissions from cigarette smoking, cooking, hand flares, and color smoke bombs by high-resolution aerosol mass spectrometry, Atmos. Environ., 77, 1043 – 1051, 2013.