FOSSIL AND NON-FOSSIL SOURCE CONTRIBUTIONS TO ATMOSPHERIC CARBONACEOUS AEROSOLS DURING EXTREME SPRING GRASSLAND FIRES IN EASTERN EUROPE by *V. Ulevicius et al. 2015.*

We thank both Referees for their helpful comments that improve the quality of the manuscript. Below are the answers to each specific point. Our replies (in blue) to specific comments and text corrections in MS (*italic*) are given below.

Anonymous Referee #1

General comments:

Authors present an investigation of impact of biomass burning on the composition of atmospheric carbonaceous aerosol in Lithuania. The ACSM measurement was coupled with PMF model for source apportionment. Satellite observations proved the obtained results. Radiocarbon measurement of OC and EC combined with the ACSM-PMF, the aethalometer measurement of BC and the measurement of organic marker as well as OC/EC were used to deduce the relative contribution of fossil and non-fossil primary and secondary OC and EC to total OC and EC. The measurements are interesting and of high quality. The paper will provide more insights into the pollution sources due to biomass burning in Lithuania. However, there are a few issues that need to be addressed before acceptance the paper for publication in journal Atmospheric Chemistry and Physics. Major revisions of the paper taking into consideration the comments reported below are requested.

Major comments:

p. 5, lines 9 –18:

The ASCM collection efficiency (CE) depends on a few variables that change from day to day. Therefore, the calculation of average CE and its use for the measurement over the whole campaign does not seem to be correct. It is necessary to state estimation of the uncertainty in the measurement of concentration by ACSM associated with use of average CE value.

Response: We have calculated the CE value for each measurement according to Middlebrook (2012). Then, the daily mean values were determined. For the measurement campaign (March 2014) we calculated the mean CE value of all daily mean values. It was found to be 0.52 with standard deviation of 0.08. The CE changes were small and therefore we use the mean value to not introduce additional noise. The main reasons for that CE value (higher than 0.5) were the low nitrate fraction (15% on average) and the fact that a high acidity of aerosols is not observed at Preila (EMEP).

Additional information was added in the manuscript: “*Middlebrook et al., (2012) had proposed a collection efficiency calculation method. The collection efficiency for each measurement and daily mean CE values were calculated. The CE variation was small during the entire measurement campaign (March 2014), so the determined mean CE value was 0.52 with a standard deviation of 0.08, which is very close to other works (Aiken et al. 2009; Timonen et al. 2010). This is not surprising because the sampled aerosol was dried to RH< 50%, moreover, the nitrate fraction was quite low (15% on average) and a high acidity of aerosols was not expected at Preila station (EMEP). Thus, we used the CE=0.52 in our investigation*”.

Reference: EMEP database: http://ebas.nilu.no/Pages/DataSetList.aspx?key=0A2E0E57813745568A5CD19604D6471C

p. 9, lines 3 -11:

Description of POC_{nf} estimation is very strict, addition of more details is necessary.

Response: Description has been modified as suggested: “*^{14}C measurements and ACSM-PMF results were coupled as follows. Daily OC_{nf} measurements from radiocarbon analysis as well as average daily POA from ACSM-PMF results provided two upper boundaries for the daily POC_{nf} contribution. In this manner we identified a possible daily range of POC_{nf} contributions. In order to determine more precisely the POC_{nf} daily contributions within the aforementioned possible daily ranges, we performed a sensitivity analysis. Briefly, in the sensitivity analysis we considered a uniform distribution of possible POC_{nf} contributions within the identified possible daily ranges, meaning that each POC_{nf} value in the selected ranges was considered as equally probable (however, as discussed in the next section, in order to explore the influence of this assumption we also performed the same sensitivity analysis assuming a non-uniform distribution). Assuming no POC_{nf} contribution from other sources than BBOC, each POC_{nf} contribution in the acceptable daily ranges could be written either as $[BBOC] = [levoglucosan]/\alpha$ or as $[BBOC] = [EC_{nf}]/\beta$, where α represents the levoglucosan/BBOC ratio and β represents the EC_{nf}/BBOC ratio. In two separated sensitivity analyses we scanned broad α and β ranges covering the possible POC_{nf} daily ranges and we retained only POC_{nf}, $[levoglucosan]/\alpha$, and $[EC_{nf}]/\beta$ combinations associated to selected acceptance criteria described in the following. From the acceptable solutions we then derived the daily probability distribution function of POC_{f}, SOC_{nf}, SOC_{f}, POC_{f}, α, and β*”.

p. 13, lines 13 - 14:

Text concerning the composition of NR-PM1 is not sufficiently supported by data to be able to compare the composition of aerosols before and during the grass burning event.

Response: We have considered modifying the following text: *During the campaign on average organic aerosol (46 %, 3.2 $\mu g\ m^{-3}$ (σ = 4.8 $\mu g\ m^{-3}$)) constituted the major fraction of the NR-PM1 aerosol concentration composition measured by ACSM with lower contributions of sulfate (17 %, 1.2 $\mu g\ m^{-3}$ (σ = 1.1 $\mu g\ m^{-3}$)), nitrate (20 %, 1.4 $\mu g\ m^{-3}$ (σ = 1.8 $\mu g\ m^{-3}$)), ammonium (15 %, 1.0 $\mu g\ m^{-3}$ (σ = 0.9 $\mu g\ m^{-3}$)), and chloride (2 %, 0.1 $\mu g\ m^{-3}$ (σ = 0.3 $\mu g\ m^{-3}$)). The average composition of $NR\text{-}PM_1$ showed similar dominance of organics to previous observations in Europe (e.g. Crippa et al., 2014). OA contribution to $NR\text{-}PM_1$ was found to be much higher during the grass burning period (61 %, 8.6 $\mu g\ m^{-3}$ ((σ = 5.0 $\mu g\ m^{-3}$)), followed by sulfate (5 %, 1.4 $\mu g\ m^{-3}$ (σ = 0.5 $\mu g\ m^{-3}$)), nitrate (19 %, 3.0 $\mu g\ m^{-3}$ (σ = 1.4 $\mu g\ m^{-3}$)), ammonium (13 %, 1.6 $\mu g\ m^{-3}$ (σ = 0.7 $\mu g\ m^{-3}$)), and chloride (3 %, 0.4 $\mu g\ m^{-3}$ (σ = 0.3 $\mu g\ m^{-3}$)) (Fig. 5A).*

p. 13, line 30 - p. 14, line 1:

Mannosan and galactosan have mostly the identical emission sources, therefore, relatively big difference in the correlation of levoglucosan with mannosan and levoglucosan with galactosan needs detailed interpretation.

Response: In deed, mannosan, galactosan and levoglucosan have similar emission sources. However, this does not imply that their emission ratios must be same for all sources. The reason for different mannosan and galactosan values could indicate that the impact of different burning material is significant. The grass/field burning resulted in uncontrolled wildfires over forested/bush/grass areas. As reported by Sullivan et al., (2008) such components as pine duff, fern, southern pine and ponderosa pine produce a higher amount of mannosan than galactosan (11.97/4.49; 9.17/1.46; 6.42/1.34 and 40.15/14.98), while grasses, leaves and marsh grasses emit mannosan/galactosan of 0.85, 0.3 and 0.06, respectively (Sullivan, 2014). Thus, it is difficult to interpret differences in correlations. We observe good correlations excluding the extreme values indicating different burning conditions or sources. We rephrased the paragraph as follows: *"Concentrations of mannosan varied from 3.1 to 68.0 ng* m^{-3} *and those of galactosan from 1.0 to 12.0 ng* m^{-3}*. The levoglucosan to mannosan (L/M), levoglucosan to galactosan (L/G) and levoglucosan to OC (L/OC) ratios were used before to separate different BB sources (Fabbri et al., 2009; Oanh et al., 2011; Harrison et al., 2012). We measured average L/M and L/G ratios of 16.4 and 135.8, respectively. This is similar to the values found by Orasche et al. (2012) from wood combustion in residential wood appliances and in the range of L/M ratios reported (2.0–33.3) for grass fires by Oros et al. (2006). Excluding the strong event days of March 9 and 10 the sugars showed a good correlation with each other (*$R^2 > 0.86$*). On March 9 and 10 the mannosan/galactosan was lower at 2-6, indicating different source contribution to the other days. Low mannosan/galactosan ratios were observed for grass and leaves (Sullivan, May et al. 2014)".*

p. 14, line 8:

Average value of ratio L/OC was 0.08. In such case, the average value over the whole study cannot comply with the value of 0.08 valid for grass burning (see Sullivan et al, 2008). What is the range of this ratio during the studied period? Add values of this ratio for period during grass burning and periods before and after the grass burning event.

Response: We agree with the reviewer's comment that values of the non-event days could be useful. The text was extended by additional ratios during the days without biomass burning events as: *"We observed an L to OC ratio from 0.06 to 0.16 during the biomass burning period and of ~ 0.03 during the days without biomass burning events. The values observed during biomass burning are in the range of those (0.04–0.20) reported for wildland fuels (Sullivan et al. 2008).*

p. 15, line 4:

Compare value 0.67 of EC_{bb} to total EC ratio for biomass burning event with those during days before and after the BB event. Discuss the value of the ratio with the value for grass burning reported in literature.

Response: This paper reports filter-based measurements focusing on extraordinary peaks of OC during a biomass burning event. For that reason five selected filter samples were further analysed to obtain the radiocarbon content of OC and EC. We agree with the reviewer's comment that EC_{bb} to total EC ratio calculation of the contribution of biomass burning during event and non-event days could be useful. We provided background values reported over Scandinavia: *"For* EC_{bb} *the mean relative contribution to total carbon in background areas of Northern countries was found to be <1.5 % on non-event days (Yttry et al., 2011). It was also reported that a major peak in* EC_{bb} *values between March and April was observed at the Zeppelin atmospheric observatory (Yttri et al. 2014)".*

p. 16, lines 2-4:

The value of ratio levoglucosan/BBOC during the whole campaign is not clear. The value of levoglucosan/BBOC ratio of 0.15 was constant during the rest of campaign as well as during the grass burning event?

Response: Sentence was reworded as: *"Note that on 5 March a different Levoglucosan/BBOC ratio was found (0.31) compared to the non-event days (~0.15)."*

p. 34, legend of Figure 5:

Picene and hopanes are mentioned as tracer species, however, the concentration of these compounds was not previously discussed in the text of paper.

Response: We believe that plotting major molecular markers in Figure 5 will help the readers see the BB impact easier. Moreover, we provided new ambient samples in the supplementary materials: *"The high fraction of biomass burning was corroborated by measurements of levoglucosan. Other molecular markers such as hopanes for traffic emissions and picene for coal combustion (Rutter et al., 2009) were also measured in order to monitor the possible contribution of fossil fuel combustion during the high pollution event. Although their concentrations increased during the episode, suggesting a contribution of co-transported fossil fuel combustion aerosols, the radiocarbon analysis revealed the contribution of this fraction to be minor (*EC_f *ranged from 0.3 to 1.1;* OC_f *ranged from 0.5 to 1.6 (Fig. 5). Values of molecular markers are provided in Table 1 of the Supplementary material".*

Minor comment:

p. 4, line 11: Add type and producer of used HV sampler.

Response: To clarify, the sentence was changed: *"A high-volume sampler (Digital model Aerosol Sampler DHA-80, 500 l* min^{-1}*) was used to collect* PM_1 *aerosol particles onto 150 mm diameter Pallflex quartz fibre filters (pre-baked for 24 h at 550 °C) over a 24-hour sampling period".*

Anonymous Referee #3

The paper of Ulevicius et al. describes the event of grassland fires observed in Preila, Lithuania. They investigated the evolution and chemical composition of particles during the fires and the impact of biomass/grass burning. Authors measured the chemical composition of PM1 by aerosol chemical speciation monitor (ACSM) and the source apportionment for OA was performed by utilizing positive matrix factorization (PMF). Carbonaceous species were separated into fossil and non-fossil primary and secondary components by combining ACSM PMF-results with radiocarbon measurements. Additionally, satellite data was used to indicate the burning areas and biomass burning tracers, i.e. levoglucosan, was determined from filter samples. The results of this paper showed that the dominant factor in PM1 was non-fossil organic carbon consisting of primary and secondary fractions. Primary and secondary fossil organic carbon had smaller portions in PM1. Regarding elemental carbon, non-fossil fraction was higher than fossil fraction. This paper is relevant and interesting as it combines different methods to investigate the impact of biomass burning emissions by using aerosol mass spectrometry, statistical analysis and radiocarbon determination. This paper addresses relevant scientific questions, however, it presents relatively narrow portion of the data provided by the instruments available. Therefore the main issue of this paper is the lack of results, and relevant discussion, related to the general characteristics of biomass burning particles. Overall, this paper is well written and the structure of the paper is clear and easy to follow. I think this paper merits publication after major revision.

General comments:

As mentioned above, the largest deficiency of this paper is the lack of results. Methods used in the paper are described in detail (more than ten pages), however, relative to that the results of the paper are presented in less than five pages. I suggest to extend the result section with more careful investigation of present results and by adding some new findings. For example size distribution data could be discussed as well as 7-wavelenght aethalometer data to investigate biomass burning BC. Also a more careful comparison between grassland fire events and other periods is needed for particle chemical composition and the concentrations of various chemical species.

The methods used however are rather complex and some of the analysis methods are novel and are worth being explained in some detail. We think the methods section as such is very interesting for people that want to do similar in-depth analyses in the future. For people that are more only interested in the results can thus skip all the methods and read only the rather crisp result part. We are sure that some people will mostly look at the paper because of the methods section. We added some discussions regarding differences in the aerosol chemical composition between events and non-events days (e.g. markers' ratios) as well aerosol size distribution and number concentration.

Specific comments:

1. Methods: page 26320; Add a collection time for the high volume filters.

Response: Text has been changed to: "*A high-volume sampler (Digital model Aerosol Sampler DHA-80, 500 l min-1) was used to collect PM$_1$ aerosol particles onto 150 mm diameter Pallflex quartz fibre filters (pre-baked for 24 h at 550 °C) over a 24-hour sampling period*".

2. Methods: page 26320: Methods: Page 26321, line 7; change "collection coefficient" to "collection efficiency" for consistency.

Response: Done as suggested.

3. Methods: Page 26321: How did you calculate the transport efficiency of the sampling line?

Response: The transport efficiency of the sampling line depends on the aerosol flowrate, geometry of the sampling line and particle size range. The used aerosol flowrate through the sampling line was 1.6 lpm. The sampling line consisted of a vertical 2.5 m long stainless steel tube with an inner diameter of 6 mm and a 30 cm long Nafion tube of i.d. 2.81 mm. So, a laminar flow (with Re=259 in the sampling tube and Re=554 in the Nafion tube) avoided particle losses by turbulence in the sampling line. The ACSM measured particles from ~40 nm to ~1 μm. In this size range, the particles are lost mainly by diffusion and impaction mechanisms. However, the particle impaction mechanism was reduced to zero by using a straight vertical stainless steel tube. We calculated the particle diffusion losses in the size range from 40 nm to 1 μm using the Gormley and Kennedy equation (Baron and Willike, 2001). The 40 nm particles were transported with an efficiency of 96.8 % through the sampling tube and 99.2 % through the Nafion dryer. The total transport efficiency was 96.0 % for particles of 40 nm. The larger particle transport efficiency reached 100 %. Additional information were added in the manuscript: "*Aerosol particle diffusion losses in the sampling line were less than 4.0 % for particles from 40 nm to 1 um according to Gormley and Kennedy (Baron and Willike, 2001) and the relative humidity lower 50 % (by SATO model SK-L200TH).*"

4. Methods: Page 26321: What was the variation for the collection efficiency (0.52)? How did you determined instrument particle counting efficiency (line 10)? Is it transport efficiency*ASCM collection efficiency? Make this transport/collection/counting efficiency section clearer.

Response: In the manuscript, we separated a section of the sampling line transport efficiency and the ACSM collection efficiency (CE). The transport efficiency calculation method was described in the Response Nr3. It was shown that the smallest Aitken mode particles (40 nm) were transported to the ACSM inlet with an efficiency of 96.0%. The transport efficiency of the largest particles

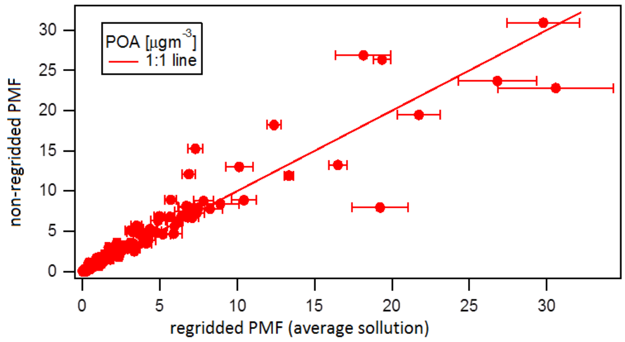
(40-1000 nm – ACSM measured range) reached 100 %. Furthermore, an impact of the smallest particles to the total PM1 mass concentration is very low. Thus, we concluded that the sampling line with Nafion dryer didn't affect the measured particle mass concentration. Then, we operated only with the ACSM collection efficiency (CE).

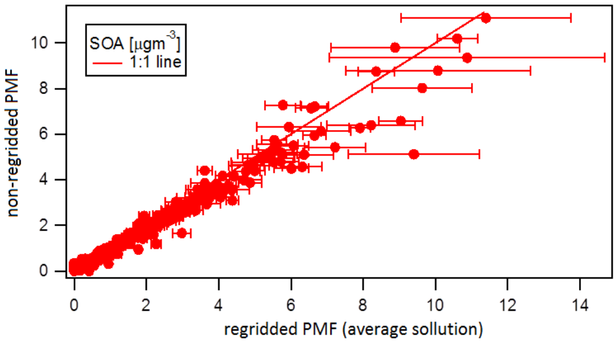
The CE values were calculated for each measurement according to Middlebrook (2012). Then, the daily mean values were determined. For the measurement campaign (March 2014) we calculated the mean CE value of all daily mean values. It was found to be 0.52 with a standard deviation of 0.08. The CE changes were small and therefore we use the mean value to not introduce additional noise. The main reasons for that CE value (higher than 0.5) were the low nitrate fraction (15% on average) and the fact that a high acidity of aerosols is not expected at Preila site (EMEP). Rewording and additional information were added in the manuscript: "*Middlebrook et al., (2012) had proposed a collection efficiency calculation method. The collection efficiency for each measurement and daily mean CE values were calculated. The CE variation was small during the entire measurement campaign (March 2014), so the determined mean CE value was 0.52 with a standard deviation of 0.08, which is very close to other works (Aiken et al. 2009; Timonen et al. 2010). This is not surprising because the sampled aerosol was dried to RH< 50%, moreover, the nitrate fraction was quite low (15% on average) and a high acidity of aerosols was not expected at Preila station (EMEP). Thus, we used the CE=0.52 in our investigation*"

Reference: EMEP database: http://ebas.nilu.no/Pages/DataSetList.aspx?key=0A2E0E57813745568A5CD19604D6471C

5. Methods; PMF analysis: page 26321; Why did you average ACSM data from 28 minutes to 1 hour? Explain if it improves the performance of PMF.

Response: Given the low background concentrations at Preila, regridding the data from 28 minutes to 1 hour enabled increasing the signal to noise of our dataset. In particular, if we consider two time points a and b, and their corresponding uncertainty σa and σb, the propagated error relative to the average of a and b will be $0.5*(\sigma a^2+\sigma b^2)^{0.5}$. If for instance as an approximation σa would be comparable to σ_b such that we can write σa= σb, then the propagated final error would be $\frac{\sqrt{2}}{2}\sigma a$, with a signal/noise improvement by a factor of 2/√2. Moreover regridding the ACSM data enabled a direct comparison with SO_x, NO_x and BC external data. Finally, we compared PMF results with and without time regridding, obtaining comparable results:





6. Methods: 7-wavelenght aethalometer; why did you show results only for BC (880 nm)? There is a method (e.g. Sandradewi et al., 2008) to calculate biomass burning contribution of BC by using other wavelengths. I suggest adding data from other wavelengths as well.

Response: A mean light absorption coefficient $\alpha_{370-950}$ (the absorption exponent calculated using the seven Aethalometer wavelengths) of 1.38 (σ = 0.11) was obtained during wildfires, which is higher than the mean $\alpha_{370-950}$ calculated for the non-event days (1.13, σ = 0.19)). The light absorption exponent values were calculated with λ = 370 – 520 nm and λ = 590 - 950 nm wavelengths for comparison purpose. The mean values of $\alpha_{370-520}$ and $\alpha_{590-950}$ were found to be 1.53 (σ = 0.19) and 1.32 (σ = 0.09) during event day and 1.25 (σ =0.27) and 1.13 (σ =0.18) during non-event days, respectively. In comparison during the same event in 2008 in Preila higher mean values of $\alpha_{370-520}$ and $\alpha_{590-950}$ nm were observed (2.4 ((σ = 0.1) and 1.5 (σ = 0.1, respectively)), as well as during the event in 2009 (2.3 (σ = 0.1) and 1.6 (σ = 0.1), respectively)) (Ulevicius et al., 2010). This is an indication of influence of the biomass burning on the Ångström exponent of the absorption coefficient α. The increase in alpha is consistent with an enhanced influence of biomass smoke. The impact of organic aerosols on the spectral dependence of light absorption was early confirmed by OC/EC ratios.

7. Methods: page 26328: line 19; remove "recently"

Response: Done as suggested.

8. Methods: page 26329: lines 26-29; add reference for SILAM (e.g. Sofiev et al., 2006)

Response: Done as suggested.

9. Results, page 26331: lines 3-8; Explain the change in the chemical composition/concentrations during the burning period. If OA contribution increased, what decreased? How much concentrations increased during the burning events?

Response: The analysis was extended: „*During the campaign on average organic aerosol (46 %, 3.2 μg* m^{-3} *(*σ *= 4.8 μg* m^{-3}*)) constituted the major fraction of the NR-PM1 aerosol concentration composition measured by ACSM with lower contributions of sulfate (17 %, 1.2 μg* m^{-3} *(*σ *= 1.1 μg* m^{-3}*)), nitrate (20 %, 1.4 μg* m^{-3} *(*σ *= 1.8 μg* m^{-3}*)), ammonium (15 %, 1.0 μg* m^{-3} *(*σ *= 0.9 μg* m^{-3}*)), and chloride (2 %, 0.1 μg* m^{-3} *(*σ *= 0.3 μg* m^{-3}*)). The average composition of* $NR\text{-}PM_1$ *showed similar dominance of organics to previous observations in Europe (e.g. Crippa et al., 2014). OA contribution to* $NR\text{-}PM_1$ *was found to be much higher during the grass burning period (61 %, 8.6 μg* m^{-3} *((*σ *= 5.0 μg* m^{-3}*)), followed by sulfate (5 %, 1.4 μg* m^{-3} *(*σ *= 0.5 μg* m^{-3}*)), nitrate (19 %, 3.0 μg* m^{-3} *(*σ *= 1.4 μg* m^{-3}*)), ammonium (13 %, 1.6 μg* m^{-3} *(*σ *= 0.7 μg* m^{-3}*)), and chloride (3 %, 0.4 μg* m^{-3} *(*σ *= 0.3 μg* m^{-3}*)) (Fig. 5A)*".

More analysis was added in this section:

"We observed L to OC ratio during the biomass burning period from 0.06 to 0.16 and during the days without biomass burning events from 0.03 to 0.04. Values observed during biomass burning were consistent with values (0.04–0.20) obtained from leaf and grass burnings reported by Sullivan et al. (2008).

10. Results: page 26334; lines 9-15; regarding the SMPS results, why don't you present (and discuss) some size distributions to show if there was an impact of biomass burning particles on size distributions (number and volume)?

Response: We think this is beyond the scope of this paper, but we added some information in MS: "*During the intensive grass burning episode, consecutive new particle formation (NPF) episodes were observed. Observed NPF could be attributed to the grass burning and secondary biomass burning product transformation as was evaluated in earlier studies over same area (Ulevicius et al., 2010b). At 13:00, there was a significant new particle formation on 9th and 10th March followed by subsequent growth up to three hours. The total particle number concentration with a daily mean value of 6440* cm^{-3} *(with maximum value of 13000* cm^{-3}*), which was extremely much higher than the daily mean observations in non-event days (1660* cm^{-3}*). Non-event day was characterized by bimodal (Aitken (44 nm) and accumulation (128 nm)) modes with a standard deviation of 1.68 and 1.87, respectively. In comparison, during biomass burning event trimodal (nucleation (9.0 nm), Aitken (31.0 nm) and accumulation (102 nm) modes with a standard deviation of 1.77, 1.71 and 1.68, respectively. However volume distribution was characterized by bimodal size distribution for non-event day (330 and 520 nm) and event day (250 and 590 nm). In this area of 2650* cm^{-3} *and comparable only with spring concentration maxima (13000* cm^{-3} *(SD = 980* cm^{-3}*)) (Byčenkienė et al., 2013)".*

11. Figure 3; Why concentrations between 5 and 14 March only? Why didn't you show them for the whole measurement period (one month)? If the filter measurement did not cover the whole period, explain it. Change the y-axes so that the change in OC and EC concentrations can be seen.

Response: This paper reports filter-based measurements focusing on extraordinary peaks of OC during a biomass burning event (5-10 March). Long-term filter based measurements were not available as filter analysis was performed only over the selected periods of the extreme wildfires and four filters (14th, 21th, 23th and 27th of March 2014 were selected as non-event days.We included now also the data of the non-event days in Figure 3.

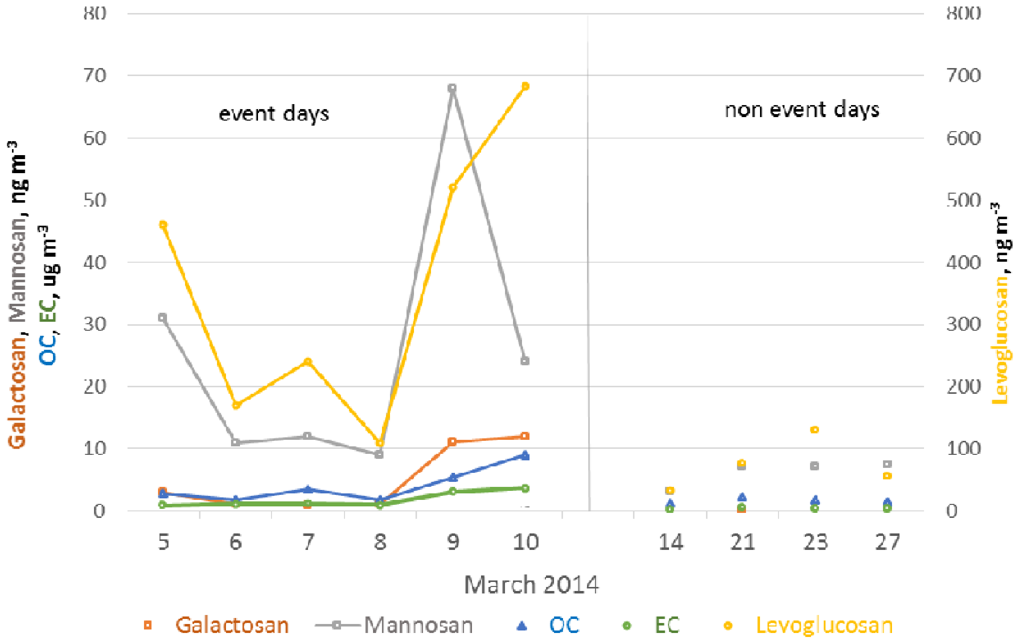


Figure 3. Average daily concentration during event days (from 5 to 10 March 2014) and non-event days (14th, 21th, 23th and 27th March 2014) for levoglucosan, galactosan, mannosan (in ng m^{-3}) and for elemental carbon (EC) and organic carbon (OC) in μg m^{-3}.

12. Figure 5; This figure is very difficult to read. Fonts are too small and there is too much information placed in one figure. Separate legends according to a), b), c) and d) and put them to corresponding figures. SOA and POA are missing from legends. Place e), f) and g) to separate figure.

Response: Done as suggested.

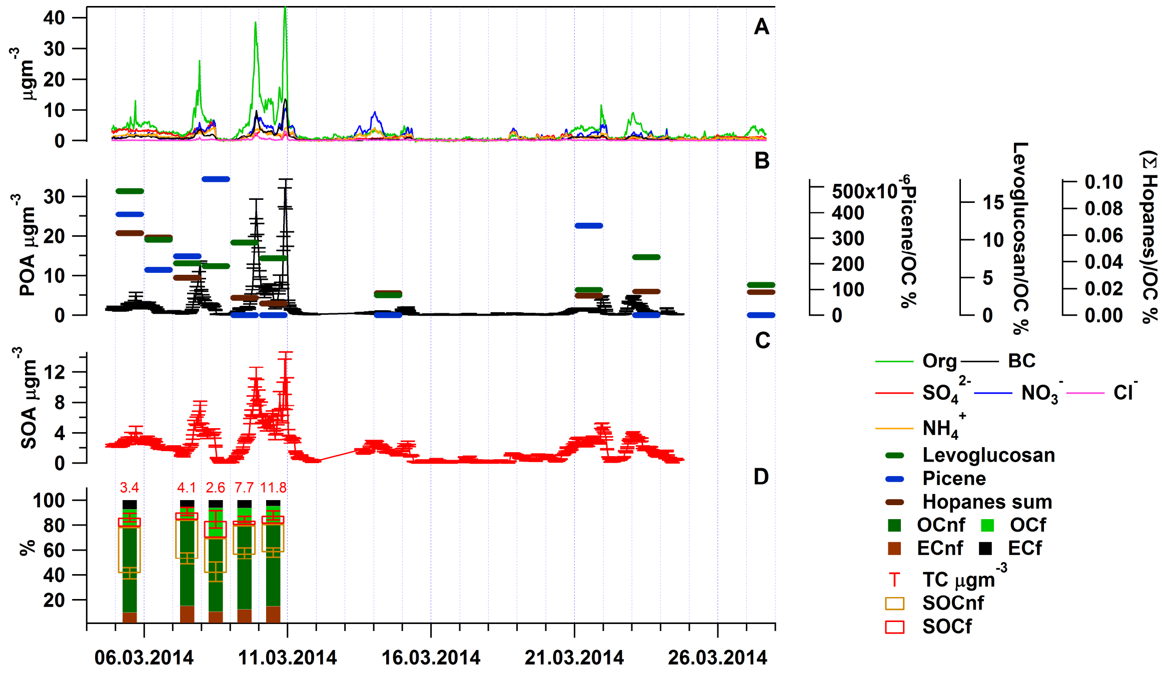


Figure 5. Average chemical composition and time series of NR-PM$_1$ OA for the entire study (A), B) Time series of the POA factor and percent contribution of the corresponding tracer species (levoglucosan, picene and hopanes) to total OA, C) Time series of the SOA factor, D) Relative source apportionment of TC during BB event. Numbers indicate the total carbon absolute concentrations in µg m^{-3}, variations of the mass concentrations of the SOC$_f$ and SOC$_{nf}$ (the whiskers above and below the boxes indicate the 1st and 3rd quartiles.

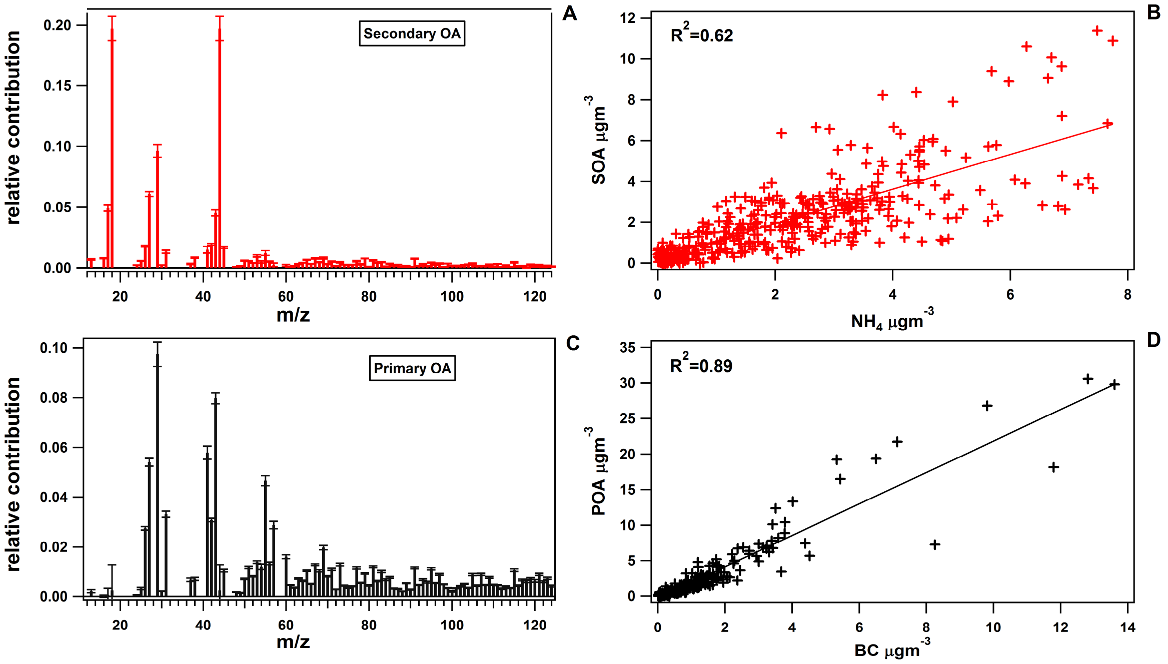


Figure 6. Mass spectra of SOA and POA, error bars represent the standard deviation of 20 PMF runs (A,C) and the scatter plots illustrate the relationship between SOA and NH$_4^+$ (B) and POA with BC (D).

Fossil and non-fossil source contributions to atmospheric carbonaceous aerosols during extreme spring grassland fires in Eastern Europe

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Abstract

In early spring the Baltic region is frequently affected by high pollution events due to biomass burning in that area. Here we present a comprehensive study to investigate the impact of biomass/grass burning (BB) on the evolution and composition of aerosol in Preila, Lithuania, during springtime open fires. Non-refractory submicron particulate matter (NR-PM_1) was measured by an Aerodyne aerosol chemical speciation monitor (ACSM) and a source apportionment with the multilinear engine (ME-2) running the positive matrix factorization (PMF) model was applied to the organic aerosol fraction to investigate the impact of biomass/grass burning. Satellite observations over regions of biomass burning activity supported the results and identification of air mass transport to the area of investigation. Sharp increases in biomass burning tracers, such as levoglucosan up to 683 ng m^{-3} and black carbon (BC) up to 17 µg m^{-3} were observed during this period. A further separation between fossil and non-fossil primary and secondary contributions was obtained by coupling ACSM PMF results and radiocarbon (^{14}C) measurements of the elemental (EC) and organic (OC) carbon fractions. Non-fossil organic carbon (OC_{nf}) was the dominant fraction of PM_1, with the primary (POC_{nf}) and secondary (SOC_{nf}) fractions contributing 26-44% and 13-23% to the TC, respectively. 5–8 % of the TC had a primary fossil origin (POC_f), whereas the contribution of fossil secondary organic carbon (SOC_f) was 4–13 %. Non-fossil EC (EC_{nf}) and fossil EC (EC_f) ranged from 13–24 % and 7–12 %, respectively. Isotope ratio of stable carbon and nitrogen isotopes were used to distinguish aerosol particles associated with solid and liquid fossil fuel burning.

1 Introduction

On global scale wood or grass burning is a major source of organic aerosol (Crutzen et al., 1979; Levine, 1996). Approximately 90 % of vegetation burning is caused by human-induced fires (Baldini et al., 2002) and only a minor fraction derives from natural processes such as lightning. The composition of biomass smoke depends on the type of wood, combustion conditions (flaming versus smoldering), and ambient weather conditions (Weimer et al., 2008, Grieshop et al., 2009, Hawkins and Russell, 2010 and Akagi et al., 2012). Fine particles emitted from biomass burning include directly emitted primary particles (POA) and secondary organic aerosols (SOA), formed in the atmosphere as the plume ages through photochemical processes driven by sunlight (Capes et al., 2008, Heringa et al., 2011).

Many studies have revealed that organic matter (OM) is the largest fraction of ambient fine particles, typically comprising 20–90 % of the submicron particulate mass (Jimenez et al., 2009). Factor analysis of aerosol mass spectra from Aerodyne aerosol mass spectrometer enables the deconvolution of OM into different factors based on their mass spectral fingerprints (Lanz et al., 2007; Aiken et al., 2009; Ulbrich et al., 2009;). Such results provided valuable insights into the source and transformation processes of organic aerosols (OA) in the atmosphere (Lanz et al., 2010; Ng et al., 2011; Hildebrandt et al., 2011; Canonaco et al. 2013; Bougiatioti et al., 2014; Huang et al., 2014).

The main type of biomass burning in Lithuania and surrounding countries in early spring during the last years is illegal grass burning for land clearing (Ulevicius et al., 2010b; Byčenkienė et al. 2013). The north-east European countries are considered to influence significantly the microphysical, chemical and optical properties of the aerosol in the Baltic Sea region (Kikas et al., 2008; Zawadzka et al., 2013; Mann et al., 2014, Beddows et al., 2014). Long-term measurements of carbonaceous aerosols performed in this area by Ulevicius et al. (2010a, 2010b) and Byčenkienė et al. (2011, 2013) reported a yearly occurrence of high biomass burning organic aerosol (BBOA) levels during March–April related to regional transport from the Kaliningrad region, Ukraine and southwestern part of Russia surrounding the Black Sea, but information on the nature and chemical composition of the biomass burning aerosol in Lithuania is still limited. There has been no systematic investigation of the impact of biomass burning on ambient organic aerosol levels in this region, and a quantitative estimate is needed to understand the possible impacts of BBOA on air quality in the south-eastern Baltic Sea region.

In many studies levoglucosan was used to assess the contribution of biomass-burning smoke to the aerosol mass concentrations (Puxbaum et al., 2007). A number of source emission studies reported that levoglucosan is not a useful tracer after long-range transport due to its transformation (Hoffmann et al., 2010, Hennigan et al., 2010; Mochida et al., 2010). In contrast to levoglucosan, determination of radiocarbon (^{14}C) offers a unique possibility for source apportionment of carbonaceous aerosol particles, as it unambiguously distinguishes fossil from non-fossil emissions (e.g. Currie, 2000; Ceburnis et al., 2011).

For this study, in the framework of the Lithuanian-Swiss Cooperation Programme joint research project (AEROLIT), an ACSM was deployed in a background area of the South Baltic Sea to measure airborne submicron particles for one month during a period of frequent grass burning pollution. The main findings include investigation of OA components (Sects.

3.1–3.2), molecular markers (Sect. 3.2), source apportionment of EC and OC using ^{14}C data and positive matrix factorization (PMF) of the ACSM organic mass spectra (Sect. 3.3).

2 Methods

2.1. Site description and filter sampling

Continuous air monitoring and time integrated particulate matter sampling were carried out in March 2014 in Preila, Lithuania (55° 55' N, 21° 04' E 5 m a.s.l.) (Fig. 1). Preila is a representative coastal background site, an ideal location for studying the long-range transport of air pollutants in the South-eastern Baltic region due to the absence of significant local sources (Fig. 1, Table 1). It served as a "super site" for the EUSAAR-EU-funded I3 (Integrated Infrastructures Initiatives) project. During the measurement period, strong biomass burning activities were observed on 9–10 March 2014. A high-volume sampler (Digital model Aerosol Sampler DHA-80, 500 l min^{-1}) was used to collect PM$_1$ aerosol particles onto 150 mm diameter Pallflex quartz fibre filters (pre-baked for 24 h at 550 °C) over a 24-hour sampling period. Filters were stored in a freezer (at -20 °C) immediately after sampling.

2.2. Instrumentation

2.2.1 Aerosol Chemical Speciation Monitor and data analysis

An ACSM (Aerodyne Research, Inc., Billerica, MA, USA) was deployed to measure PM$_1$ components in Preila (Fig. 1, Sect. 2.1). A PM$_{10}$ impactor-type inlet was utilized to remove coarse particles from the sample stream. The sampling air (1.1 L min^{-1}) passed through a vertical 2.5 m long stainless steel tube with a 6 mm i.d. and a Nafion dryer (MD-110-12S-4, PermaPure LLC, Toms River, NJ, USA) before reaching the device. Aerosol particle diffusion losses in the sampling line were less than 4.0 % for particles from 40 nm to 1 µm according to Gormley and Kennedy (Baron and Willike, 2001) and the relative humidity lower 50 % (by SATO model SK-L200TH). Thus, the used sampling line and ambient relative humidity did not affest aerosol mass concentration measured by ACSM. The transported aerosol flow was split and directed to a scanning mobility particle sizer (model 19.3.09 IFT/TT (TROPOS, Leipzig, Germany) and to the ACSM. In the ACSM particles were directed onto a resistively heated surface at ~600 °C where NR-PM$_1$ components are flash vaporized and the resulting gases are subsequently ionized by 70 eV electron impact. ACSM was operated with a time resolution of ~28 min (for typical aerosol loadings, i.e. several µg m^{-3}) and a scan rate of 220 ms amu^{-1} from *m/z* 10 to 140 (approximately 31.9 s per scan and 1.126 s pause), 56 scans and data interval 30 min. The data acquisition software used was DAQ 1.4.4.4. The mass concentrations and mass spectra were processed using ACSM standard data analysis software (v 1.5.3.0).

The instrument was calibrated using ammonium sulphate and ammonium nitrate. The determined calibration parameters were response factor (RF) $RF_{NO3} = 2.75*10^{-11}$ and relative ionization efficiency (RIE) $RIE_{NH4} = 6.16$, $RIE_{SO4} = 0.92$. The $RIE_{Org} = 1.4$, $RIE_{Chl} = 1.3$ were set as default. However, the ACSM collection efficiency varies depending on the acidity of aerosol particles, aerosol composition, and particle phase water (Matthew et al., 2008). Many atmospheric aerosol studies reported reasonable agreement and linear correlations were obtained with other measurements by using a collection efficiency of 0.5 (Aiken et al. 2009; Timonen et al. 2010). Middlebrook et al., (2012) had proposed a collection efficiency calculation method. The collection efficiency for each measurement and daily mean CE values were calculated. The CE variation was small during the entire measurement campaign (March 2014), so the determined mean CE value was 0.52 with a standard deviation of 0.08, which is very close to other works (Aiken et al. 2009; Timonen et al. 2010). This is not surprising because the sampled aerosol was dried to RH< 50%, moreover, the nitrate fraction was quite low (15% on average) and a high acidity of aerosols was not expected at Preila station (EMEP). Thus, we used the CE=0.52 in our investigation. The time series of organic aerosol mass spectra were processed using PMF analysis.

2.2.2. PMF analysis

The ACSM measured data were averaged to 1-hour time resolution. A graphical user interface SoFi (Source Finder) (Canonaco et al., 2013), developed at Paul Scherrer Institute was used to perform PMF for the source apportionment of the non-refractory OA mass spectra collected during March 2014. Only signals at *m/z*<120 were used for PMF analysis (Paatero and Tapper, 1994; Paatero, 1997)) due to the following reasons: 1) the signals above *m/z* > 120 account for a minor fraction of total signal, 2) the *m/z*'s > 120 have larger uncertainties because of poor ion transmission and the large interferences of naphthalene signals on some *m/z*'s (e.g., *m/z* 127, 128, and 129) (Sun et al., 2012). A 2-factor solution including a Primary Organic Aerosol factor (POA), and a Secondary Organic Aerosol factor (SOA) was selected for this study. 20 different PMF runs were performed using a bootstrapping approach

(Davison and Hinkley, 1997). The bootstrap creates new input data matrices by randomly resampling measured mass spectra from the original input matrices. Moreover each PMF bootstrap run is initiated from a different pseudorandom starting-point of the algorithm (seed). The bootstrapping approach, together with the seed approach allows a reasonable exploration of the PMF solution space (Paatero et al., 2014). Higher order solutions (3 factors) were explored yielding additional primary profiles, without a significant modification of the secondary contributions. Moreover the retrieved additional profiles showed very high time correlation ($R^2 = 0.98$) with the POA factor, suggesting a splitting of the same aerosol source. As the additional primary factors could not be associated to specific primary emissions, those solutions are not shown. Medium-long range transport of polluted air masses resulted in a co-variability of the sources at the sampling site, hampering a further separation of the primary organic aerosols.

2.2.3. 7-wavelength aethalometer and Scanning Mobility Particle Sizer

An aethalometer, Model AE31 Spectrum (Manufactured by Aerosol d.o.o., Ljubljana, Slovenia) provided continuous measurements of the BC mass concentrations. The aethalometer was equipped with a $PM_{2.5}$ impactor. The aethalometer data were recorded with a 5-minute time resolution. The optical transmission of light absorbing carbonaceous aerosol particles was measured at seven wavelengths (370, 450, 520, 590, 660, 880, and 950 nm). Measurements at 880 nm wavelength were used to determine BC mass concentration (Lavanchy et al., 1999). The aethalometer converts light attenuation measurements to BC mass using specific attenuation absorption cross-section (σ) of 16.6 $m^2\,g^{-1}$ (at 880 nm) (Aethalometer Operations manual). The default value for a near-infrared wavelength of 880 nm was set by the manufacturer. An empirical algorithm for loading effects compensation was used (Collaud Coen et al., 2010). Ångström exponent of the absorption coefficient computed by fitting an exponential curve was evaluated.

Aerosol size distribution measurements were performed using a Scanning Mobility Particle Sizer (SMPS) model 19.3.09 IFT/TT (TROPOS, Leipzig, Germany), with automatic sheath flow, temperature and relative humidity (RH) control (SMPS setup V2.6 TT 2006) as described in Wiedensohler et al. (2012) applying CPC UF-02M (Mordas et al., 2013). The measured particle size (8.7 to 840.0 nm) with a time resolution of 5 min having 72 channels.

2.2.4. OC/EC, ^{14}C, $\delta^{13}C$ and $\delta^{15}N$ analysis

Filter measurements were performed to determine OC, EC and TC concentrations with a thermo-optical OC/EC analyser (Sunset Laboratory Inc, USA) equipped with a non-dispersive infrared (NDIR) detector. A 1.5 cm^2 filter punch was analysed according to the EUSAAR2 protocol (Cavalli et al., 2010). The blank filter was subtracted only from the measured OC and TC concentrations, as for the EC the corresponding blank was below the detection limits of the instruments.

^{14}C in EC and TC was measured using the accelerator mass spectrometer MICADAS, equipped with a gas-capable ion source (Szidat et al., 2014). ^{14}C analysis of TC was determined after combustion of filter punches in an elemental analyser, directly coupled to the MICADAS (Salazar et al., 2015). The TC ^{14}C raw data were corrected for a representative field blank. For ^{14}C analysis of EC, the filters were first water extracted in order to minimize charring by removing the water-soluble OC (WSOC). Then the Swiss_4S protocol (Zhang et al., 2012) was used to remove the water-insoluble OC (WINSOC) and measure the EC ^{14}C, by coupling of the Sunset instrument to the MICADAS (Agrios et al., 2015). ^{14}C in OC was determined from the TC ^{14}C and the EC ^{14}C results with an isotope mass balance calculation. All the data from the ^{14}C analysis were corrected for the decay of the ^{14}C from 1950 until present. The reported uncertainty for the non-fossil fraction of EC includes both charring of OC (overestimation of EC) and EC loss (underestimation of EC) during the WINSOC removal process (Zhang et al., 2012). Non-fossil fractions of TC, EC and OC (i.e., TC_{nf}, EC_{nf} and OC_{nf}) were determined from the individual ^{14}C analyses and ^{14}C reference values. These reference values represent emissions from purely non-fossil sources and amount 1.06 ± 0.03 for TC and OC and 1.10 ± 0.03 for EC based on the calculation of Mohr et al. (2009). The fossil fractions of TC, EC and OC (i.e., TC_f, EC_f and OC_f) were determined by subtraction of the respective non-fossil fractions.

Bulk $\delta^{13}C$ and $\delta^{15}N$ values were derived by measuring filter pieces (1.4 cm^2) wraped in tin capsules (8*5 mm, Elemental Microanalysis) using an elemental analyser accompanying an isotope ratio mass spectrometer (EA-IRMS, Flash EA1112—Thermo V Advantage) via a ConFlo III interface. The autosampler of the EA was continuously flushed with He (180 ml min^{-1}) to remove all atmospheric gases. Helium flow on the oxidation column was 80 ml min^{-1}. Flash combustion occurred in the oxidation column with the presence of O_2 (the O_2 flow was 180 ml min^{-1} for 4 s). Formed gases were taken to the reduction column in which molecular nitrogen was obtained from any nitrogen oxides followed by a water trap (magnesium perchlorate). The nitrogen and the carbon dioxide were separated on a packed gas chromatographic (GC) column (PoraPlot, 3m*2cm, 35°C) and delivered to the isotope ratio mass spectrometer (via the ConFlo interface) where the measurement of carbon and nitrogen isotope ratio was made. The amount of nitrogen and carbon in the sample was determined by a thermal conductivity detector which is a part of the elemental analyser. These measurements were used in the isotope mass balance calculations (Eq. 1).

The total carbon and total nitrogen fractions of the aerosol particles were used for the isotopic ratio measurements. Stable carbon and nitrogen isotopic ratio measurements were expressed relative to the Vienna Pee Dee Belemnite (VPDB) standard using the formula:

$$\delta^{13}\mathrm{C} = \left(\mathrm{R}_{\mathrm{sample}} / \mathrm{R}_{\mathrm{standard}} - 1 \right) * 1000\,(‰), \quad (1)$$

where $\mathrm{R}_{\mathrm{sample}}$ and $\mathrm{R}_{\mathrm{standard}}$ are the ratios of ^{13}C to ^{12}C (or ^{15}N to ^{14}N) in the sample and the standard (referred to as VPDB), respectively.

Repeated analysis of certified reference material (caffeine IAEA-600) and oil (NBS 22) gave an average δ^{13}C value: mean ± σ = -27.77 ± 0.08 ‰ (certified value: mean ± σ = -27.771 ± 0.043 ‰$_{\mathrm{VPDB}}$) and δ^{13}C = -30.031 ± 0.043 ‰$_{\mathrm{VPDB}}$ respectively. These values were used for δ^{13}C measurements in order to evaluate an analytical precision and calibration of a reference gas (CO_2) to VPDB. Meanwhile, the IAEA-600 standard gave an average δ^{15}N value: mean ± σ = 1 ± 0.2 ‰ which was used for calibration of a reference gas (N_2) to air (for δ^{15}N measurements).

Stable carbon and nitrogen isotope ratios were measured in the samples with the signal intensity reaching 1000 mV or more, due to analytical restrictions (the isotope values measurements below 1000 mV did not fulfil linearity requirements of 0.07 ‰/V for the internal standard).

The mass balance equation was used to calculate the real δ values of carbon or nitrogen of the aerosol samples (blank correction):

$$m_{\mathrm{measured}} \times \delta X_{\mathrm{measured}} = m_{\mathrm{l}} \times m_{\mathrm{blank}} \times \delta X_{\mathrm{blank}}, \quad (2)$$

where m_{measured} was the mass of measured material (carbon or nitrogen) in the measured sample, $\delta X_{\mathrm{measured}}$ was the measured (aerosol + filter) δ value (carbon or nitrogen), m_{l} was the mass of pure material (carbon or nitrogen), and m_{blank} and $\delta X_{\mathrm{blank}}$ were the mass and isotope ratio (of carbon or nitrogen) of the blank filter, respectively.

2.2.5. Radiocarbon-based source apportionment of carbonaceous aerosols

An estimate of fossil and non-fossil primary and secondary organic carbon (POC_f, POC_{nf}, SOC_f, SOC_{nf}) was achieved by coupling ACSM-PMF results, ^{14}C data, and organic marker measurements using a chemical mass balance-like approach. The sensitivity of POC_f, POC_{nf}, SOC_f, and SOC_{nf} contributions to the assumed parameters and measurement errors are described in details in this section. The approach is based on the POC_{nf} estimate, for a subsequent determination of SOC_{nf}, SOC_f, and POC_f as follows:

$$SOC_{nf} = OC_{nf} - POC_{nf} \quad (3)$$

$$SOC_f = SOC - SOC_{nf} \quad (4)$$

$$POC_f = OC_f - SOC_f \quad (5)$$

^{14}C measurements and ACSM-PMF results were coupled as follows. Daily OC_{nf} measurements from radiocarbon analysis as well as average daily POA from ACSM-PMF results provided two upper boundaries for the daily POC_{nf} contribution. In this manner we identified a possible daily range of POC_{nf} contributions. In order to determine more precisely the POC_{nf} daily contributions within the aforementioned possible daily ranges, we performed a sensitivity analysis. Briefly, in the sensitivity analysis we considered a uniform distribution of possible POC_{nf} contributions within the identified possible daily ranges, meaning that each POC_{nf} value in the selected ranges was considered as equally probable (however, as discussed in the next section, in order to explore the influence of this assumption we also performed the same sensitivity analysis assuming a non-uniform distribution). Assuming no POC_{nf} contribution from other sources than BBOC, each POC_{nf} contribution in the acceptable daily ranges could be written either as [BBOC] = [levoglucosan]/α or as [BBOC] = [EC_{nf}]/β, where α represents the levoglucosan/BBOC ratio and β represents the EC_{nf}/BBOC ratio. In two separated sensitivity analyses we scanned broad α and β ranges covering the possible POC_{nf} daily ranges and we retained only POC_{nf}, [levoglucosan]/α, and [EC_{nf}]/β combinations associated to selected acceptance criteria described in the following. From the acceptable solutions we then derived the daily probability distribution function of POC_f, SOC_{nf}, SOC_f, POC_f, α, and β.

The assumption that each input POC_{nf} contribution in the selected possible range is equally probable (hereafter referred to as "uniform distribution approach") has advantages and drawbacks: while this assumption doesn't consider any a priori information about levoglucosan/POC_{nf} and EC_{nf}/POC_{nf}, it considers those ratios as equally possible. To explore the influence of this assumption on our results we performed the same sensitivity analysis assuming an input levoglucosan/POC_{nf} distribution derived from 33 profiles for combustion of hard or softwoods in domestic fireplaces or woodstoves (Fine et al. 2001, 2002, 2004a, 2004b, Schmidl et al. 2008, the approach is hereafter referred to as "non-uniform distribution approach"). We eventually derived the probability distribution functions of the levoglucosan/POC_{nf} and EC_{nf}/POC_{nf} ratios relative to the acceptable solutions. The two approaches provided similar results. From the uniform distribution approach, a median levoglucosan/POC_{nf} ratio of 0.18 (1st quartile = 0.14; 3rd quartile = 0.23) and a median EC_{nf}/POC_{nf} ratio of 0.32 (1st quartile = 0.28; 3rd quartile = 0.36) were retrieved, whilst from the non-uniform distribution approach a median levoglucosan/POC_{nf} ratio of 0.15 (1st quartile = 0.13; 3rd quartile = 0.18) and a median EC_{nf}/POC_{nf} ratio of 0.33 (1st quartile = 0.28; 3rd quartile = 0.36) were obtained.

In the following section a technical description of the sensitivity analysis implementation is reported. For each filter sample i, 10000 random combinations (r) of input data, $[TC]_{i,r}$, $[EC]_{i,r}$, $[EC_f]_{i,r}$, $[OC_f]_{i,r}$, and $[Levoglucosan]_{i,r}$, were generated. In this process, we assume a normal distribution of the errors around the average $[X]_i$ value (X being one of the input values mentioned above), and a distribution width equal to the standard deviation $\sigma[X]_i$:

For each random combination of input data, the corresponding $[OC]_{i,r}$, $[EC_{nf}]_{i,r}$, and $[OC_{nf}]_{i,r}$ values were determined as:

$$[OC]_{i,r} = [TC]_{i,r} - [EC]_{i,r}, \tag{6}$$

$$[EC_{nf}]_{i,r} = [EC]_{i,r} - [EC_f]_{i,r}, \tag{7}$$

$$[OC_{nf}]_{i,r} = [OC]_{i,r} - [OC_f]_{i,r}. \tag{8}$$

10000 random $[SOC]_s$ values were generated by randomly selecting a daily average $[SOA]_s$ value from one of the 20 ACSM-PMF runs (s). The corresponding $[SOC]_s$ values were derived as:

$$[SOC]_s = [SOA]_s/(OM/OC)_{SOA(s)} \tag{9}$$

$(OM/OC)_{SOA(s)}$ and $\sigma(OM/OC)_{SOA(s)}$ were calculated according to Aiken et al., 2009 as function of the fractional contribution of the *m/z* 44 (*f44*) to the SOA_s mass spectra. Fröhlich et al. (2015) showed a systematic difference between *f44* measured from ACSM and AMS, therefore an empirical correction factor was accordingly applied to rescale *f44* from ACSM (*f44*$_{\mathrm{ACSM}}$) data to the corresponding AMS *f44* value (*f44*$_{\mathrm{AMS}}$). The uncertainty relative to the *f44* correction factor was propagated into $\sigma(\mathrm{OM/OC})_{\mathrm{SOA(s)}}$ which includes the $\mathrm{O/C_s}$ uncertainty as well. Each $[\mathrm{SOC}]_{i,\mathrm{r}}$ value was obtained by randomly varying $[\mathrm{SOC}]_{\mathrm{s}}$ assuming a normal distribution of errors around the average value $[\mathrm{SOC}]_{\mathrm{s}}$ and a distribution width equals $\sigma(\mathrm{OM/OC})_{\mathrm{SOA(s)}}$. $[\mathrm{BBOC}]_{i,\mathrm{r}}$ contributions for each sample *i* were derived as follows:

$$[\mathrm{BBOC}]_{i,\mathrm{r}} = [\mathrm{levoglucosan}]_{i,\mathrm{r}}/\alpha, \qquad (10)$$

$$[\mathrm{BBOC}]_{i,\mathrm{r}} = [\mathrm{EC_{nf}}]_{i,\mathrm{r}}/\beta, \qquad (11)$$

where α represents the levoglucosan/BBOC ratio. This ratio was systematically varied between 0.01 and 0.31 according to Huang et al. (2014) and references therein (scan step equals 0.01). β corresponds to the EC/BBOC ratio. Values of β were systematically varied between 0.1 and 0.4 according to Zhang et al. (2015) and references therein (scan step equals 0.01). 10000 $[\mathrm{BBOC}]_{i,\mathrm{r},\alpha}$ and 10000 $[\mathrm{BBOC}]_{i,\mathrm{r},\beta}$ were determined as in Eq. (8) and (9). Only acceptable $[\mathrm{BBOC}]_{i,\mathrm{r},\alpha/\beta}$ (= $[\mathrm{POC_{nf}}]_{i,\mathrm{r},\alpha/\beta}$) values were considered for the sensitivity analysis. The criteria to consider a $[\mathrm{BBOC}]_{i,\mathrm{r},\alpha/\beta}$ value as acceptable were:

a) $[\mathrm{BBOC}]_{i,\mathrm{r},\alpha/\beta} \leq [\mathrm{POC}]_{i,\mathrm{r}}$ and b) $[\mathrm{BBOC}]_{i,\mathrm{r},\alpha/\beta} \leq [\mathrm{OC_{nf}}]_{i,\mathrm{r}}$ (12)

$[\mathrm{POC}]_{i,\mathrm{r}}$ was determined as follows:

$$[\mathrm{POC}]_{i,\mathrm{r}} = [\mathrm{OC}]_{i,\mathrm{r}} - [\mathrm{SOC}]_{i,\mathrm{r}}, \qquad (13)$$

Only acceptable $[\mathrm{POC}]_{i,\mathrm{r}}$ values were considered. The criterion to consider a $[\mathrm{POC}]_{i,\mathrm{r}}$ value as acceptable was:

c) $[\mathrm{POA}]_{\mathrm{s}}/[\mathrm{POC}]_{i,\mathrm{r}} \geq 1.3$ according to Mohr et al. (2009), Aiken et al. (2009).

$[\mathrm{SOC_{nf}}]_{\mathrm{i,r}}$ values were then derived as:

$$[\mathrm{SOC_{nf}}]_{i,\mathrm{r}} = [\mathrm{OC_{nf}}]_{i,\mathrm{r}} - [\mathrm{POC_{nf}}]_{i,\mathrm{r}} \qquad (14)$$

Only acceptable $[\mathrm{SOC_{nf}}]_{i,\mathrm{r}}$ values were considered, where

d) $[\mathrm{SOC_{nf}}]_{i,\mathrm{r}} \leq [\mathrm{SOC}]_{i,\mathrm{r}}$ (15)

Only solutions where all 4 criteria a), b), c), and d) held were considered acceptable and retained.

Finally, $[\mathrm{SOC_f}]_{i,\mathrm{r}}$ and $[\mathrm{POC_f}]_{i,\mathrm{r}}$ were calculated as:

$$[\mathrm{SOC_f}]_{i,\mathrm{r}} = [\mathrm{SOC}]_{i,\mathrm{r}} - [\mathrm{SOC_{nf}}]_{i,\mathrm{r}}, \qquad (16)$$

$$[POC_f]_{i,r} = [OC_f]_{i,r} - [SOC_f]_{i,r}. \quad (17)$$

2.2.6. Satellite products and organic markers

Determination of organic marker concentrations were performed using developed in-situ derivatization thermal desorption gas chromatography time of flight mass spectrometry (IDTD-GC-MS) method (Orasche et al., 2011).

Biomass burning episodes were explored using a variety of remote sensing datasets and their derived properties. Satellite data and ground based observations of aerosol properties from the MODIS, HYSPLIT and SILAM (Sofiev et al., 2006) were coupled to analyse the variability of carbonaceous aerosols in Lithuania (Fig. 2).

The MODIS sensors on-board NASA's Terra and Aqua satellites provides multiple thermal observations of the Earth on 9–10 March 2014 at a spatial resolution of 1 km using the latest version of the MODIS Active Fire Product (MOD14/MYD14) algorithm (MODIS, 2011). To identify the influence of air masses from different transport pathways on the large BB event occurring at Preila, 72-h back trajectories at an arrival height of 100, 200 and 500 m were calculated by Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model Version 4.8. All air mass back trajectories were generated using Gridded Meteorological Data archives of the Air Resource Laboratory (ARL), National Ocean and Atmospheric Administration (NOAA) (Fig. 2A).

The Navy Aerosol Analysis and Prediction System (NAAPS) model results were used to define the distribution of BB aerosols from wildfires area (model description and results are available from the web pages of the Naval Research Laboratory, Monterey, CA, USA; http://www.nrlmry.navy.mil/aerosol/) (Fig. 2B). The NAAPS model has been adapted to combine real-time observations of biomass burning based on the joint Navy/NASA/NOAA Fire Locating and Modelling of Burning Emissions system (FLAMBE, http://www.nrlmry.navy.mil/flambe/) (Reid et al., 2004). The method has proven helpful in previous studies of long-range and regional transport of smoke (Honrath et al., 2004). The resolution of 2.5° longitude × 2.5° latitude National Centers for Environmental Prediction (NCEP) reanalysis data (Kanamitsu et al., 2002) during grass burning episode were analysed to illustrate the sub synoptic-scale weather feature among the biomass burning events over Lithuania issued every 6 h for March 2014 (Fig. 2C). SILAM is an air quality and emergency open code system (http://silam.fmi.fi/) providing $PM_{2.5}$ emission maps by Eulerian dynamics and a combination of basic acid and ozone chemistry with inert particles for fire and anthropogenic primary PM emission to account for the fire induced aerosol contribution (Fig. 2D).

Results and discussion

2.1 Identification of grass burning event

Massive active fires occurred throughout the Kaliningrad region (Russia), Belorussia and Ukraine (Fig. 2A) when a high atmospheric pressure system was situated over the study area, as illustrated in the weather map of Fig. 2C. The plumes from those fires covered a large area south of the Baltic region and were transported thousands of kilometres downwind affecting the background air in Lithuania (Fig. 2). Although the number of fires was similar to that one of previous years, the impact of the fire events on the Lithuanian air quality was enhanced in March 2014 due to air mass transport of smoke entrained in deep convection by the large scale circulation around the pressure maximum of the anticyclonic system (Fig. 2C). This is consistent with the relatively high concentrations of smoke reaching Preila as predicted by NAAPS (Fig. 2B).

The weather maps showed that the high concentration of pollutants during this BB event was caused by the anticyclonic large-scale movement, which persisted throughout the lower troposphere causing stagnant conditions and extended aerosol residence time.

2.2 Investigation of PM_1 composition and ambient concentrations of organic tracers

The climatic conditions in West Europe as well as in west part of Lithuania are particular, as the moderate warm climate dominating by air mass transport from Atlantic Ocean, leading to higher humidity. Annual mean temperature increases in west-east direction. The average temperature of March was ~3–4 ºC. During the BB event (9–11 March) combustion products were spread over the study region by the large-scale atmospheric circulation processes. At the beginning of the BB episode, the wind speed was up to 3 m s^{-1} on average in the daytime of 9th March, causing weaker dilution of the pollutants while the BC concentration were higher than 12 μg m^{-3}.

During the campaign on average organic aerosol (46 %, 3.2 μg m^{-3} ($\sigma = 4.8$ μg m^{-3})) constituted the major fraction of the NR-PM_1 aerosol concentration composition measured by ACSM with lower contributions of sulfate (17 %, 1.2 μg m^{-3} ($\sigma = 1.1$ μg m^{-3})), nitrate (20 %, 1.4 μg m^{-3} (σ = 1.8 μg m^{-3})), ammonium (15 %, 1.0 μg m^{-3} (σ = 0.9 μg m^{-3})), and chloride (2 %, 0.1 μg m^{-3} (σ = 0.3 μg m^{-3})). The average composition of NR-PM_1 showed similar dominance of organics to previous observations in Europe (e.g. Crippa et al., 2014). OA contribution to NR-PM_1 was found to be much higher during the grass burning period (61 %, 8.6 μg m^{-3} ((σ = 5.0 μg m^{-3})), followed by sulfate (5 %, 1.4 μg m^{-3} (σ = 0.5 μg m^{-3})), nitrate (19 %, 3.0 μg m^{-3} (σ = 1.4 μg m^{-3})), ammonium (13 %, 1.6 μg m^{-3} (σ = 0.7 μg m^{-3})), and chloride (3 %, 0.4 μg m^{-3} (σ = 0.3 μg m^{-3})) (Fig. 5A).

Quantification of monosaccharide anhydrides together with OC and EC are presented in Fig. 3. It is evident that during the event, when grass burning was most intense, the levoglucosan concentration increased up to 680 ng m^{-3}. That was significantly lower than values reported during extreme event of August 2010 in Moscow – 3100 ng m^{-3} (Popovicheva et al., 2014) and are higher than values (220–290 ng m^{-3}) reported during a major biomass burning episode over northern Europe in Helsinki (Saarikoski et al., 2007), while background values in Nordic rural background sites were found to be 2.1–9.8 ng m^{-3} (Yttri et al., 2011). Concentrations of mannosan varied from 3.1 to 68.0 ng m^{-3}, with a mean value of 19.0 ng m^{-3}, and concentrations of galactosan varied from 1.0 to 12.0 ng m^{-3}. Concentrations of mannosan varied from 3.1 to 68.0 ng m^{-3} and those of galactosan from 1.0 to 12.0 ng m^{-3}. The levoglucosan to mannosan (L/M), levoglucosan to galactosan (L/G) and levoglucosan to OC (L/OC) ratios were used before to separate different BB sources (Fabbri et al., 2009; Oanh et al., 2011; Harrison et al., 2012). We measured average L/M and L/G ratios of 16.4 and 135.8, respectively. This is similar to the values found by Orasche et al. (2012) from wood combustion in residential wood appliances and in the range of L/M ratios reported (2.0–33.3) for grass fires by Oros et al. (2006). Excluding the strong event days of March 9 and 10 the sugars showed a good correlation with each other ($R^2 > 0.86$). On March 9 and 10 the mannosan/galactosan was lower at 2-6, indicating different source contribution to the other days. Low mannosan/galactosan ratios were observed for grass and leaves (Sullivan, May et al. 2014). We observed an L to OC ratio from 0.06 to 0.16 during the biomass burning period and of ~ 0.03 during the days without biomass burning events. The values observed during biomass burning are in the range of those (0.04–0.20) reported for wildland fuels (Sullivan et al. 2008). The OC/EC ratio ranged from 1.5 to 6.2 being lower on event days (2.4–3.0) indicating an aerosol composition dominated by organic aerosol. During the intensive grass burning episode, consecutive new particle formation (NPF) episodes were observed.

Observed NPF could be attributed to the grass burning and secondary biomass burning product transformation as was evaluated in earlier studies over same area (Ulevicius et al., 2010b). At 13:00, there was a significant new particle formation on 9th and 10th March followed by subsequent growth up to three hours. The total particle number concentration with a daily mean value of 6440 cm^{-3} (with maximum value of 13000 cm^{-3}), which was extremely much higher than the daily mean observations in non-event days (1660 cm^{-3}). In this area annual total particle concentration of 2650 cm^{-3} was observed (Byčenkienė et al., 2013). Non-event day was characterized by bimodal (Aitken (geometric mean diameter (D_g) of 44 nm) and accumulation (D_g = 128 nm)) modes with a standard deviation of 1.68 and 1.87, respectively. In comparison, during biomass burning event trimodal (nucleation (D_g = 9.0 nm), Aitken (D_g = 31.0 nm) and accumulation (D_g = 102 nm) modes with a standart deviation of 1.77, 1.71 and 1.68, respectively. However volume distribution was characterized by bimodal size distribution for non-event day (D_g = 330 and 665 nm) and event day (D_g = 250 and 590 nm).

The measured $\delta^{13}C$ values varied from -28.2 to -26.7 ‰. The lowest stable carbon isotope ratio values (-28.5 ‰) were detected during the period with the highest total carbon concentration of 12.2 µg m^{-3} (2014.03.10) and 8.5 µg m^{-3} (2014.03.09). The highest concentration 14.0 µg m^{-3} of nitrogen was detected on 10 March 2014. The nitrogen isotope ratio values varied from +1.0 to +13.0 ‰ (Fig. 4).

Stable carbon and nitrogen isotope ratios values of aerosol particles derived from biomass burning (C3 plants) and liquid fossil fuel are overlapping (Garbaras et al., 2015, Masalaite et al., 2015, Turekian et al., 1998). Coal derived aerosol particles are characterised by higher $\delta^{13}C$ and lower $\delta^{15}N$ values (Fig. 4, solid lines). $\delta^{13}C$ values of aerosol particles during wild grass burning events distinguish in low $\delta^{13}C$ values (Garbaras et al. 2008, Ulevicius et. al. 2010b). The above mentioned distribution of $\delta^{13}C$ and $\delta^{15}N$ values allowed excluding coal burning as main source for aerosol particles at Preila during the investigated event. Aerosol particles with the $\delta^{13}C$ values equal -28 ‰ and below originated mainly from grass burning events. This interpretation of the data is consistent with the radiocarbon analysis shown below.

2.3 Source apportionment of EC and OC using ^{14}C data

Relative fossil and non-fossil contributions to OC and EC were evaluated using ^{14}C analysis (Szidat et al., 2014) to enable a more detailed source attribution of the carbonaceous aerosol mass. Widely used, two-source simple models (Currie, 2000; Lemire et al., 2002; Lewis et al., 2004; Szidat et al., 2004) can only distinguish fossil from non-fossil TC emissions. Here, carbonaceous aerosol was described to be composed of the following 4 categories: OC_f and EC_f attributed to primary and secondary fossil fuel combustion; and OC_{nf}, and EC_{nf} typically emitted by to primary and secondary biomass burning, cooking, biogenic emissions and non-fossil OC combustion (Table 2, Fig. 5). There was day-to-day variation in the fractional contributions to TC throughout the BB event. The fraction of elemental carbon from biomass burning EC_{bb} (= EC_{nf}) to total EC was found to be on average 67±3 %. For EC_{bb} the mean relative contribution to total carbon in background areas of Northern countries was found to be <1.5 % on non-event days (Yttry et al., 2011). It was also reported that a major peak in EC_{bb} values between March and April was observed at the Zeppelin atmospheric observatory (Yttri et al. 2014). Such high values are unusual and have only been found in wood burning dominated places like villages in Alpine valleys (Zotter et al., 2014). This shows, together with high levels of levoglucosan, that biomass burning contributed to a large extent to OC_{nf} during this event. A mean light absorption coefficient $\alpha_{370–950}$ (the absorption exponent calculated using the seven Aethalometer wavelengths) of 1.38 (σ = 0.11) was obtained during wildfires, which is higher than the mean $\alpha_{370–950}$ calculated for the non-event days (1.13, σ = 0.19)). The light absorption exponent values were calculated with λ = 370 – 520 nm and λ = 590 - 950 nm wavelengths for comparison purpose. The mean values of $\alpha_{370–520}$ and $\alpha_{590–950}$ were found to be 1.53 (σ = 0.19) and 1.32 (σ = 0.09) during event day and 1.25 (σ =0.27) and 1.13 (σ =0.18) during non-event days, respectively. In comparison during the same event in Preila higher mean values of $\alpha_{370–520}$ and $\alpha_{590–950}$ nm were observed (2.4 ((σ = 0.1) and 1.5 (σ = 0.1, respectively)) in 2008, as well as during the event in 2009 (2.3 (σ = 0.1) and 1.6 (σ = 0.1), respectively)) (Ulevicius et al., 2010). This is an indication of infuence of the biomass burning on the Ångström exponent of the absorption coefficient α. The impact of organic aerosols on the spectral dependence of light absorption was early confirmed by OC/EC ratios. PMF analysis of OA spectra resolved two OA components, which are attributed to POA and SOA, whose mass spectra and time series are presented in Fig. 5 B, C. Combining these results with the ^{14}C measurements as described in section 2.2.4 shows that the high grass burning pollution event is characterized by a high non-fossil organic compound fraction, which accounts for up to ~90 % of total carbon mass.

SOA showed reasonable correlation ($R^2 = 0.62$) with average NH_4^+ mass concentration during the BB event. NH_4^+ is in this case a good tracer for secondary aerosol, as it correlates well with the sum of NO_3^- and SO_4^{2-} ($R^2 = 0.96$; linear fit: y = 0.816+ 0.005) (Fig. 6). There was day-to-day variation throughout the study period with the non-fossil contribution to organic carbon between 67–86 %. OC_{nf} was estimated to be ~65 % primary, while the primary fraction of the OC_f in Preila was estimated to be ~93 %. Conversely, when EC_f showed a lower contribution (2014.03.07 and 2014.03.10; 26 % and 24 %, respectively), OC_f was also lower (15 %) (Table 3). The high fraction of biomass burning was corroborated by measurements of levoglucosan. Other molecular markers such as hopanes for traffic emissions and picene for coal combustion (Rutter et al., 2009) were also measured in order to monitor the possible contribution of fossil fuel combustion during the high pollution event. Although their concentrations increased during the episode, suggesting a contribution of co-transported fossil fuel combustion aerosols, the radiocarbon analysis revealed the contribution of this fraction to be minor (EC_f ranged from 0.3 to 1.1; OC_f ranged from 0.5 to 1.6 (Fig. 5). Values of molecular markers are provided in Table 1 of the Supplementary material. The combination of both techniques allowed a better characterization of the carbonaceous aerosol sources. POA determined with the ACSM is mostly non-fossil and originates from grass burning. The lines in Fig. 7 represent the absolute contribution of each source during 5–10 March 2014. It is shown that POC_{nf} and SOC_{nf} concentrations increase drastically (from 1.1 to 5.4 $\mu g m^{-3}$ for POC_{nf}; from 0.9 to 3.1 $\mu g m^{-3}$ for SOC_{nf}) with increasing influence of biomass burning, whereas the concentrations of the respective fossil fractions show a smaller increase during this episode. From the acceptable solutions obtained from the sensitivity test described in section 2.2.7, we derived the probability distribution functions of the different daily contributions for POC_f, SOC_{nf}, SOC_f, POC_f fractions (Fig. 7). The median Levoglucosan/BBOC and EC/BBOC ratios obtained from the sensitivity tests is consistent with values reported in Zhang et al. (2015) and Huang et al. (2014) (Fig. 8).

In Zhang et al. (2015) agricultural waste combustion is considered to be the main contributor to the total biomass burning. Note that on 5 March a different Levoglucosan/BBOC ratio was found (0.31) compared to the non-event days (~0.15). Also, this is consistent with different wind back-trajectories, associated to air masses originating in the Southern and Central Russian Federal districts, i.e. air masses with a different geographical origin and associated to potentially different types of biomass burning.

3 Conclusions

In March 2014, an intensive field campaign was conducted in the marine background of South Eastern Baltic region during a period of intensive grass burning. This paper provides the biomass burning related aerosol concentrations during grass burning estimated by data that stem from a synthesis of various techniques including surface online/ offline and satellite based measurements. Lidar vertical profiles allowed confirming smoke plume from wild fire regions. Levels of source specific tracers, i,e, levoglucosan as well as ^{14}C of TC, EC and OC have been used as input for source apportionment of the carbonaceous aerosol approach. Overall, EC and OC were dominated by non-fossil sources. The total POC fraction was separated into POC_f and POC_{nf}. In term of OC mass, POC_{nf} contributes on average 56 %, while relative contribution to TC was found to be on average 39 %. In case of SOC, the contribution of OC_f reached on average 10.3 % (non-fossil – 25 %). The δ^{13}C value of -28.5 % indicated the dominance of the aerosol derived from the vegetation burning as no significant carbon isotope fractionation occurs between the aerosol particles from biomass burning and the raw biomass material.

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Figure 1. A) Map of the observation site, Preila (indicated by the red marker). Nearest major cities are Klaipeda (40 km north) and Kaliningrad (90 km south), B) Environmental pollution research station Preila and site surroundings (C).

Table 1. Preila site surroundings 10 km

Site altitude	5 (m) a.s.l.	Terrain below site	50.0 (%)
Median altitude	0 (m) a.s.l.	Standard deviation of altitude	7 (m)
Total population	6831	Standard deviation of population	159
Mean population density	20 (km^{-2})	Standard deviation of population density	13 (km^{-2})
Local population density	29.5 (km^{-2})		
Dominating land cover types (based on GLC2000)			
Water bodies (natural & artificial) (20)			84.9 (%)
Tree cover, needle-leaved, evergreen (4)			13.2 (%)
Tree cover, mixed leaf type (6)			1.1 (%)
Herbaceous cover, closed-open (13)			0.4 (%)

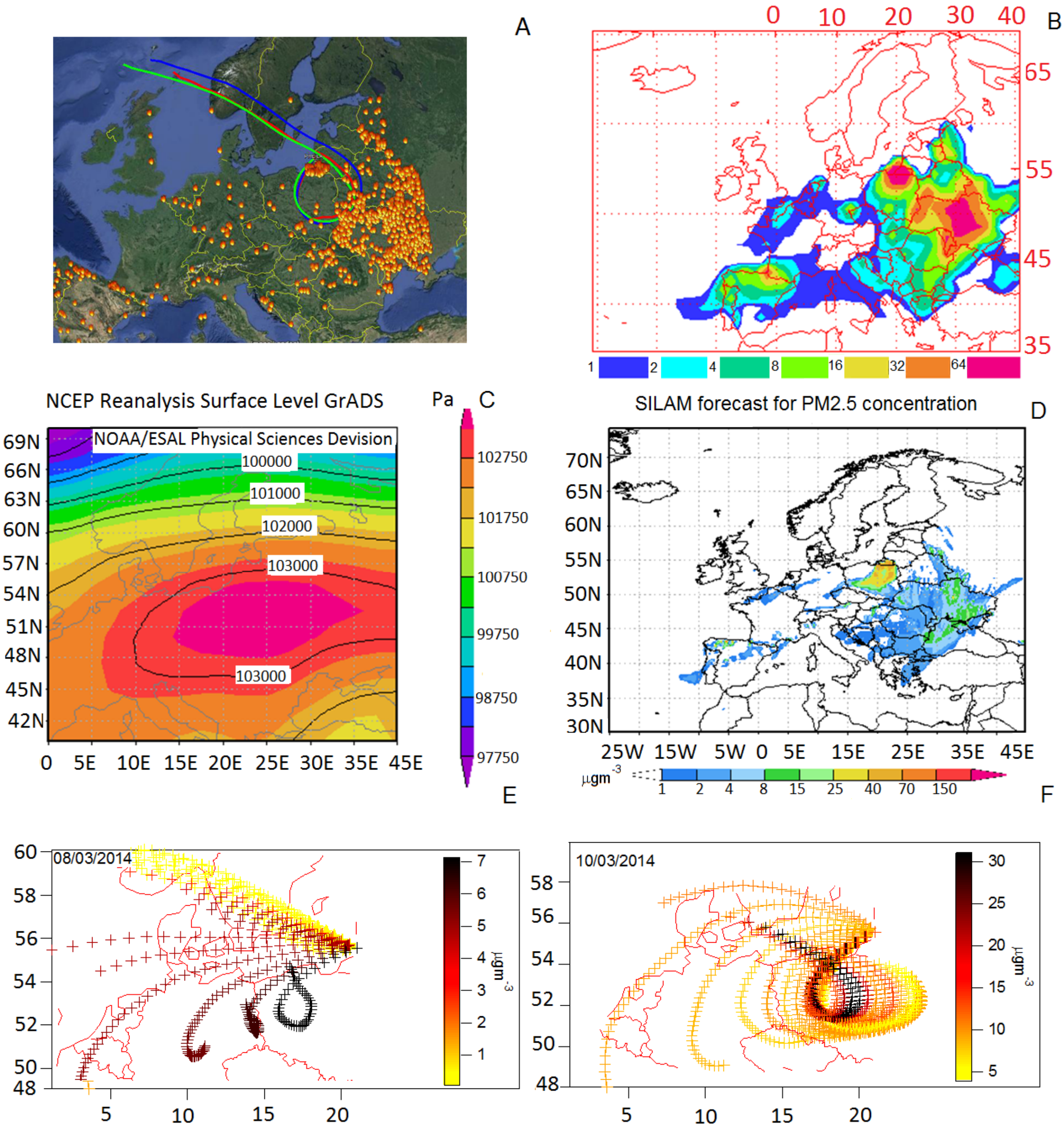

Figure 2. (A) Combined MODIS images observed from the Aqua satellite on 10 March 2014, showing numerous fires due to seasonal grass burning and 72-hour air mass backward trajectories from the fire regions arriving at Preila at 100 (red), 200 (blue) and 500 (green) m above ground level (AGL). (B) NAAPS model results showing surface smoke concentrations for the strongest stage (10 March 2014) (the color scale (from blue to purple) corresponds to the 7 levels of the contours that indicate the smoke mass mixing ratio (µg m^{-3}) at the surface. Smoke optical depth at a wavelength of 0.55 microns. The contouring begins at 1 µg m^{-3} and

doubles in magnitude for each successive contour. (C) Pressure level at surface at 2.5 degree latitude × 2.5 degree longitude global grids in Pa (NCEP/NCAR Reanalysis 1, 10 March 2014). (D) $PM_{2.5}$ concentration (μg m^{-3}) forecast utilized by the SILAM chemical transport model during the event of grass fires, E,F) ACSM organic concentration ACSM organics concentration (μg m^{-3}) (measured in Preila) weighted air mass back trajectories of 48 h (an arrival on 8 (left) and 10 (right) March 2014) with an altitude endpoint of 500 m AGL.

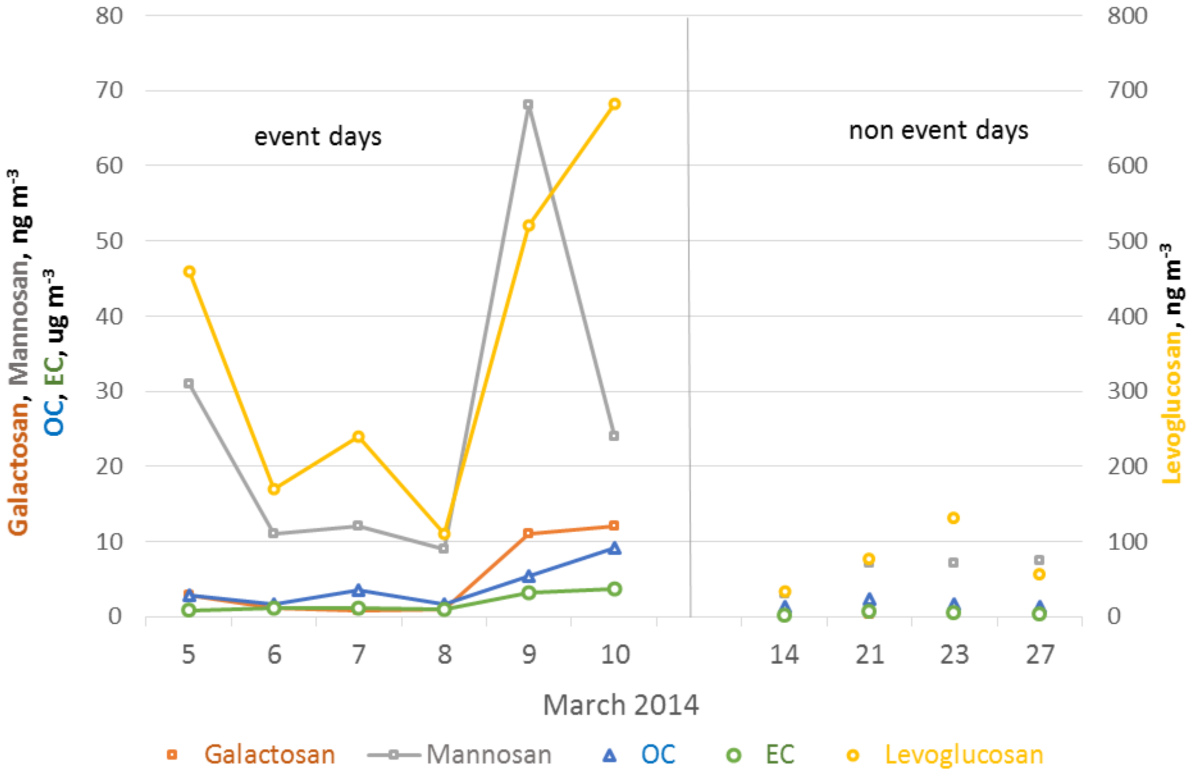

Figure 3. Average daily concentration during event days (from 5 to 10 March 2014) and non-event days (14th, 21th, 23th and 27th March 2014) for levoglucosan, galactosan, mannosan (in ng m^{-3}) and for elemental carbon (EC) and organic carbon (OC) in µg m^{-3}.

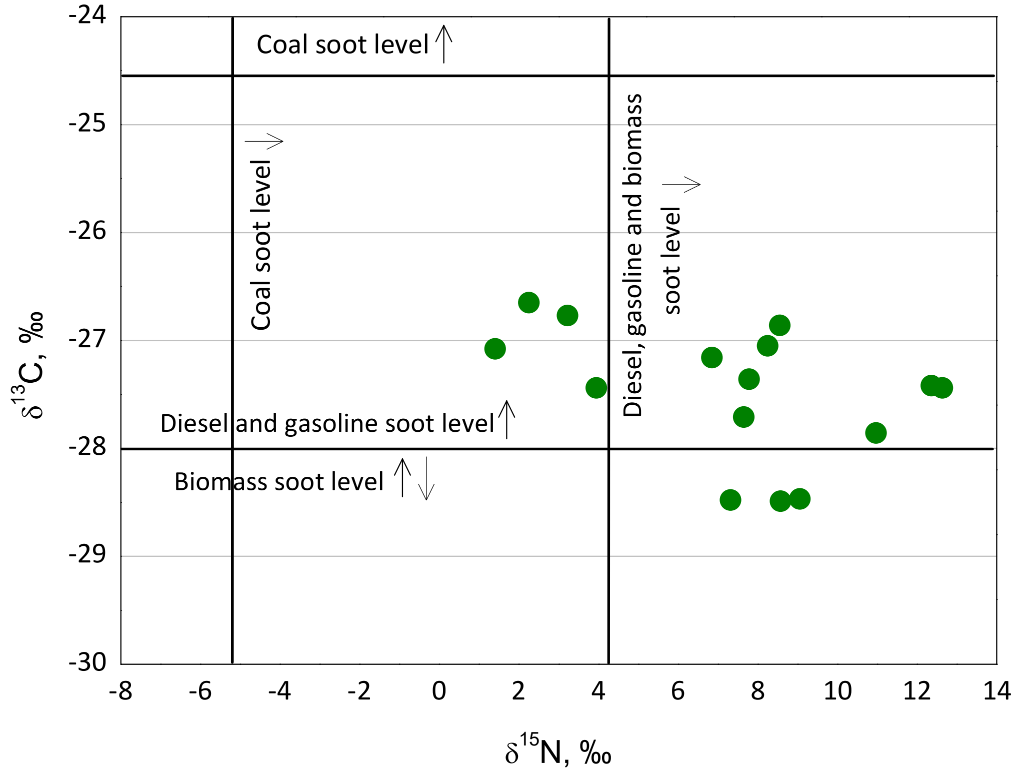

Figure 4. Stable carbon and nitrogen isotope ratio values of PM_1 in Preila station. Vertical and horizontal lines represent carbon and nitrogen, respectively, isotope ratio characteristic values for the sources of aerosol particles (Garbaras et al., 2008, 2015; Ulevicius et al., 2010a; Widory 2007).

Table 2. Variation of the fractions of EC_f, EC_{nf}, OC_f, OC_{nf} and TC, EC and OC values during the study periods.

μg m^{-3}/date of collection	EC_f	EC_{nf}	OC_f	OC_{nf}	TC	EC	OC
2014.03.05	0.25±0.04	0.33	0.47±0.10	2.34±0.18	3.39±0.18	0.59±0.17	2.80±0.18
2014.03.07	0.21±0.04	0.61	0.39±0.12	2.80±0.20	4.01±0.23	0.81±0.24	3.31±0.20
2014.03.08	0.15±0.05	0.26	0.56±0.07	1.46±0.12	2.43±0.13	0.41±0.18	2.24±0.15
2014.03.09	0.46±0.16	0.95	0.95±0.18	4.98±0.36	7.28±0.43	1.36±0.63	6.32±0.35
2014.03.10	0.56±0.18	1.64	1.64±0.28	7.77±0.50	11.72±0.64	2.31±0.75	9.47±0.51

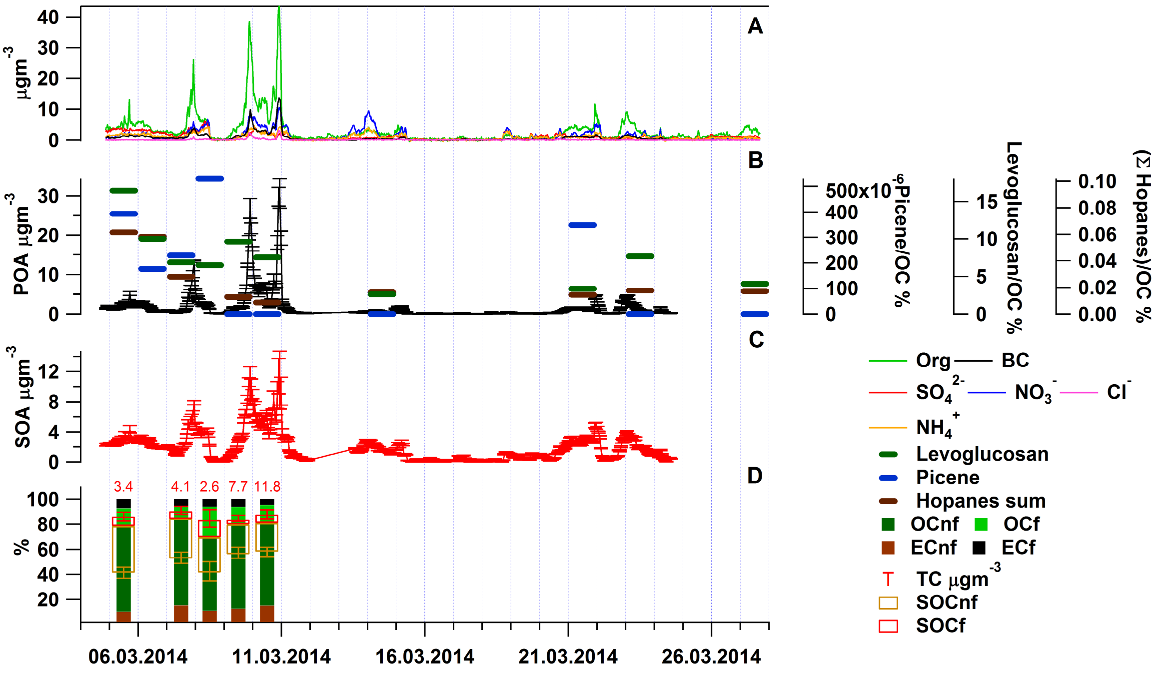

Figure 5. Average chemical composition and time series of NR-PM$_1$ OA for the entire study (A), B) Time series of the POA factor and percent contribution of the corresponding tracer species (levoglucosan, picene and hopanes) to total OA, C) Time series of the SOA factor, D) Relative source apportionment of TC during BB event. Numbers indicate the total carbon absolute concentrations in µg m^{-3}, variations of the mass concentrations of the SOC$_f$ and SOC$_{nf}$ (the whiskers above and below the boxes indicate the 1st and 3rd quartiles.

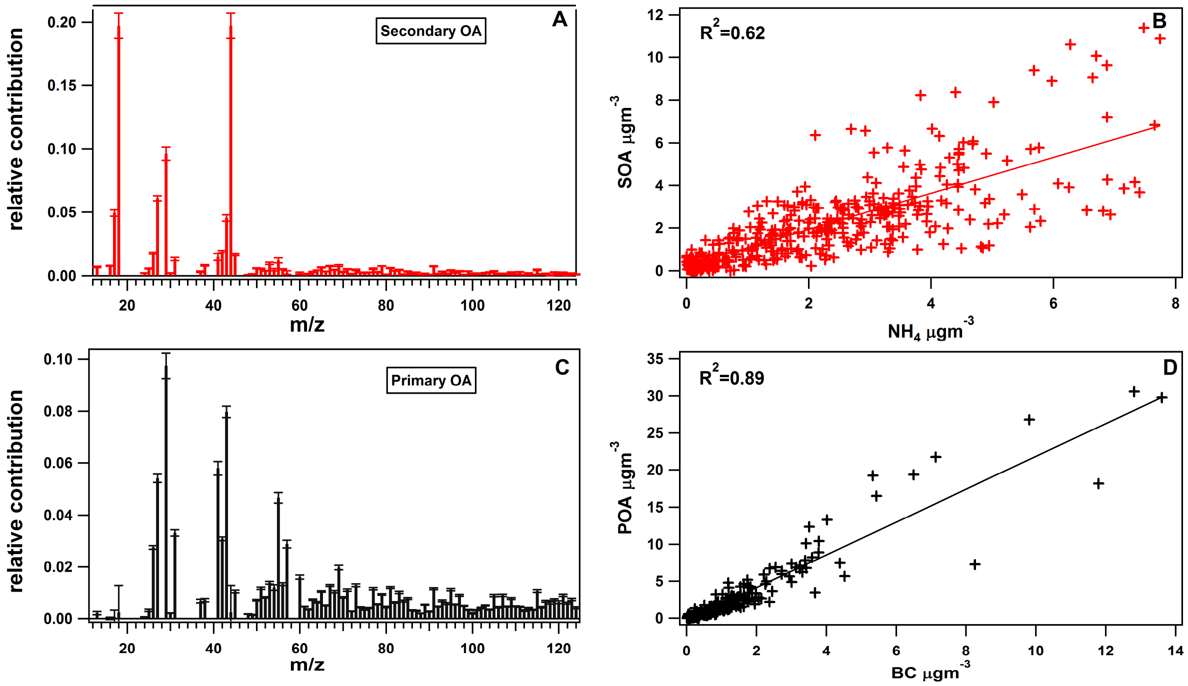

Figure 6. Mass spectra of SOA and POA, error bars represent the standard deviation of 20 PMF runs (A,C) and the scatter plots illustrate the relationship between SOA and NH_4^+ (B) and POA with BC (D).

Table 3. Average Percentage Contributions of Different Sources

Relative contributions [%] to TC	POC$_f$	POC$_{nf}$	SOC$_f$	SOC$_{nf}$	EC$_f$	EC$_{nf}$	TC to PM1
2014.03.05	5.07	43.23	6.69	22.51	9.66	12.83	28.44
2014.03.07	6.26	43.58	5.66	19.14	6.58	18.79	37.62
2014.03.08	7.73	26.28	13.36	18.65	12.60	21.38	24.80
2014.03.09	4.55	41.30	4.38	13.12	12.48	24.17	51.27
2014.03.10	6.82	43.02	5.9	14.83	7.18	22.26	43.91
Relative contributions [%] to OC	POC$_f$	POC$_{nf}$	SOC$_f$	SOC$_{nf}$			
2014.03.05	6.55	55.78	8.63	29.04			
2014.03.07	8.39	58.38	7.59	25.64			
2014.03.08	11.70	39.80	20.24	28.25			
2014.03.09	7.18	65.20	6.91	20.71			
2014.03.10	9.66	60.96	8.36	21.02			

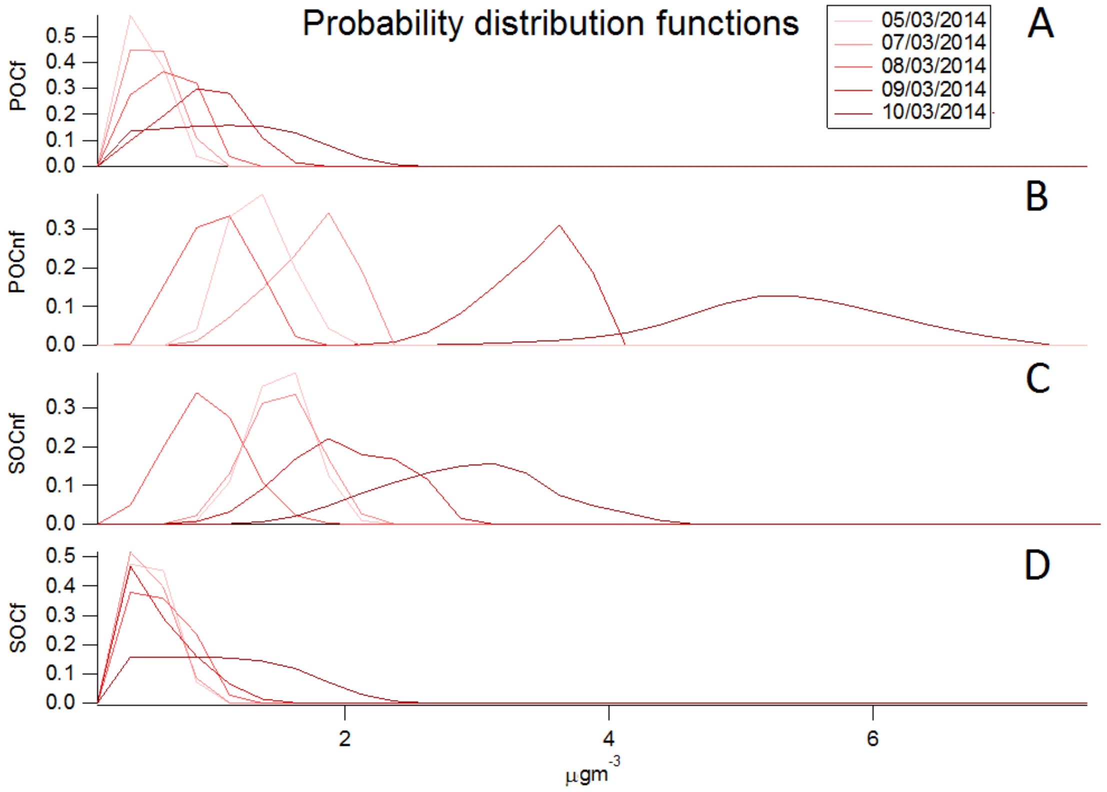

Figure 7. Probability distribution functions of the absolute daily contribution of POC_f (A), POC_{nf} (B), SOC_{nf} (C), SOC_f (D).

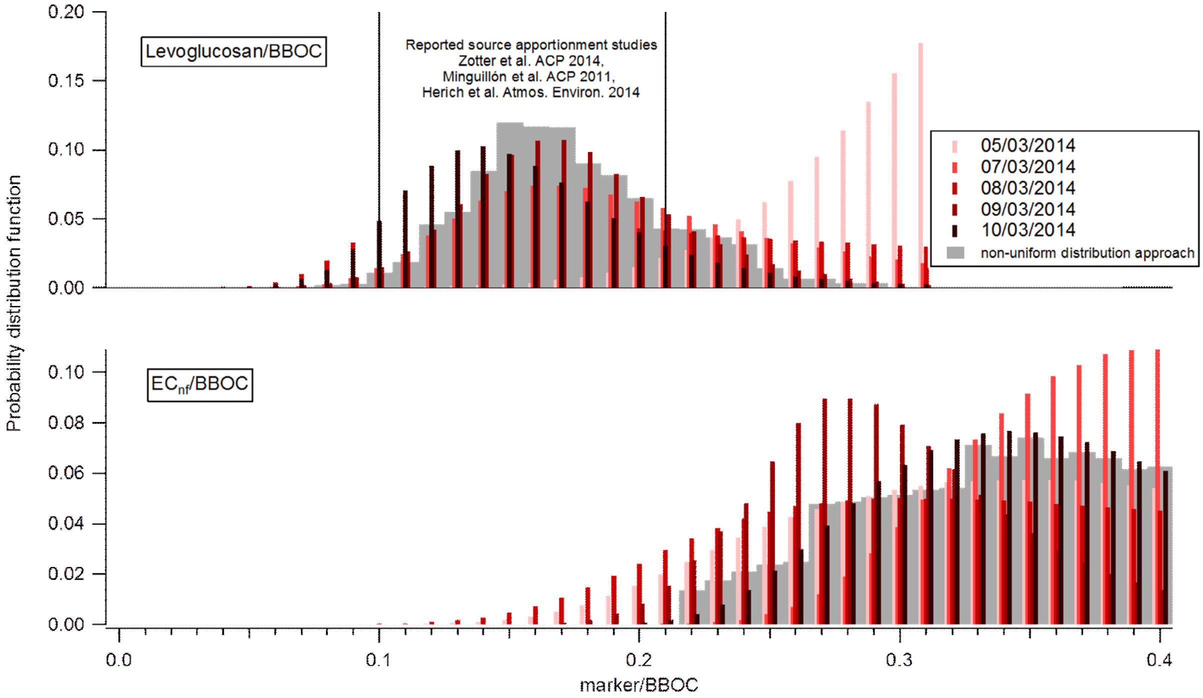

Figure 8. Probability distribution functions of Levoglucosan/BBOC (A) and EC$_{nf}$/BBOC (B).