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 Referee for 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 #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.

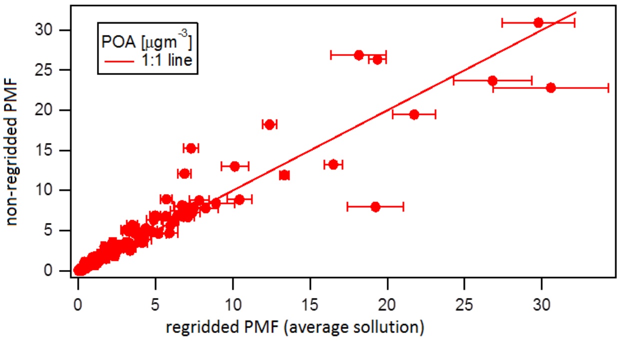
Response: In the manuscript, we separated a section of the sampling line transport efficiency and the ACSM collection efficiency (CE). The transport efficiency calculation method was described in the Response Nr3. It was shown that the smallest Aitken mode particles (40 nm) were transported to the ACSM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

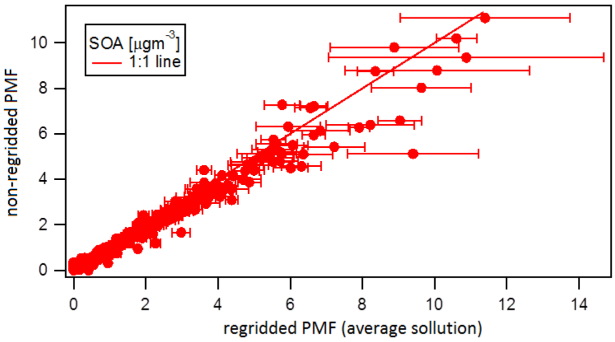
The CE values were calculated for each measurement according to Middlebrook (2012). Then, the daily mean values were determined. For the measurement campaign (March 2014) we calculated the mean CE value of all daily mean values. It was found to be 0.52 with a standard deviation of 0.08. The CE changes 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 $\sigma a= \sigma b$, then the propagated final error would be $\frac{\sqrt{2}}{2}\sigma a$, with a signal/noise improvement by a factor of $2/\sqrt{2}$. 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 $\mu g\ m^{-3}$ (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-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 $\mu g\ m^{-3}$ ((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)*".

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: More analysis was added in this section: "*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)"*.

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.

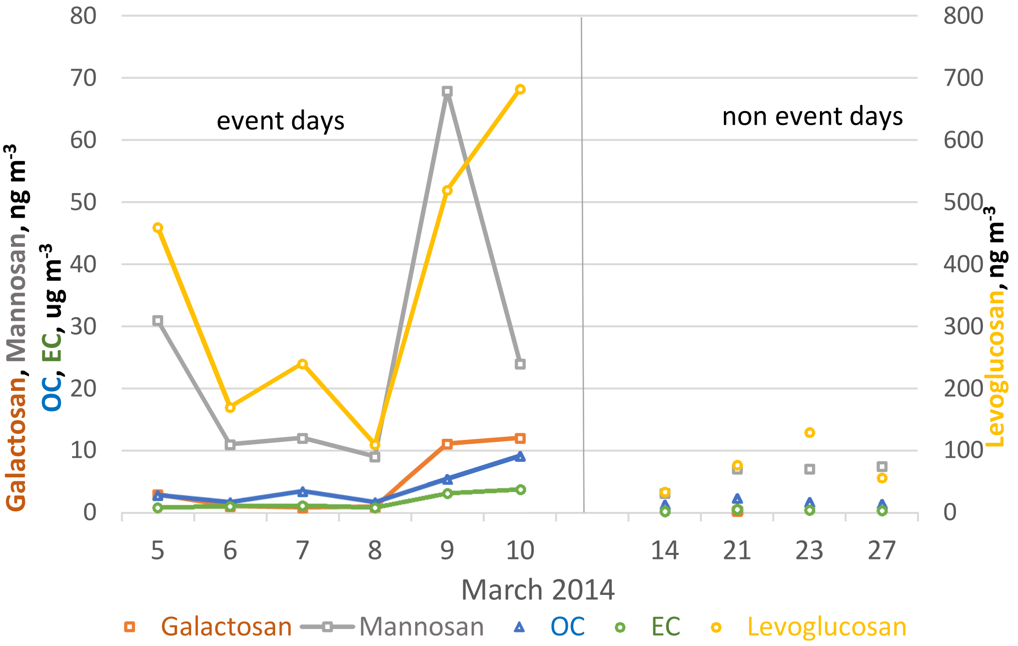


Figure 3. Average daily concentration during event days (from 5 to 10 March 2014) and non-event days (14th, 21th, 23th and 27th March 2014) for levoglucosan, galactosan, mannosan (in ng m^{-3}) and for elemental carbon (EC) and organic carbon (OC) in µg m^{-3}.

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.

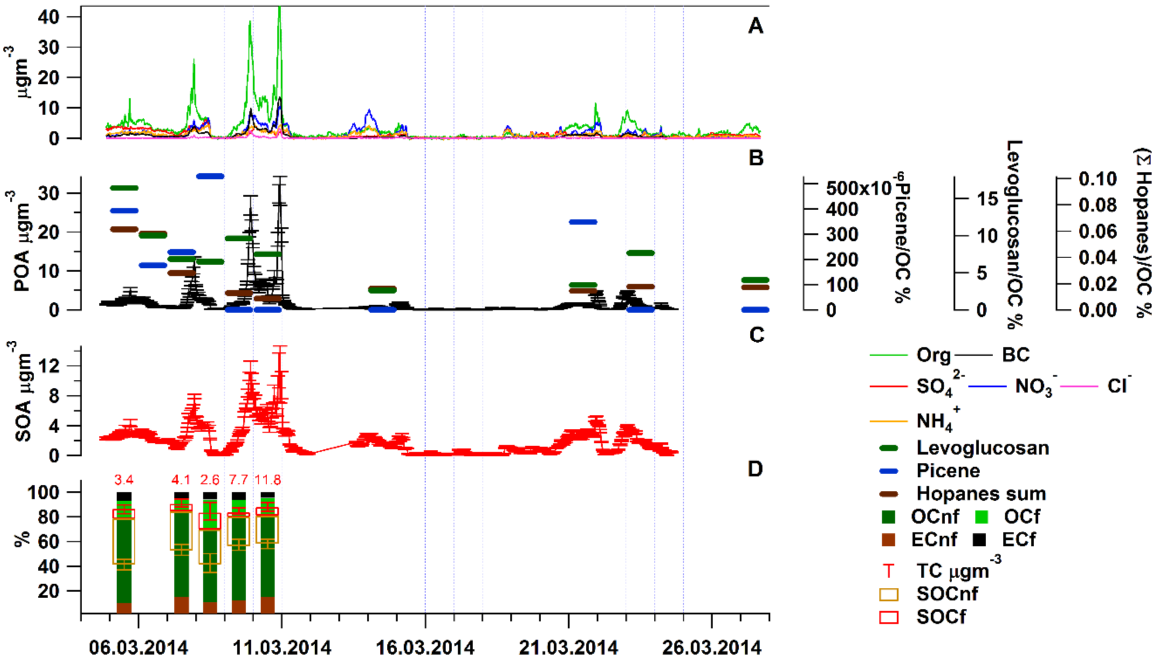


Figure 5. Average chemical composition and time series of NR-PM_1 OA for the entire study (A), B) Time series of the POA factor and percent contribution of the corresponding tracer species (levoglucosan, picene and hopanes) to total OA, C) Time series of the SOA factor, D) Relative source apportionment 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.

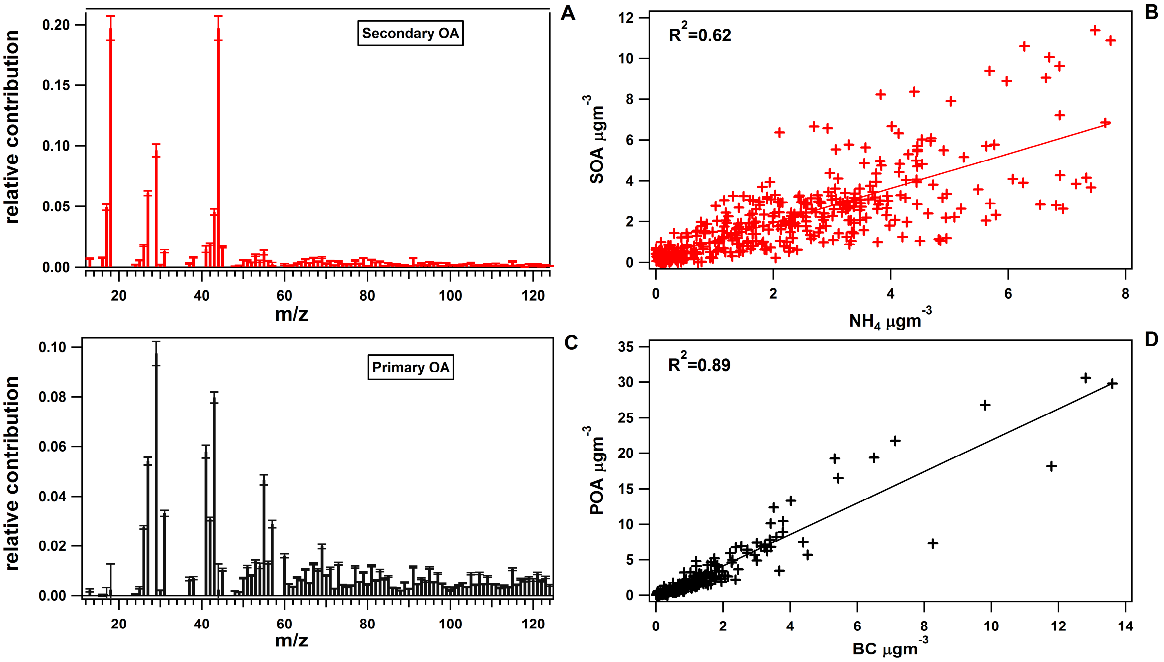


Figure 6. Mass spectra of SOA and POA, error bars represent the standard deviation of 20 PMF runs (A,C) and the scatter plots illustrate the relationship between SOA and NH_4^+ (B) and POA with BC (D).