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 #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]/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*".

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 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-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).*

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*".

Supplementary:

Table 1. Concentrations of molecular markers during grass burning event.

Concentration, analyte ng/m^3	**5.3.14**	**6.3.14**	**7.3.14**	**8.3.14**	**9.3.14**	**10.3.14**	**14.3.14**	**21.3.14**	**23.3.14**	**27.3.14**
Fluoranthene	0,54	0,35	0,57	0,65	1,00	1,18	0,08	0,50	0,15	0,21
Pyrene	0,49	0,29	0,45	0,52	0,78	0,84	0,06	0,42	0,12	0,19
Benz[a]anthracene	0,17	0,07	0,12	0,16	0,26	0,22	0,01	0,13	0,03	0,03
Chrysene	0,53	0,22	0,54	0,44	0,83	0,90	0,03	0,34	0,08	0,13
sum Benzo[b,j,k]fluoranthene	0,92	0,31	0,85	0,59	1,13	1,22	0,05	0,54	0,16	0,20
Benz[e]pyrene	0,43	0,13	0,37	0,26	0,46	0,51	0,02	0,08	0,07	0,08
Benz[a]pyrene	0,29	0,08	0,24	0,18	0,33	0,29	0,01	0,16	0,03	0,06
Perylene	0,07	0,01	0,03	0,03	0,04	0,06	<DL	0,02	0,01	0,01
Dibenz[ah]anthracene	0,014	0,004	0,012	0,01	0,016	0,012	<DL	0,01	0,004	0,003
Indeno[1,2,3-cd]pyrene	0,17	0,05	0,15	0,10	0,16	0,15	0,01	0,08	0,03	0,03
Picene	0,011	0,003	0,008	0,009	<DL	<DL	<DL	0,008	<DL	<DL
Benzo[ghi]perylene	0,35	0,12	0,28	0,22	0,11	0,41	0,02	0,17	0,07	0,08
Coronene	0,09	0,06	0,10	0,06	0,46	0,42	<DL	0,08	0,03	0,08
Retene	0,13	0,06	0,07	0,12	0,14	0,12	<DL	0,05	0,02	0,02
1(2H)-Acenaphthylenone	4,02	1,70	5,98	5,21	3,17	4,52	<DL	2,10	1,21	0,84
9H-Fluoren-9-one	0,06	0,07	0,14	0,15	0,10	0,14	<DL	0,06	0,03	0,03
Xanthone	0,03	0,02	0,05	0,06	<DL	0,05	<DL	<DL	<DL	<DL
9,10-Anthracenedione	11	4,7	8,3	9,3	8,5	21	<DL	4,2	3,9	2,2
Cyclopenta(def)phenanthrenone	0,06	0,03	0,08	0,06	0,09	0,11	0,01	0,04	0,02	0,02
1,8-Naphthalic anhydride	22	11	19	19	28	62	4,0	10	8,4	4,2
11H-Benzo[a]fluoren-11-one	0,08	0,04	0,08	0,09	0,09	0,14	0,01	0,04	0,02	0,02
11H-Benzo[c]fluoren-11-one	0,03	0,01	0,03	0,03	0,04	0,05	<DL	0,02	0,01	0,01
11H-Benzo[b]fluoren-11-one	0,13	0,05	0,14	0,12	0,16	0,22	0,01	0,07	0,03	0,02
7H-Benz[de]anthracen-7-one	0,25	0,09	0,25	0,16	0,25	0,29	0,01	0,11	0,05	0,04
Benz[a]anthracene-7,12-dione	0,07	0,05	0,08	0,07	0,16	0,16	<DL	0,06	0,04	<DL
29ab	0,44	0,28	0,25	0,65	0,38	0,31	0,09	0,16	0,18	0,13
30ab	0,71	0,37	0,45	0,62	0,31	0,47	0,12	0,17	0,12	0,11
31abS	0,23	0,18	0,16	0,19	<DL	<DL	<DL	<DL	<DL	<DL
31abR	0,34	0,16	0,12	0,27	<DL	<DL	<DL	<DL	<DL	<DL
Galactosan	2,90	1,07	0,84	1,02	11,1	12,0	<DL	0,23	<DL	<DL
Mannosan	31	11	12	9,0	68	24	3,10	7,1	7,1	7,5
Levoglucosan	460	170	240	110	520	683	34	77	130	56

DL – detection limit