

Development of a versatile source apportionment analysis based on positive matrix factorization: a case study of the seasonal variation of organic aerosol sources in Estonia

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Author's response to Referee #1:

We thank Referee #1 for the careful revision and comments which helped improving the overall quality of the manuscript. A point-by-point answer (in regular typeset) to the referees' remarks (in the *italic typeset*) follows. Changes to the manuscript are indicated in blue font.

In the following page and lines references refer to the manuscript version reviewed by anonymous Referee #1.

1) *This article presents source apportionment of OA contained in PM10 in Estonia using PMF technique on off-line AMS data sets. It also estimate the uncertainty of the PMF solution by a bootstrap analysis. Overall, this manuscript is well written, and the findings of the study are in agreement with previous studies. I have minor concerns for the manuscript as listed in the following:*

Number of samples: The author collected only 39 samples from KJ. I am afraid that only 10 samples/ season is not enough to present for the seasonal variation of organic aerosols. It would be more useful if the author could describe in more details of sampling time for 150 samples. Do those samples collected from three sites in same sampling days/ time?

We agree with anonymous referee #1 that 39 samples are in general not enough to perform a robust PMF analysis. However, these 39 samples refer only to those from KJ and the PMF analysis was performed on 150 samples collected from three cities during the same period, where aerosol sources are very similar (except for the enhancement in OilOA in KJ). In addition, the errors on the PMF time-series estimated by the bootstrap analysis are similar at the three different locations (Table S3).

Aerosols were sampled for 24h (Page 3, line 32) at the three sites. The samples were not collected on the exact same dates at the 3 sites. Following the reviewer's comment, the dates are now displayed in the

Μορφοποιήθηκε: Απόσταση κεφαλιδας από τα άκρα: 1,25 εκ., Απόσταση υποσέλιδου από τα άκρα: 1,25 εκ.

following Fig. S1 and Table S1, added in the supplementary. According to the suggestions of anonymous referee#1 we also changed the text in the Methods (Page 3, Line 33) as follows:

The measurements were performed with 24 h integrated PM₁₀ quartz fibre filter samples from KJ (31/08/2013 to 25/08/2014), Tallinn (05/09/2013 to 01/09/2014) and Tartu (05/09/2013 to 31/08/2014) (see Table S1, [S2](#) and Fig. S1 for details).

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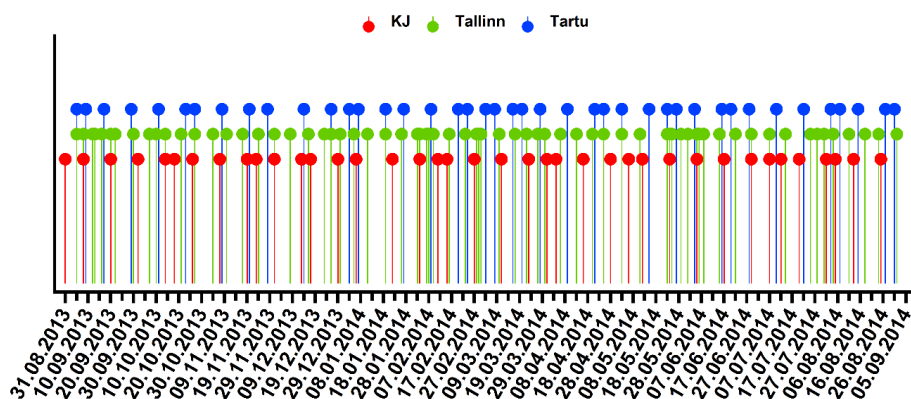


Figure S1. Dates per site. KJ represented in red, Tallinn in green and Tartu in blue.

Table S1. Dates per site.

KJ	Tallinn	Tartu	KJ	Tallinn	Tartu
2013			2014		
31.08.2013					03.01.2014
	05.09.2013	05.09.2013		05.01.2014	
08.09.2013	08.09.2013		06.01.2014		
		09.09.2013		11.01.2014	07.01.2014
	12.09.2013			19.01.2014	19.01.2014
	13.09.2013		22.01.2014		
	16.09.2013	17.09.2013		26.01.2014	
20.09.2013	20.09.2013			02.02.2014	
	22.09.2013				27.01.2014
		29.09.2013	03.02.2014	03.02.2014	
	30.09.2013			06.02.2014	
02.10.2013	07.10.2013			07.02.2014	
	10.10.2013			09.02.2014	08.02.2014
		11.10.2013	11.02.2014		
14.10.2013	14.10.2013		15.02.2014		
18.10.2013				16.02.2014	
	21.10.2013				20.02.2014
		23.10.2013		23.02.2014	
26.10.2013					24.02.2014
	27.10.2013	27.10.2013	27.02.2014		
	04.11.2013			28.02.2014	

07.11.2013		08.11.2013		01.03.2014	
	10.11.2013			02.03.2014	04.03.2014
	17.11.2013				08.03.2014
19.11.2013		20.11.2013	11.03.2014	10.03.2014	
23.11.2013					16.03.2014
	24.11.2013	28.11.2013		17.03.2014	
01.12.2013	01.12.2013			22.03.2014	20.03.2014
	08.12.2013		23.03.2014	27.03.2014	
13.12.2013		14.12.2013		30.03.2014	28.03.2014
	16.12.2013		31.03.2014		
17.12.2013			04.04.2014	06.04.2014	
	23.12.2013	26.12.2013		13.04.2014	09.04.2014
29.12.2013				20.04.2014	
	30.12.2013		16.04.2014	25.04.2014	21.04.2014
				28.04.2014	25.04.2014
			28.04.2014	03.05.2014	03.05.2014
			06.05.2014	11.05.2014	
			12.05.2014		15.05.2014
				23.05.2014	23.05.2014
			24.05.2014	24.05.2014	
				25.05.2014	27.05.2014
				29.05.2014	
				01.06.2014	04.06.2014
			05.06.2014	05.06.2014	
				06.06.2014	
				08.06.2014	
				15.06.2014	16.06.2014
			17.06.2014		
					20.06.2014
				22.06.2014	
					28.06.2014
			29.06.2014	29.06.2014	
			07.07.2014	07.07.2014	
					10.07.2014
			12.07.2014		
				14.07.2014	
			20.07.2014		

		25.07.2014	22.07.2014
		28.07.2014	
		31.07.2014	
	01.08.2014		03.08.2014
		04.08.2014	
	05.08.2014		07.08.2014
		11.08.2014	
	13.08.2014		15.08.2014
		18.08.2014	
		24.08.2014	
	25.08.2014		27.08.2014
			31.08.2014
		01.09.2014	

2) *PMF techniques: The bootstrap techniques were commonly used to check uncertainty of PMF solutions for decades. I do not think it is "novel technique" as the author state in Page 3, Line 10. Could the author explain more the novelty of their bootstrap techniques?*

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We did not intend to claim that the bootstrap technique used here for the uncertainty exploration of PMF is novel. We apologize for this misunderstanding. The novelty corresponds to the selection technique applied after the bootstrap analysis, which enables evaluating the quality of a large set of solutions. We changed the text accordingly (Page 3, Line 10):

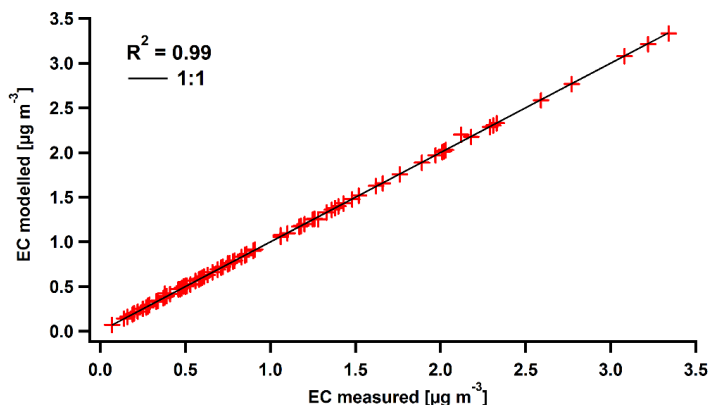
10 *In this study, we propose a novel technique to evaluate the selection of the PMF solutions generated through a large number of bootstrap iterations.*

3) *In equation 3, do the authors assume the EC/WSOA ratio for each source is constant? If yes, please provide any references for that. In addition, the author should provide the correlation between measured EC and modeled EC concentration based on equation (3).*

15

According to the definition of PMF (Paatero, 1999), the sources are represented by constant profiles and varying intensities; therefore, as noted by the reviewer the EC/WSOA ratio for each source is constant. We note that this ratio is not assumed a priori, but determined through the PMF analysis. We also note that the PMF analysis performed to assess the EC sources is fully constrained. Therefore, EC modelled corresponds to the measured EC as shown by the figure below:

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Correlation between EC measured by the thermal/optical method and the modelled EC calculated by PMF ($EC = EC_{tr} + EC_{bb} + EC_{oil} + EC_{md}$).

5 | **Author's response to Referee #2:**

We thank Referee #2 for the careful revision and comments which helped improving the overall quality of the manuscript. A point-by-point answer (in regular typeset) to the referees' remarks (in the *italic typeset*) follows. Changes to the manuscript are indicated in blue font.

10 In the following page and lines references refer to the manuscript version reviewed by anonymous Referee #2.

1) *This manuscript investigates a year of organic aerosol in PM10 at three sites in Estonia. The organic aerosol was characterized by analyzing the water-soluble filter extract with an HR-ToF-AMS. The PM10 samples were 24-hour integrated PM10 quartz fiber filter samples using a high-volume sampler. Source apportionment of the AMS mass spectra was performed using positive matrix factorization. Seven factors were found between the three sites including an oil factor, sulfate-rich factor, summer oxygenated OA, winter oxygenated OA, dust, primary biological OA, and biomass burning OA. The BBOA, PBOA, WOOA, and SOOA factors were all validated with externally measured organic markers. The dust factors were validated with external measurements of Ca²⁺. A bootstrap analysis is used to analyze the results and factor uncertainties. The paper thorough in its investigation and very well written. With some minor changes I suggest this paper be accepted.*

Specific comment: For the estimation of traffic contribution to EC calculation what are the EC/WSOA values used? The ratio of EC/OC measured in biomass burning emissions highly variable (Pokhrel et al., 2016), as is SOA formation in biomass burning plumes (Jolleys et al., 2012; May et al., 2015). Given this range of possible EC/WSOA values, language as to uncertainties regarding this analysis should be added.

30 We need to add some clarifications about the PMF analysis performed to apportion the EC contribution to the different sources. The analysis includes 4 variables: the time-series of the concentrations of EC, water soluble BBOA (WSBBOA), WSSCOA, and WSOilOA. Four factors are considered only representing primary anthropogenic sources: traffic, biomass burning, road dust resuspension/tire-wear, and oil related processes. The contribution of EC in all profiles is not constrained (i.e., in none of the profiles is the EC/OA ratio fixed a priori). The contribution of the water-soluble organic aerosol from a certain source is also not constrained in the factor profile
 35 representing the source in question, while the organic aerosol from all other sources are set to 0 in this profile. As mentioned in the response to reviewer#1, such setting means that the EC variability is fully

explained. In such setting, we do not assume any EC/WSOA in the traffic profile. As mentioned above, we also do not include any factor representing secondary OA. Therefore, uncertainties related to the EC/WSOA in aged biomass burning do not affect the analysis. We indeed agree with the reviewer comment that WSOA/EC is highly variable in primary sources, e.g. biomass burning. Therefore, we have performed a bootstrap analysis to assess the uncertainties in retrieving the contributions of the different sources to EC. These are represented as PDFs in Figure S4.

We have adapted the text in the manuscript as follows (Page 7, line 11):

Here, EC_{bb} , EC_{oil} and EC_{rrd} represent the EC concentration time-series related to the primary sources biomass burning, oil shale industry and resuspension of road dust/tire wear, respectively, while, a , b , and c are the EC_{tr} :WSOA ratios characteristic of the emissions from the same sources and were obtained as outputs of the model. This new methodology, based on PMF, is especially pertinent as unlike other inversion techniques it sets positive constraints on a , b and c and offers the possibility of resolving the contributions of factors for which no constraints are available, here EC_{tr} .

We found that EC_{tr} contributed $57\% \pm 5\%$ to the total EC (on a yearly average), while $36\% \pm 5\%$ of EC was attributed to biomass burning, $4\% \pm 1\%$ to road dust resuspension and $3\% \pm 1\%$ to the oil shale emissions (Fig. S4). The contribution of EC from fossil fuel combustion (EC_{ff}) measured at a site similar to Tartu, i.e., an Alpine valley in Southern Switzerland, Magadino in 2014 (Vlachou et al., 2018) was in agreement with our EC_{tr} contribution, with a yearly average of $55\% \pm 7\%$. Also in Zurich, an urban site, EC_{ff} ranged from 40% to 55% during winter 2012 (Zotter et al., 2014). From the EC_{tr} contribution, we estimated that the HOC (obtained by multiplication of the EC_{tr} time series with the HOC:EC ratio) contributed 4% to the total OC on a yearly average.

Μορφοποιήθηκε: Δείκτης

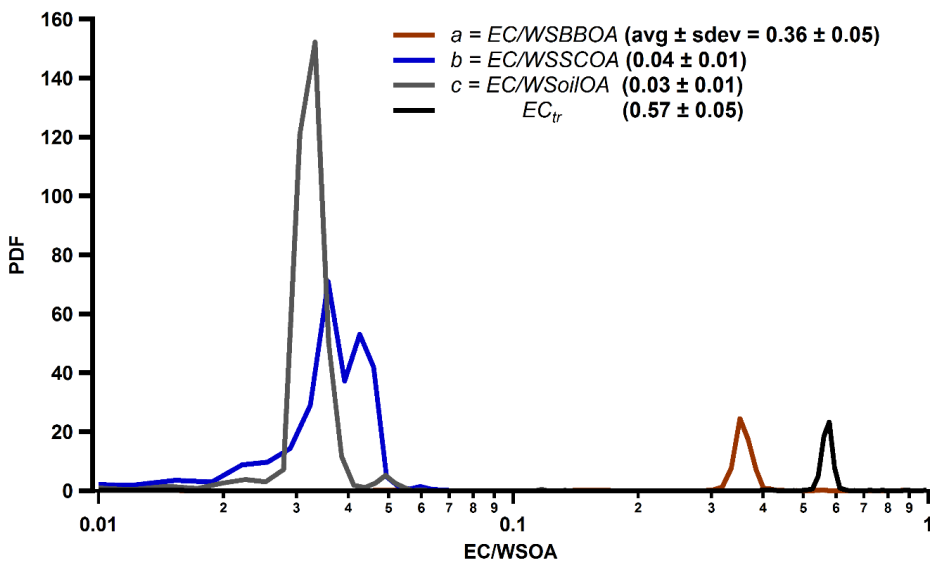


Figure S4. Probability density functions for the EC:WSOA ratios (a for WSBBOA, b for WSSCOA and c for WSoilOA) characteristic of the emissions from the same sources obtained by the 1000 PMF runs.

2) How many samples per season per site were there?

We gathered all the information in the following table. We will include it in the supplementary along with Table S1 and Fig. S1 which contain all the dates per site (as mentioned in the response to reviewer#1).

Table S2. Number of samples per season per site.

Seasons	Number of samples per season		
	KJ	Tallinn	Tartu
Summer	11	16	11
Autumn	9	18	10
Winter	10	18	9
Spring	9	17	12

5

3) Fig 7. The colours of the two bars are very similar and hard to distinguish.

We agree with anonymous referee#2 and therefore we changed the colours from light and dark green to red and blue as shown in the plot below.

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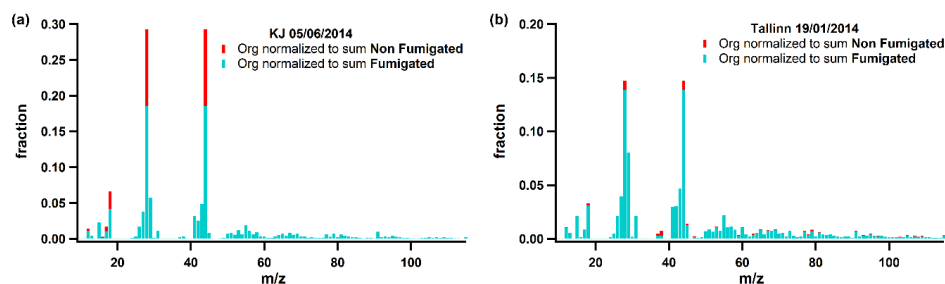


Figure 7. Examples of fumigated and non-fumigated mass spectra from two samples, with a high (KJ 05/06/2014, a), and a low dust concentration (Tallinn 19/01/2014, b).

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References

Paatero, P.: The multilinear engine – A table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model, J. Comput. Graph. Stat., 8, 854–888, 1999.

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Development of a versatile source apportionment analysis based on positive matrix factorization: a case study of the seasonal variation of organic aerosol sources in Estonia.

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Abstract. Bootstrap analysis is commonly used to capture the uncertainties of a bilinear receptor model such as the positive matrix factorisation (PMF) model. This approach can estimate the factor related uncertainties and partially assess the rotational ambiguity of the model. The selection of the environmentally plausible solutions though can be challenging and a systematic approach to identify and sort the factors is needed. For this, comparison of the factors between each bootstrap run and the initial PMF output, as well as with externally determined markers, is crucial. As a result, certain solutions that exhibit sub-optimal factor separation should be discarded. The retained solutions would then be used to test the robustness of the PMF output. Meanwhile, analysis of filter samples with the Aerodyne aerosol mass spectrometer and the application of PMF and bootstrap analysis on the bulk water soluble organic aerosol mass spectra has provided insight into the source identification and their uncertainties. Here, we investigated a full yearly cycle of the sources of organic aerosol (OA) at three sites in Estonia, Tallinn (urban), Tartu (suburban) and Kohtla-Järve (KJ, industrial). We identified six OA sources and an inorganic dust factor. The primary OA types included biomass burning, dominant in winter in Tartu accounting for $73\% \pm 21\%$ of the total OA, primary biological OA which was abundant in Tartu and Tallinn in spring ($21\% \pm 8\%$ and $11\% \pm 5\%$, respectively) and two other primary OA types lower in mass. A sulphur containing OA was related to road dust and tire abrasion which exhibited a rather stable yearly cycle, and an oil OA was connected to the oil shale industries in KJ prevailing at this site comprising $36\% \pm 14\%$ of the total OA in spring. The secondary OA sources were separated based on their seasonal behaviour: a winter oxygenated OA dominated in winter ($36\% \pm 14\%$ for KJ, $25\% \pm 9\%$ for Tallinn and $13\% \pm 5\%$ for Tartu) and was correlated with benzoic and phthalic acid implying an anthropogenic origin. A summer oxygenated OA was the main source of OA in summer at all sites ($26\% \pm 5\%$ in KJ, $41\% \pm 7\%$ in Tallinn and $35\% \pm 7\%$ in Tartu) and exhibited high correlations with oxidation products of α -pinene like pinic acid and 3-methyl-1, 2, 3-butanetricarboxylic acid (MBTCA) suggesting a biogenic origin.

1. Introduction

40 Particulate matter of aerodynamic diameter smaller than $10 \mu\text{m}$ (PM_{10}) has been extensively explored at many sites around the globe due to their various adverse effects upon human health and climate. In Europe, several monitoring networks have been measuring PM_{10} for long time periods and an increasing trend in concentrations from north to south was noticed (Fuzzi et al., 2015, Putaud et al., 2010). Despite of this, some North European countries are still suffering from PM_{10} daily limit exceedances (European Environment Agency report No

13/2017), and according to modelling studies following the “current legislation” scenarios, some of these sites will remain exposed to high PM₁₀ standards up to 2030 (Kiesewetter et al., 2015). Therefore, understanding the origins of the pollutants can play a crucial role for future abatement policies.

5 While large efforts have been devoted to the investigation of the sources and the chemical composition of PM₁₀ and in particular the organic fraction in ~~western-Western~~ and ~~central-Central~~ Europe, measurements in Eastern Europe and the Baltic region are scarce. More specifically, ~~the~~ organic aerosol (OA) composition in Estonia has received little attention so far. PM_{2.5} organic aerosol source apportionment was extensively studied by Elser et al. (2016) who performed mobile lab measurements during March 2014 at two different sites, Tallinn and Tartu. They found similar sources of OA at both sites where residential biomass burning, traffic and long-range transported OA were the major sources of OA. They also found a localised residential influenced OA factor, which was connected to cooking activities and possibly coal and waste burning. Whilst the long-range transported OA was dominating during night time and during several events when polluted air masses were transported from Northern Germany, the remaining factors were important during day time. These results provided insights into the spatial resolution of OA; nevertheless, they were limited to short time periods, hence, the seasonal variation of the pollutants remains unknown. Residential wood combustion and traffic were also presented as important sources of PM in previous long-term air pollution studies in Estonia (Urb et al., 2005, Orru et al., 2010). However, they did not provide any quantitative source apportionment on OA.

The offline AMS technique was recently developed by Daellenbach et al. (2016) where aqueous filter extracts are measured after nebulisation with an Aerodyne high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS, Canagaratna et al., 2007) and the resulting organic mass spectra are analysed with positive matrix factorisation (PMF, Paatero 1997). This technique has significantly increased our capability in investigating and identifying the seasonal behaviour of OA sources at several sites around the globe (Huang et al., 2014, Daellenbach et al., 2017, Bozzetti et al., 2017a). In addition, this technique allows for OA measurements of different size fractions overcoming the limitation given by the transmission window of the AMS, resulting in 25 quantifying sources from the coarse mode, such as primary (i.e. OA directly emitted in the atmosphere) biological (Bozzetti et al., 2016) or sulphur containing primary OA sources (Daellenbach et al., 2017).

PMF is widely used to analyse ambient aerosol measurement data by decomposing the input aerosol mass spectra into factor concentration time series and factor profiles. To do so, PMF iteratively solves the bilinear Eq. (1), where $\mathbf{X}_{i,j}$ represents the measured input data matrix in which i is the number of samples and j the chemical species measured, $\mathbf{G}_{i,k}$ represents the concentration time series matrix in which k is the number of factors, $\mathbf{F}_{k,j}$ represents the factor profiles matrix and \mathbf{E} the residual matrix. The goal of PMF is to solve Eq. (1) such that the object function Q (Eq. 2) is minimised. In Eq. (2), \mathbf{U} represents the corresponding error matrix.

$$\mathbf{X}_{i,j} = \sum_k \mathbf{G}_{i,k} \mathbf{F}_{k,j} + \mathbf{E}_{i,j} \quad (1)$$

$$Q = \sum_i \sum_j [\mathbf{E}_{i,j} / \mathbf{U}]^2 \quad (2)$$

Bilinear models suffer from rotational ambiguity; that is mathematically similar goodness of fit (Henry, 1987), leading to uncertainties in extracting the contributions of different OA sources. Additional modelling errors may occur due to the user subjectivity in analysing natural phenomena, when for example selecting the number of interpretable factors or estimating the error matrix.

40 The bootstrap analysis (Davison and Hinkley, 1997), a resampling technique of the original data and error matrices, has been widely adopted to assess to a certain extent the rotational ambiguity related to PMF analysis (Brown et al., 2015). For each bootstrap iteration a random number of samples are selected with repeats from the original input matrices (*base case*), to recreate new input matrices with the same dimensions (*bootstrap iteration*) that will be analysed with PMF. As a result, the bootstrap analysis results in a great number of solutions, whose environmental representativeness has to be assessed, which requires a systematic approach in 45 relating the separated factors to specific sources. This factor classification has been typically based on the

contributions of certain markers (e.g. $C_2H_4O_2^+$ to identify biomass burning OA or CO_2^+ to identify secondary OA) (Daellenbach et al., 2017, 2018, Bozzetti et al., 2017a, Vlachou et al., 2018) in the case of the application of PMF to AMS data. However, in datasets with similar factor profiles, for example two oxygenated OA factors or more, this type of sorting can become challenging, especially when a bootstrap iteration does not provide the expected factors. To assess the quality of the different bootstrap solutions, users typically compare the factor time-series to external marker measurements, when available, and discard suboptimal solutions using a set of acceptance criteria (Ulbrich et al., 2009, Zhang et al., 2011, Norris and Brown, 2014, Bozzetti et al., 2017a, 2017b, Zhang et al., 2017).

In this study, we propose a novel technique [to evaluate the selection of the PMF solutions generated through a large number of bootstrap iterations](#). The method is based on the examination of the correlation matrix between the base case and bootstrap iterations for both time series and profiles, without setting a priori a defined threshold in the correlation coefficient. We assess the performance of the technique (accuracy and probability of false positive and false negative results) by comparing the factors' time-series to the available specific markers. We have applied the technique to an unprecedented dataset of 150 PM_{10} filter samples from 3 sites in Estonia covering a full year (Sept. 2013 - Sept. 2014), where anthropogenic and natural emissions of primary and secondary organic aerosols could be extracted.

2. Methods

2.1 Sampling sites

The samples were collected at three different sites in Estonia: Tallinn, Tartu and Kohtla-Järve. Tallinn is the capital and the largest city of Estonia located on the northern coast facing the Gulf of Finland. The measurement station is located about 9 km from the city centre, in the sub-district Õismäe (59°24'50.927", 24°38'57.207", 8.5 m a.s.l.). Tartu is the second largest city of Estonia, located in the south-eastern part of the country, in the valley of the Emajõgi River, a location that favours temperature inversions and the trapping of air pollutants. The measurement station (58°22'14.183", 26°44'5.517", 39.5 m a.s.l.) is positioned in the city centre. According to Orru et al. (2010) traffic and local heating are important sources of air pollution at these sites. In both cities the fleet of cars increases in contrast to the limited street network capacity. Moreover, the local heating is more pronounced in Tartu compared to Tallinn. Kohtla-Järve (KJ) is a coastal industrial city located in the north-eastern part of Estonia (59°24'34.513", 27°16'43.166", 55.5 m a.s.l.). The main industries are related to large production of petroleum products, oil shale processing and electricity generation. As it is not a highly populated area, residential heating or traffic are not as important as in the other two cities.

The measurements were performed with 24 h integrated PM_{10} quartz fibre filter samples from KJ (31/08/2013 to 25/08/2014), Tallinn (05/09/2013 to 01/09/2014) and Tartu (05/09/2013 to 31/08/2014) (see Tables S1, S2 and Fig. S1 for details). PM was collected onto 15 cm diameter quartz filters, using a high volume sampler (500 l min^{-1}). After exposure, the filter samples were wrapped in lint-free paper, sealed in polyethylene bags and stored at -20 °C.

2.2 Major ionic species, sugar and acid analyses

The additional filter measurements, performed to corroborate and support the source apportionment, are listed in Table 1.

2.3 Offline AMS technique

The offline AMS technique was established by Daellenbach et al. (2016) and is briefly described in the following. From each filter sample, 4 punches of 16 mm diameter were extracted in 15 ml of ultrapure water (18.2 MΩ cm at 25 °C with total organic carbon < 3 ppb). The liquid extracts were inserted into an ultra-sonic bath for 20 minutes at 30 °C. The ultra-sonicated samples were then filtered through a nylon membrane syringe of 0.45 μm. Out of the resulting solutions, aerosols were generated in Ar (≥ 99.998% Vol., Carbagas, 3073, Gümliigen, Switzerland) via an Apex Q nebulizer (Elemental Scientific Inc., Omaha, NE, USA) operating at 60 °C and subsequently directed into the AMS after getting dried by a Nafion dryer.

Μορφοποιήθηκε: Γραμματοσειρά: Όχι Έντονα

The technique was performed on 150 filter samples in total: 39 from KJ, 69 from Tallinn and 42 from Tartu (Tables S1 and S2). The resulting organic spectra were analysed by PMF with the use of the Multilinear engine 2 (ME-2; Paatero, 1999). The interface for the data processing was provided by the Source finder toolkit (SoFi version 4.9; Canonaco et al., 2013) for Igor Pro (WavemetricsInc, Portland, Oregon, USA).

- 5 The NH_4NO_3 artefact on the CO_2^+ signal (Pieber et al., 2016) was also accounted for. For a thorough description of the artefact and the correction procedure the reader is referred to Pieber et al. (2016) and to Daellenbach et al. (2017).

2.4 PMF input and uncertainties

10 As stated in the introduction, the input data matrix for the PMF is the organic mass spectra data matrix $\mathbf{X}_{i,j}$ that which consists of a combination of factor profiles, and time-series and the input error matrix \mathbf{U} includes the blank variability and the measurement uncertainties. Before using the PMF algorithm, all the fragments with signal-to-noise ratio (SNR) below 0.2 were removed from the input matrix and the ones with SNR below 2 were down-weighted according to Paatero and Hopke's (2003) recommendations. Note that the PMF input matrix $\mathbf{X}_{i,j}$ included the data from all 3 sites.

15 To obtain quantitative results, both data and error matrices were multiplied by the externally measured water soluble OC (WSOC) times the OM:OC ratio retrieved from the factor profiles of the matrix $\mathbf{X}_{i,j}$.

20 Even though traffic is expected to be one of the primary sources of air pollutants especially in Tallinn and Tartu, a clear hydrocarbon like OA (HOA) which mainly contains non water soluble compounds could not be identified due the extraction procedure used. To assess a potential effect of the water soluble HOA (WSHOA) on the PMF results we estimate the WSHOA contribution to the different fragments in the data matrix. The calculation was based on the time series of the concentration of EC, and the averaged high resolution HOA reference factor profiles from Crippa et al. (2013) and Mohr et al. (2012) multiplied by the HOA_2EC ratio ($=0.4$) reported by El Haddad et al. (2013) times the recovery $R_{\text{HOA}} = 0.11$ reported by Daellenbach et al. (2016) (see Section 4 for more information on the recoveries). The calculated WSHOA data matrix was then subtracted from the original data matrix. The PMF output did not change with the subtraction of WSHOA even though the calculated concentration of the latter was a high estimate due to the assumption that EC only originates from traffic. A thorough apportionment of EC and the calculation of HOC will be discussed in Section 4.1.

30 The variability of the AMS input dataset was best described by a seven factor solution which will be thoroughly described in Section 3.1 below. To assess the stability of the PMF solution and the sensitivity of the model for the WSHOA subtraction, we performed 250 bootstrap runs by perturbing the HOA_2EC and R_{HOA} parameters within their errors (1 standard deviation, σ) assuming a normal distribution. Note that this number of runs was restricted by computational limitations.

35 The sorting of the factors and the concomitant selection of the retainable solutions out of the 250 runs was based on the correlation (R Spearman, R_s) of the time series between the base case (which is the PMF result before bootstrapping) and each bootstrap iteration n , as well as the correlation (R_s) of each factor profile between the base case and each iteration n . In the following, the sorting based on the time series is denoted as "ts" and the sorting based on profiles is denoted as "pr". The criteria, followed for the selection or rejection of each solution, are described in Section 3.2.

3. Source apportionment

3.1 Interpretation of PMF factors

40 As already mentioned, the variability of the water soluble organic mass spectra was best explained by a seven factor solution, to which we refer as *base case*. The factors found were:

1. An oil related OA which was rich in hydrocarbons (Fig. 1a) and showed elevated concentrations mainly in KJ (Fig. 1b).

2. A sulphur containing OA (SCOA) factor with a pronounced peak at m/z 79 (CH_3SO_2^+) (Fig. 1a) and rather stable contributions at all sites (Fig. 1b). As this factor was significantly enriched in the coarse mode (Vlachou et al., 2018), mainly found in urban areas influenced by traffic at other European sites (Daellenbach et al., 2017) and clearly associated with fossil carbon (Vlachou et al., 2018), we have previously related it to asphalt abrasion or tire wear.
3. A summer oxygenated OA (SOOA) with enhanced m/z 43 ($\text{C}_3\text{H}_2\text{O}^+$) and 44 (CO_2^+) peaks (Fig. 1a) which was highest during summer at all sites (Fig. 1b).
4. A winter oxygenated OA (WOOA) with enhanced peaks at m/z 28 (CO^+) and 44 (CO_2^+) (Fig. 1a) dominating in winter at all sites (Fig. 1b). Both of these two oxygenated factors (SOOA and WOOA) were also found in different European sites and were connected to non-fossil sources; biogenic and anthropogenic respectively (Vlachou et al., 2018, Daellenbach et al., 2018). Such a distinction was also found in Canonaco et al. (2015) where an online ACSM was used.
5. A factor with a significantly pronounced peak at m/z 44 (CO_2^+) (Fig. 1a) and elevated concentrations in summer (Fig. 1b), which was identified as dust. This factor will be more thoroughly examined in Section 4.
6. A primary biological OA (PBOA) which exhibited high contributions of the fragment $\text{C}_2\text{H}_5\text{O}_2^+$ (at m/z 61, Bozzetti et al., 2016) (Fig. 1a) and increased concentrations during late spring and summer at all sites (Fig. 1b).
7. A biomass burning OA (BBOA) with a characteristic peak at m/z 60 ($\text{C}_2\text{H}_4\text{O}_2^+$) (Alfarra et al., 2007) (Fig. 1a) and elevated concentrations during late fall and winter in Tallinn and especially Tartu (Fig. 1b).

3.2 PMF uncertainty analysis: factor sorting and solution selection

The framework for factor sorting and solution selection proceeded as follows:

1. A correlation matrix was composed including all the correlations between base case factor time series (profiles) represented in rows and bootstrap iteration n time series (profiles) represented in columns, demonstrating the R_s per correlation (Fig. 2).
2. Factors were sorted according to the highest correlation of their time series (profiles) with the base case factor time series (profile).
3. Solutions were discarded, if any of the correlation coefficients occurring in the matrix diagonal was not statistically significantly higher than at least one of the coefficients in the respective column or row (significance level $\alpha=0.05$). These selection criteria have two implications. (1) Every factor separated in a bootstrap run should correspond to a unique factor of the seven factors separated in the base case. (2) All factors that could be identified in the base case have one unambiguous corresponding factor in the bootstrap run. We have statistically evaluated the comparison between the Spearman coefficients by treating them as if they were Pearson coefficients (Myers et al., 2006) and applying the standard Fisher's z-transformation and subsequent comparison using a t -test. This approach was reported to be more robust with respect to Type I error (false positive) than ignoring the non-normality and using Pearson instead of Spearman coefficients.

An example of the correlation matrix of a retained solution is shown in Fig. 2a for time series and 2b for profiles. Meanwhile, Fig. 2c and 2d represent ~~an~~ examples of a bootstrap iteration ($n=140$) where the solution was rejected because SCOA was not resolved, based on both ts and pr analysis, respectively. In Fig. 2c, the highest correlation between the time series of factor 2 and the factors of the base case was found with ~~d~~Dust instead of SCOA, yet much weaker ($R_s=0.34$) than the correlation between factor 7 and ~~d~~Dust ($R_s=0.79$). Therefore, factor 7 could be identified as ~~d~~Dust and factor 2 could not be identified as an interpretable factor. In Fig. 2d factor profile 2 correlated most with the base case SCOA profile; however this correlation was not significantly higher than the correlation between factor 2 and ~~d~~Dust. Moreover, base case SCOA correlated better with factor 6, which was related to SOOA, indicating that SCOA could not be unambiguously related to factor 2.

To validate the selection of the solutions we compared the factors of each bootstrap iteration with an externally measured marker; more specifically BBOA with levoglucosan, PBOA with cellulose, WOOA with phthalic acid and SOOA with 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). The retained solutions exhibited the highest correlations between the external markers and the respective factors (red markers in Fig. 3). To seal the validity of the retained solutions, we also compared the R_s between the base case factors and their respective external marker with the R_s between the bootstrap iteration factors and their respective external markers. We performed the bootstrap technique for a second time on the time series of the base case factors and the respective external markers for 1000 times. The resulting R_s coefficients are represented in probability density functions (PDF) indicated as red curves in Fig. 3, centred at 0.8 for BBOA (Fig. 3a), 0.7 for WOOA (Fig. 3c) and 0.9 for SOOA (Fig. 3d) and a broader one centred at 0.45 for PBOA (Fig. 3b). In all four cases the retained solutions, either coming from the “ts” or the “pr” approach, spanned around the centre of each PDF (Fig. 3 and S4-Fig. S2 for the “pr”) and most of the solutions where at least one factor was not resolved (black markers in Fig. 3) were not included within the PDF boundaries. The general agreement between the PDFs and the retained solutions ratified the solution selection approach, however, there were still some cases of possible misallocation of retained or rejected solutions (for example a few black markers appearing at the centre of the PDF, Fig. 3c).

To assess whether the retained bootstrap solutions share the same quality with the base case solution with regard to correlations between factors and markers, we calculated the probability of type I (false positive) and type II (false negative) errors associated with the solution selection approach (Fig. 4). The analysis entailed a quantitative comparison of the Spearman coefficients obtained between markers and factor time series from the bootstrap iterations, $R_{s_{\text{boots}}}$, with the respective Spearman coefficients obtained between markers and factor time series from the base case $R_{s_{\text{base}}}$, considering the same samples as in the corresponding bootstrap iterations. The comparison between $R_{s_{\text{boots}}}$ and $R_{s_{\text{base}}}$ was performed by applying a Fisher transformation followed by a t -test. We defined true positive and false negative as the red (retained solutions) and black (non-resolved factors) points, respectively lying within the PDF boundaries with regard to the total number of red and black points within the PDF boundaries. True negative and false positive were defined as the black and red points lying outside the PDF boundaries with respect to the total number of red and black points outside the PDF boundaries. The limits between false positive and false negative were set by 2 standard deviations from the one-to-one line. The percentages of the accuracy and the probability of false positive or false negative cases are compiled in Table S4-S3. Sorting based on profiles seemed less reliable and is more prone to false negative solutions (Tables S4-S3 and S2-S4), as the profiles often look similar and therefore the R_s exhibits high values for all factors (Fig. 2b and d). On the contrary, sorting based on time series showed clearer results as the R_s spanned over a greater range of values (Fig. 2a and 2c). Still the “ts” method produced false negative solutions, for example 53% for PBOA due to the combination of (i) limited number of points available for cellulose and (ii) the representativeness of the marker time series after the resampling (bootstrap analysis). Note that PBOA was important only during a few days in spring and therefore it is possible that these days were not always selected in the resampling process. The SOOA on the other hand exhibited 0% false negative and 16% false positive cases always demonstrating high $R_{s_{\text{boots}}}$ and $R_{s_{\text{base}}}$ values.

However, in any of the two methods “ts” and “pr”, the Fisher-transformed correlation coefficient rendered the selection of the solution evident, and eventually the two sorting methods yielded a very similar retained solution space (Fig. 4 and 5). Figure 5 depicts the correlation between the averaged common retained solutions and the averaged retained solutions coming from either the “ts” or the “pr” sorting method for the example of BBOA (correlations for the other factors are shown in Fig. S2-S3). There is a minor deviation from the one to one line for the standard deviation scatter plot (Fig. 5b) for the “ts” sorting method. However, as soon as the solutions got weighted according to the correlation between external marker and bootstrap run time series, then the deviation decreased (blue markers in Fig. 5). The weighting factor w_i was calculated as:

$$w_i = \frac{1}{\sqrt{\sum_i (SE)^2}} \quad (4),$$

where SE is the standard error resulting from the regression between external marker and bootstrap iteration.

4. Investigation of sources and discussion

4.1 Estimation of traffic contribution to EC and OC

We estimated above that the traffic contribution to WSOA (<1%) can be neglected and has little effect on the PMF outputs. However, traffic might be an important source of EC and OA, which is assessed in the following.

5 To estimate the percentage of EC coming from traffic (EC_{tr}) we used the ME-2 model (with SoFi standard version 6.399, Canonaco et al., 2013) assuming that the sources of EC are biomass burning, resuspension of road dust, industrial emissions from the oil shale factories and traffic. Here the input data matrix included the time series of water soluble BBOA (WSBBOA), WSSCOA, WSOiOA and EC. PMF was called 1000 times varying the initial seed to solve Eq. (3).

$$10 \quad EC = EC_{tr} + EC_{bb} + EC_{oil} + EC_{rd} = EC_{tr} + a \cdot WSOA_{bb} + b \cdot WSOA_{oil} + c \cdot WSOA_{soil} \quad (3)$$

15 Here, EC_{bb} , EC_{oil} and EC_{rd} represent the EC concentration time-series related to the primary sources biomass burning, oil shale industry and resuspension of road dust/tire wear, respectively, while, a, b, and c are the $EC:WSOA$ ratios characteristic of the emissions from the same sources and were obtained as outputs of the model. This new methodology, based on PMF, is especially pertinent as unlike other inversion techniques it sets positive constraints on a, b and c and offers the possibility of resolving the contributions of factors for which no constraints are available, here EC_{tr} .

20 We found that EC_{tr} contributed $57\% \pm 5\%$ to the total EC (on a yearly average), while $36\% \pm 5\%$ of EC was attributed to biomass burning, $4\% \pm 1\%$ to road dust resuspension and $3\% \pm 1\%$ to the oil shale emissions (Fig. S4). The contribution of EC from fossil fuel combustion (EC_{ff}) measured at a site similar to Tartu, i.e., an Alpine valley in Southern Switzerland, Magadino in 2014 (Vlachou et al., 2018) was in agreement with our EC_{tr} contribution, with a yearly average of $55\% \pm 7\%$. Also in Zurich, an urban site, EC_{tr} ranged from 40% to 55% during winter 2012 (Zotter et al., 2014). From the EC_{tr} contribution, we estimated that the HOC (obtained by multiplication of the EC_{tr} time series with the HOC:EC ratio) contributed 4% to the total OC on a yearly average.

25 Here, EC_{bb} , EC_{oil} and EC_{rd} represent the EC concentration time series related to biomass burning, oil shale industry and resuspension of road dust, respectively, and a, b, and c are the $EC:WSOA$ ratios characteristic of the emissions from the same sources. This new methodology, based on PMF, is especially pertinent as unlike other inversion techniques it sets positive constraints on a, b and c and offers the possibility of resolving the contribution of factors for which no constraints are available, here EC_{tr} .

30 We found that EC_{tr} contributed 57% to the total EC (on a yearly average), while 36% of EC was attributed to biomass burning, 2% to road dust resuspension and 4% to the oil shale emissions. The contribution of EC from fossil fuel combustion (EC_{ff}) measured in a similar site to Tartu, i.e. an Alpine valley in Southern Switzerland, Magadino in 2014 (Vlachou et al., 2018) was in agreement with our EC_{tr} contribution as the yearly average was $55\% \pm 7\%$. Also in Zurich, an urban site, EC_{tr} ranged from 40% to 55% during winter 2012 (Zotter et al., 2014). From the EC_{tr} contribution, we estimated that the HOC (multiplication of the EC_{tr} time series with the ratio HOC/EC) contributed 4% to the total OC on a yearly average.

4.2 Scaling to organic carbon

40 All the retained solutions (in total 62%) were averaged per factor and their seasonal behaviour as well as their correlations with the external markers are presented in Section 4.4. Note that all the water soluble factors were recovered following the method described in Daellenbach et al. (2016) and Vlachou et al. (2018). The recoveries were calculated by fitting Eq. (4).

$$45 \quad OC_{i,n} = \sum_k \frac{WSOC_{i,n,k}}{R_k} \quad (4)$$

where $OC_{i,n}$ is the OC concentration per bootstrap run n per sample i , R_k is the recovery R per factor k , and $WSOC_{i,n,k}$ is the water soluble OC concentration calculated based on the measured WSOC and the OM:OC per factor. From the $OC_{i,n}$ the part of hydrocarbon like OC as well as the inorganic carbon related to dust were removed. The carbonate carbon investigation and calculation is discussed in Section 4.3. To define the

recoveries we used a non-negative multilinear fit. The starting points of the fitting for each R_k with the exception of R_{oil} were obtained from the literature (Bozzetti et al., 2016, Daellenbach et al. 2016 and Vlachou et al., 2018) and were randomly varied within their literature range with an increment of 10^{-4} . The final distributions of the recoveries are shown in the Supplementary (Fig. S3S5). The recoveries in this study were all shifted to the lower end of the recoveries reported in the literature. While the reason remains unclear, the water solubility of OA is dataset specific therefore we can expect differences to other datasets. Moreover, we re-measured in a different laboratory the OC concentrations from a subset of 21 samples covering all sites and all seasons. The agreement between the two differently determined OC concentrations was excellent (Fig. S4S6, slope = 0.93, $R^2 = 0.99$).

4.3 Exploration of the dust factor

Mineral dust can contain a significant amount of inorganic carbon in the form of CO_3^{2-} . The water extracts used in the offline AMS technique have a pH that is always < 8 . Therefore, the CO_3^{2-} in our samples is all solubilized into HCO_3^- (pKa ($\text{HCO}_3^-/\text{CO}_3^{2-}$) = 10.33, Bruice, 2010). The latter is shown to release CO_2 when it undergoes thermal decomposition on the AMS vaporiser (at 600°C) (Bozzetti et al., 2017b). Thus, the contribution of CO_2 to organic aerosols is overestimated and the fraction coming from the inorganic carbon should be removed from the OA spectra.

To remove the influence of the inorganic dust, we estimated the carbonate carbon concentrations (C_CO_3) corrected for the relative ionisation efficiency, as discussed in the Supplementary. This estimated C_CO_3 concentration was compared to measured carbonate on a subset of 19 filter samples. While the agreement between measured and estimated concentrations is poor for Tartu, a decent agreement ~~washad been~~ found for KJ and Tallinn, especially given the large uncertainties in both variables (Fig. S5S7). On an absolute basis, PMF seems to overestimate the C_CO_3 concentrations by $\sim 20\%$ compared to the measured concentrations.

Ca^{2+} is one of the most common constituents of mineral dust and therefore can be used to trace this source. The time series of C_CO_3 and Ca^{2+} , available for the entire set of samples, displayed in Fig. 6, show that the two variables exhibit similar trends (except for Tallinn). Despite the large errors in the C_CO_3 estimates, an uncertainty weighted correlation analysis (SI and Fig. S6S8) shows that C_CO_3 and Ca^{2+} correlate statistically significantly ($R=0.4$, p-value $< 10^{-5}$) with a slope of 0.2, consistent with C_CO_3 and Ca^{2+} being in the form of calcium bicarbonate.

We have validated the identity of the dust factor even further, by measuring the same subset of 19 filters with the offline AMS technique before and after fumigation with HCl (as described in Zhang et al., 2016). The comparison of the mass spectra of fumigated and non-fumigated samples is illustrated in Figure 7 for two samples: with high and low contribution of dust. In the example of KJ (05/06/2014) where the dust factor exhibited the highest contribution, f_{44} was substantially decreased after fumigation (Fig. 7a). In the case of Tallinn (19/01/2014), where the dust factor concentration was negligible, f_{44} remained stable after fumigation (Fig. 7b). Overall, the comparison of the Δf_{44} modelled ($= f_{44\text{total}} - f_{44\text{org}}$) from the initial data set of 150 filters and the Δf_{44} measured ($= f_{44\text{non_fum}} - f_{44\text{fum}}$) from the subset of 19 filters showed consistent results (Fig. 8). Taken together these results provide strong confidence on the nature of the dust factor extracted by PMF.

4.4 Seasonal variation of organic aerosol sources

The sources were quantified after removing the contribution of the dust factor from the total OA. All the factor concentrations with their uncertainties averaged per season are presented in Table S3. In general, the relative uncertainties decreased with increasing concentrations per factor (Fig. S7S9). For concentrations above $\sim 1 \mu\text{g m}^{-3}$ the percentage error became more important than the error related to noise and thus more stable for all factors. Consistent with the factor separation and uncertainty analysis above, the factors that were well separated, such as SOOA, exhibited low relative uncertainty (0.15), while the factors that were more difficult to extract, such as BBOA exhibited higher relative uncertainty (0.45).

BBOA exhibited high concentrations in Tallinn during winter (on average $3.7 \pm 2.7 \mu\text{g m}^{-3}$) and fall ($1.2 \pm 0.9 \mu\text{g m}^{-3}$) and in Tartu (8.4 ± 3.9 and $3.8 \pm 1.9 \mu\text{g m}^{-3}$, winter and fall, respectively) (Fig. 9a, Table S3S5). In both

cities BBOA and the marker levoglucosan correlated very well (Fig. 9b) confirming the identity of the factor. For KJ the concentrations of BBOA were lower in winter ($1.3 \pm 0.8 \mu\text{g m}^{-3}$) as expected, due to the low number of residents and low biomass burning activities in the region. At all sites the levoglucosan:BBOA ratio (0.08 for KJ, 0.05 for Tallinn and 0.05 for Tartu) assessed in this study was consistent with the one reported in the neighbouring country, Lithuania (Bozzetti et al., 2017). Potassium (K^+), which is often used as a wood burning marker, especially for ash, also correlated well with BBOA for Tallinn ($R^2=0.80$) and Tartu ($R^2=0.58$). Different BBOA: K^+ ratios were used in the past to describe burning conditions (Zotter et al., 2014, Daellenbach et al., 2018) and higher values were linked to inefficient burning conditions. Here, the BBOA: K^+ ratio (14.3 for Tallinn and 18.1 for Tartu) was in agreement with the one found at Southern Alpine valley sites (Magadino and San Vittore, Switzerland, Daellenbach et al., 2018) where older stoves are still used. In Estonia more than 80% of households use old type stoves for heating purposes (Maasikmets et al., 2015), therefore, BBOA could be linked to inefficient residential wood burning.

The recognition of PBOA as described in Section 3.2 was also supported by the high correlations of this factor with cellulose and erythritol (Fig. 9d). Cellulose is related to plant debris and is typically used as a marker for primary biological aerosols (Bozzetti et al., 2016) while erythritol, among other sugar alcohols, reflects airborne biogenic detritus (Graham et al., 2002). The seasonal behaviour of PBOA was very similar to the respective behaviour of both markers (Fig. 9c) with average spring concentrations of $0.2 \pm 0.2 \mu\text{g m}^{-3}$ for KJ, $1.2 \pm 0.8 \mu\text{g m}^{-3}$ for Tallinn and $0.7 \pm 0.4 \mu\text{g m}^{-3}$ for Tartu.

SOOA exhibited a clear yearly cycle at all sites with the highest concentrations witnessed in summer and early fall (in summer on average $1.8 \pm 0.7 \mu\text{g m}^{-3}$ for KJ, $2.8 \pm 0.6 \mu\text{g m}^{-3}$ for Tallinn and $2.1 \pm 0.4 \mu\text{g m}^{-3}$ for Tartu) (Fig. 9e). In previous studies this factor showed an exponential increase (Fig. S8S10) with temperature and was linked to terpene oxidation products (Daellenbach et al. 2017, Leaitch et al., 2011). In another study in an Alpine valley site, this factor was also found to be 79% non-fossil, supporting the connection to biogenic secondary OA (Vlachou et al., 2018). Here, SOOA was not only correlated with temperature ($R_s = 0.77$, Fig. S7S10) but also with two oxidation products of α -pinene, i.e., with pinic acid and even better with MBTCA (Fig. 9f). The latter was shown to be produced by reaction of pinonic acid with the OH-radical (Mueller et al., 2012).

WOOA was more pronounced during fall and winter at all sites with average concentrations in winter of $1.4 \pm 0.5 \mu\text{g m}^{-3}$ for KJ, $2.2 \pm 0.8 \mu\text{g m}^{-3}$ for Tallinn, and $1.5 \pm 0.5 \mu\text{g m}^{-3}$ for Tartu (Fig. 9g). In earlier studies WOOA was characterised as non-fossil (Vlachou et al., 2018) and was identified based on its correlation with NH_4^+ coming mainly from NH_4NO_3 in winter time (Lanz et al., 2007, Daellenbach et al., 2017). It was also related to long-range transported oxygenated OA stemming from anthropogenic emissions during winter, such as biomass burning. Also, WOOA demonstrated high correlations with two anthropogenic organic acids: benzoic and phthalic acid (Fig. 9h), formed via the photo-oxidation of aromatic hydrocarbons, such as toluene and naphthalene, and therefore suggested to be tracers for anthropogenic sources (Kawamura and Yasui 2005, Deshmukh et al., 2016). Recently, Bruns et al. (2016) found that aromatic compounds, such as benzene and naphthalene emitted by wood combustion can indeed produce highly oxidized-oxygenated SOA. Taking all the above into account, it was concluded that WOOA might be linked mostly to aged wood burning OA.

Figure 10 illustrates the relative contributions per factor per site to the total OA (all averaged contributions per season per factor with their uncertainties are shown in Table S4S6). Out of the primary sources, the major contributor was BBOA during winter and fall (on average and one standard deviation: $39\% \pm 16\%$ and $27\% \pm 13\%$ in Tallinn and $73\% \pm 21\%$ and $53\% \pm 14\%$ in Tartu). However, in KJ during winter and fall WOOA was the dominant source ($36\% \pm 14\%$ and $39\% \pm 13\%$, respectively) indicating that for this site regional transport of OA is important. In spring, PBOA was the major source in Tartu ($21\% \pm 88\%$) while in Tallinn BBOA and SOOA were the dominating sources during that season ($30\% \pm 14\%$ and $18\% \pm 5\%$, respectively). This could be due to the fact that temperatures in early spring are still low (2°C on average in Tallinn in March) and wood burning for residential heating is still widely used. Towards the end of spring (15°C on average in Tallinn in May) the rising temperature favours the biogenic emissions. In KJ, the most important source was oil OA ($36\% \pm 14\%$ in spring), most possibly coming from the oil shale industries in the region. The presence of the oil factor

at the other two sites could be an indication that this factor is mixed with coal or waste burning, as also found by Elser et al. (2016). Besides, the oil OA profile resembled the coal profile identified in Cork city, Ireland (Dall'Osto et al., 2013). During the summer months and early fall, SOOA was prevailing over all sources at all sites, with 26% \pm 5% in KJ, 41% \pm 7% in Tallinn and 35% \pm 7% in Tartu. Even though KJ is highly industrialised, SOOA can still be related to the production of secondary OA from biogenic volatile organic compounds. The least significant source, especially in Tartu, with rather stable seasonal behaviour was SCOA. The yearly average contribution of SCOA was 12% \pm 4% in KJ, 14% \pm 5% in Tallinn and 4% \pm 2% in Tartu. Although it is generally found that the secondary sources are prevailing over the primary, here in general the primary sources seem to dominate the secondary ones. This-which is also observed in other European sites such as Payerne (Bozzetti et al., 2016 for coarse particles) or Magadino especially in winter (Vlachou et al., 2018 for PM₁₀) as well as in China, Beijing (Zhang et al., 2017 for PM₁).

5. Conclusions

The offline AMS technique was applied on a set of 150 filter samples covering a yearly cycle at three sites in Estonia. The uncertainties of the PMF solution were assessed by bootstrap analysis. In order to identify the factors the Spearman *R* (*Rs*) coefficients between base case time series and bootstrap run time series (“ts”) as well as base case profiles and bootstrap run profiles (“pr”) were monitored. The results showed that the retained solution space if one follows the “ts” or the “pr” sorting method was very similar. Weighting with the *Rs* between external markers and bootstrap run increased our confidence towards the solution space. The source apportionment results revealed four primary OA sources, two secondary OA and a dust factor. The dust factor was identified by measurements of calcium carbonate as well as by acidification with HCl of a selected batch of filters. Out of the primary sources, three had an anthropogenic influence. BBOA was mainly present in winter and autumn in Tallinn and Tartu, the two largest cities of Estonia, where residential heating activities are common. SCOA was mostly important in winter in Tallinn and KJ in contrast to Tartu. The third anthropogenic primary factor was oil OA which exhibited the highest concentrations in KJ, as expected. The reason why this factor was evident in Tallinn and Tartu could be that it may include coal combustion for residential heating purposes. PBOA was the only primary OA not related to anthropogenic emissions and was prevailing in spring at all sites. The two oxygenated OA factors were separated according to their seasonal behaviour: WOOA was linked to anthropogenic wood burning activities as it dominated in winter and autumn at all sites and also correlated with phthalic and benzoic acid. SOOA was significant during summer at all sites and was related to biogenic emissions and strong aging as it was highly correlated with a second generation oxidation product of *a*-pinene.

Competing interests. The authors declare that they have no conflict of interest.

Author Contribution. AV performed the offline AMS measurements, data curation and formal analysis, AV and IEH wrote the paper, AT assisted with the formal analysis, HL provided expertise on AMS measurements, FC and KD provided expertise on software, JLJ performed additional measurements including major ions, sugars, organic acids, cellulose, OC/EC and WSOC, MCM performed the carbonate measurements, MM and ET organised the filter sampling, UB, ASHP and IEH were involved with the supervision and conceptualisation. All authors commented on the paper and assisted in the interpretation of the results.

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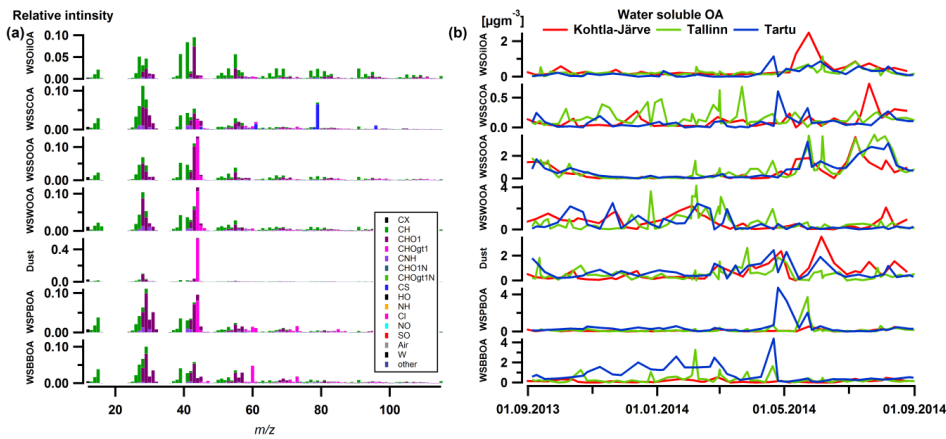
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Table 1. Detailed overview of the additional measurements.

Method	Compounds	Number of filters
Ion chromatography (Jaffrezo et al., 1998)	K ⁺ , Na ⁺ , Mg ²⁺ , Ca ²⁺ , NH ₄ ⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ and methane sulfonic acid	All (150)
Liquid chromatography-electrospray ionisation mass spectrometry (Jacob et al., 2018, 2019)	Organic acids (e.g. benzoic acid, pinic acid)	69 (Tallinn)
High performance liquid chromatography with pulsed amperometric detection (Waked et al., 2014)	Anhydrous sugars (e.g. levoglucosan, mannosan) and sugar alcohols (e.g. erythritol, mannitol)	150
Enzymatic conversion of cellulose (Kunit and Puxbaum, 1996)	Cellulose	69 (Tallinn)
Sunset EC/OC analyser (Birch and Carry, 1996) with the EUSAAR2	Organic (OC) and elemental (EC)	150

protocol (Cavalli et al., 2010)	carbon	
Total organic carbon analyser (Piot et al., 2012) with the use of catalytic oxidation and detection of CO ₂ with a non-dispersive infrared detector	Water soluble OC (WSOC)	150
Thermal Optical Transmittanceusing Sunset EC/OC analyser (Karanasios et al., 2011)	CO ₃ ²⁻	19 (from all sites)



5 Figure 1. Factor profiles (a) and time series (b) of the seven factor solution: Biomass burning OA (BBOA), sulfur-containing OA (SCOA), primary biological OA (PBOA), Industrial/ Oil combustion OA (OilOA), winter oxygenated OA (WOOA), summer oxygenated OA (SOOA) and a dust related OA (Dust). Note that the water soluble parts are illustrated here.

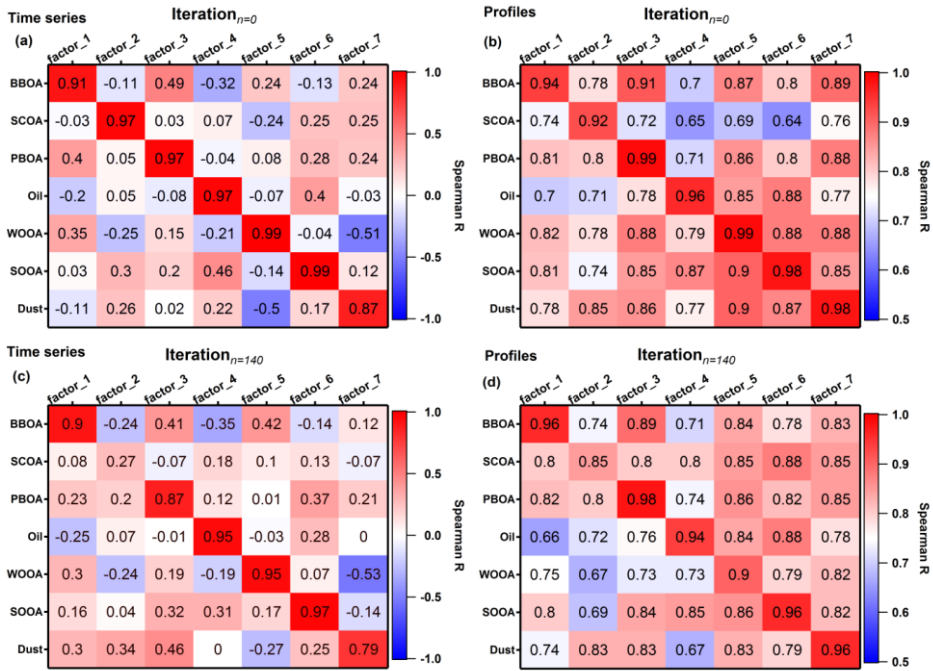


Figure 2. Explanatory tables for the factor sorting based on the time series: (a) accepted bootstrap iteration where all highest correlations (R_s) lay in the diagonal, (c) failure to resolve SCOA as for this bootstrap iteration both factors 2 and 7 showed the highest correlation with Dust factor. The respective tables for the case of profiles are in (b) and (d). Note the different scales of R_s for the profiles.

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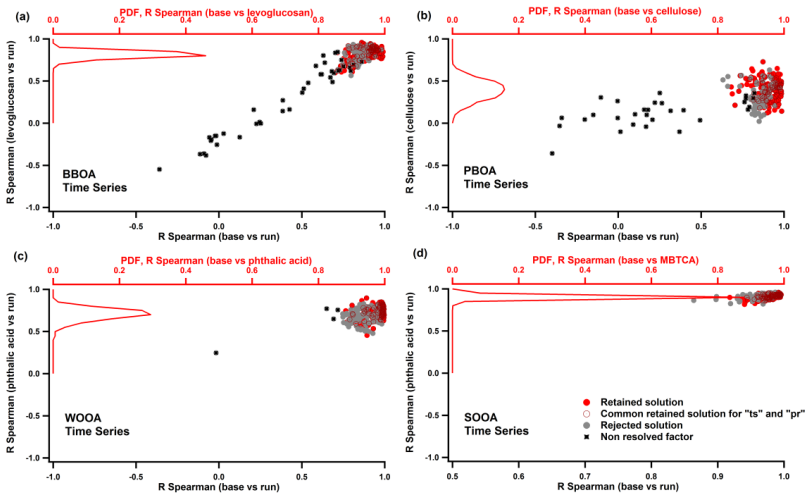
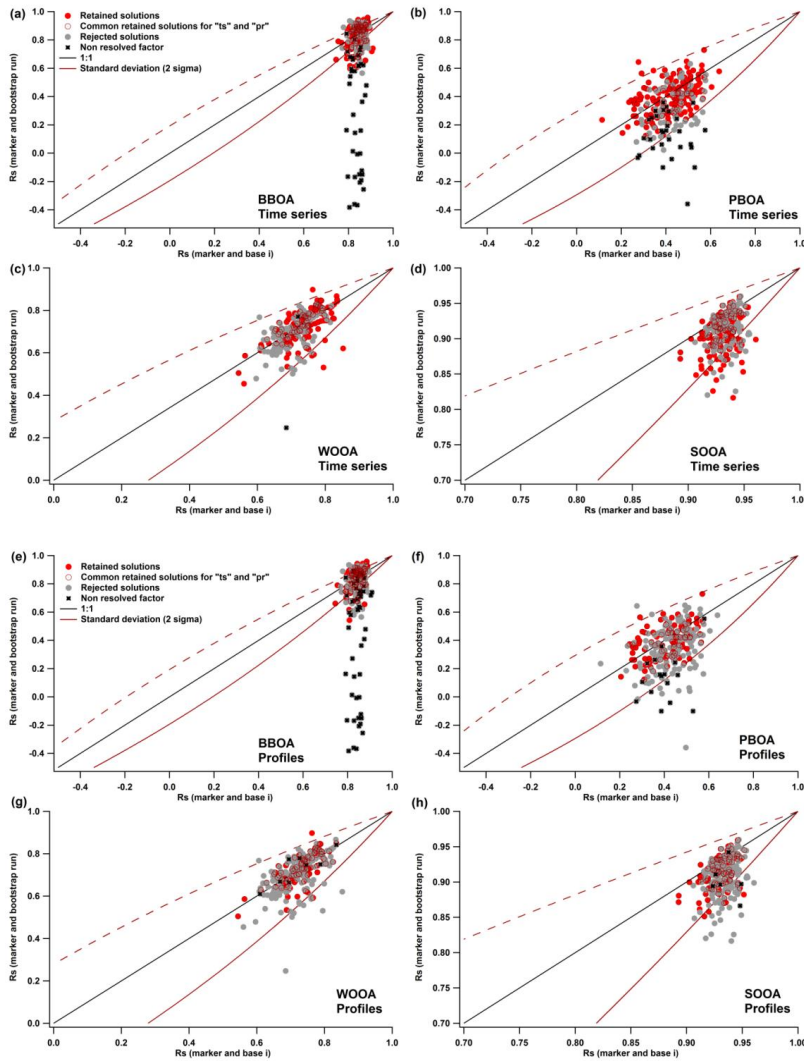


Figure 3. Solution space per factor defined by investigation of the correlation (R_s) between base case time series and bootstrap runs (bottom x-axis) and external markers and bootstrap runs (y-axis): BBOA with levoglucosan (a), PBOA with cellulose (b), WOOA with phthalic acid (c) and SOOA with MBTCA (d). The retained solutions are indicated in red and the rejected ones in grey. The points in black represent the runs where the

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specific factor was not resolved at all. Each PDF (top x-axis) includes the range of R coming from the correlations between the time series of the base case factors with their respective markers.



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Figure 4. Scatter plots of $R_{s_{boots}}$ between markers and bootstrap runs and $R_{s_{base}}$ between markers and base cases per factor: BBOA with levoglucosan (a), PBOA with cellulose (b), WOOA with phthalic acid (c) and SOOA with MBTCA (d) for the “ts” sorting method. The black points that lie below the 1σ line (in solid dark red) indicate true negative solutions, whereas the black points within 2σ indicate false negative solutions. The red points below 1σ represent the false positive solutions, while the red points above are the true positive solutions. The respective scatter plots for the “pr” method are shown in (e), (f), (g) and (h). Note the different R_s scales per factor.

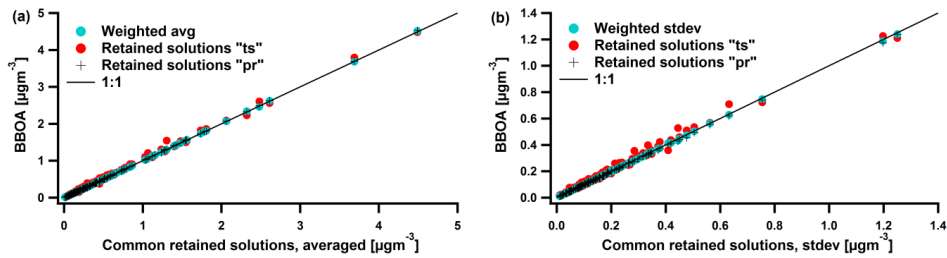


Figure 5. (a) Scatter plots between BBOA time series averaged (avg) over the common solutions coming from both the time series ("ts") and profile ("pr") sorting method plotted in the x-axis, and plotted in the y-axis the BBOA time series averaged over the solutions coming from the "ts" method in red, from the "pr" in black cross and from the weighted average based on the marker, here levoglucosan, in blue. The respective scatter plot for the standard deviation (stdev) is shown in (b).

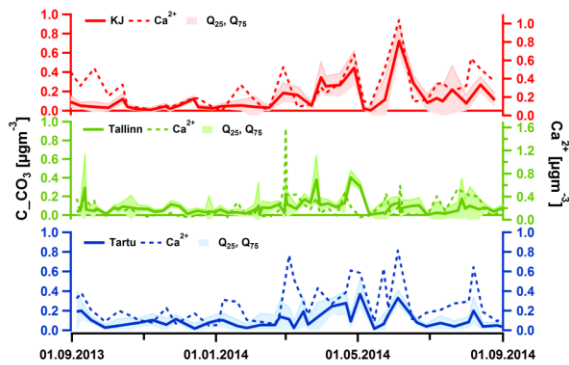


Figure 6. Time series of the inorganic dust factor (C_{CO_3}) with interquartile ranges (Q_{25} and Q_{75}) and of Ca^{2+} per site.

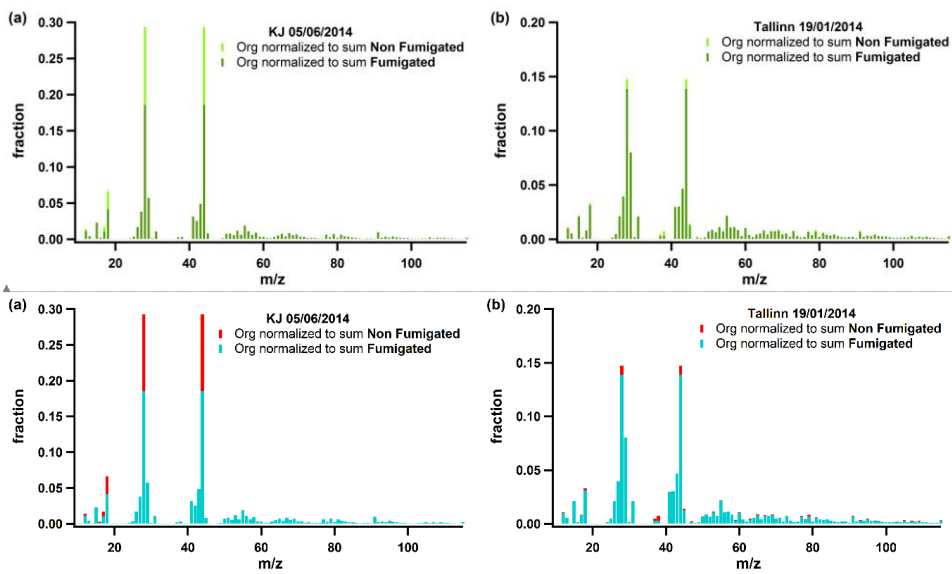


Figure 7. Example mass spectra from two of fumigated and non-fumigated mass spectra from two samples, with a high (KJ 05/06/2014, a), and a low dust concentration (Tallinn 19/01/2014, b).

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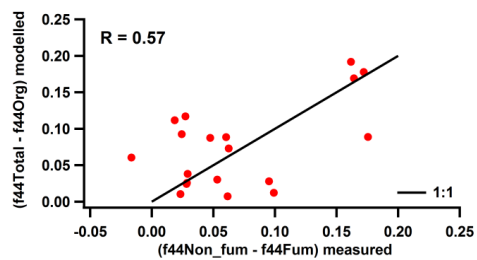


Figure 8. Scatter plot between the calculated Δf_{44} and the measured Δf_{44} coming from dust.

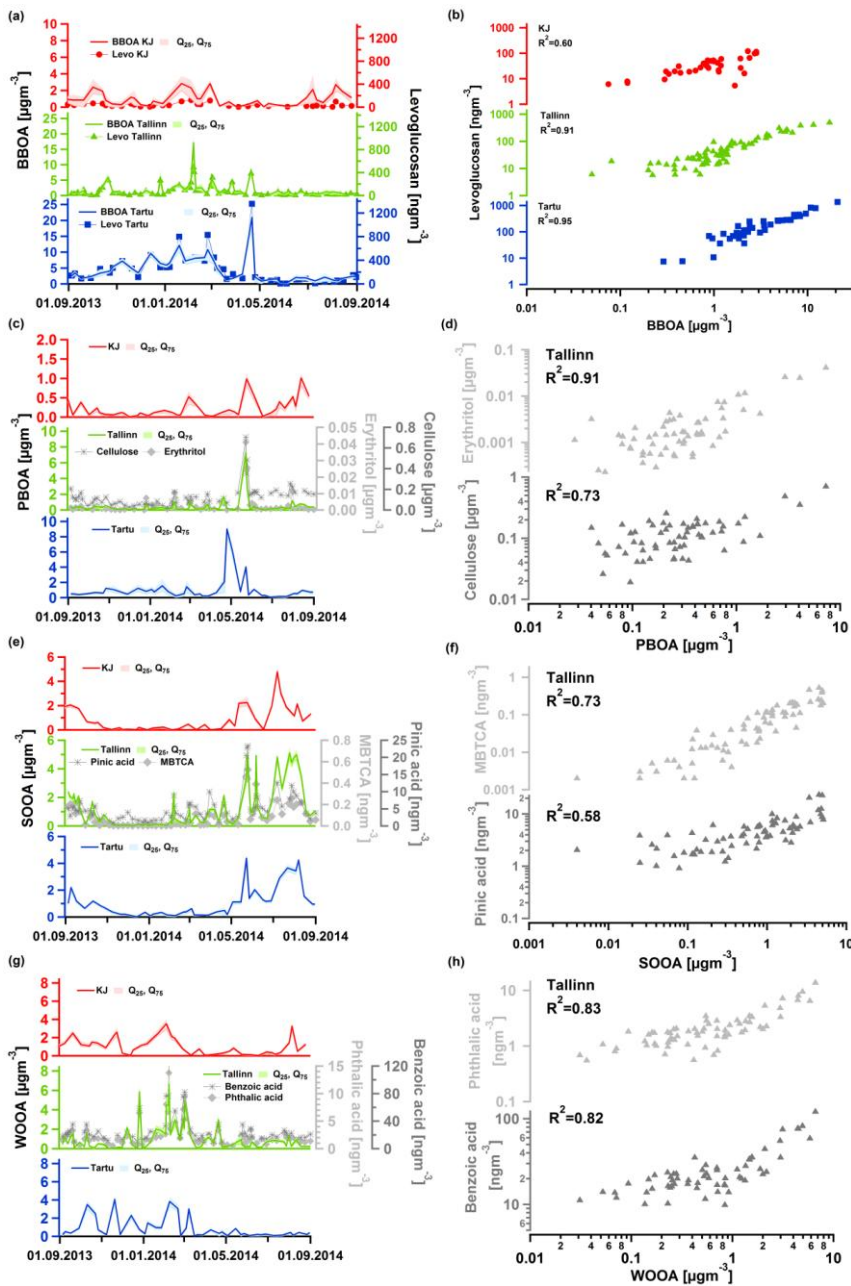


Figure 9. Factor median and external marker concentration time series for all three sites; (a) BBOA and levoglucosan (note the change of the scale for KJ), (c) PBOA, cellulose and erythritol, (note the change of the scale for KJ) (e) SOOA, pinic acid and MBTCA and (g) WOOA, benzoic and phthalic acid, with the respective scatter plots between factors and external markers in (b), (d), (f) and (h). The colours red, green and blue denote the site (Kohla-Järve KJ, Tallinn and Tartu) and the markers in light and dark grey denote the concentrations of the external markers. The shaded areas represent the first (Q₂₅) and third (Q₇₅) quartiles.

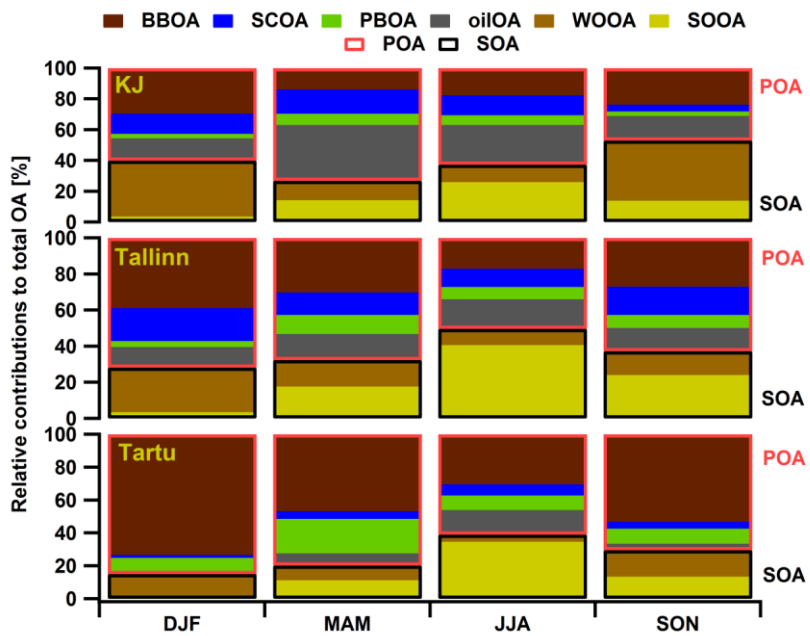


Figure 10. Seasonally averaged relative contributions of each factor to the total OA per site. The red and black boxes indicate the contributions of primary and secondary OA, respectively.

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