Authors’ response to reviewers’ comments

We would like to thank the reviewers for their careful reading and comments which helped to clarify the message of the manuscript. Our responses to each of the reviewers’ comments are written in blue. Changes in the manuscript are marked in yellow.

Interactive comment on "Carbonaceous aerosol source apportionment using the aethalometer model – Evaluation by radiocarbon and levoglucosan analysis at a rural background site in southern Sweden" by Johan Martinsson et al.

Anonymous Referee #1

Received and published: 19 January 2017

Martinsson et al. present analysis of a yearlong dataset of carbonaceous aerosols at a rural background site. Long-term source apportionment studies of carbonaceous aerosols are rare, and in addition the authors propose a new modification to the 'aethalometer model' that they suggest can apportion biogenic sources in addition to wood burning and fossil fuel from aethalometer data. However, while the source apportionment results are promising for wood burning and biogenic carbon, there is a clear shortcoming in its ability to apportion carbon from fossil fuel. The authors are upfront with this issue and have tried alternative methods to improve the source apportionment model, but these did not offer any improvements. I would have liked to see more discussion on why the proposed aethalometer model over-estimated fossil fuel carbon, apart from the blaming the poor correlation between fossil fuel aerosol light absorption and carbon mass concentration. Why do the authors think there was such a poor fit?

We have performed a sensitivity analysis where we increased or decreased the carbon in Eq. 10-11, while not changing the b_{abs} parameters. This would be analogous to change the mass of non-light absorbing carbon. We have written a detailed discussion regarding this in section 3.4. Our results from this analysis suggest that interference of non-light absorbing carbon (presumably biogenic carbon) may be responsible for the observed overestimation of CM_{FF}. Hence, we have re-written our abstract, discussion and conclusion where we have added this information. We have omitted that the poor fit would be the reason for the overestimation.

Overall, the paper is well written and structured with a wide range of relevant references and I would recommend it for publication after consideration to the comments below.

Comments:

1. Page 11, line 15-20: While I would agree that the in Fig 3d, the BCFF diurnal trend is bimodal like traffic emissions (though with a peak at night?) I am not sure I agree that the diurnal trend in BCFF for winter especially (Fig 3c), is similar to NOx (Fig 3g). The diurnal trends in NOx in winter are more what would be expected for traffic emissions, and are dissimilar to that observed for BCFF. The flat diurnal trend in BCFF for winter instead to me suggests that the model did not apportion the FF fraction correctly.

We agree with the reviewer that the BC_{FF} during winter (Fig. 3c) appears to have less pronounced (if any) bimodal behavior in comparison to NO_X concentrations during winter (Fig. 3g). However, we would still claim that there are features in common. Both BC_{FF} and NO_X start with decreasing concentrations from 1:00-6:00, and then increase and stay on an elevated level until 22:00 when both concentrations show indications of decrease.

It is possible that the elevated precipitation during the winter (described in section 3.1) was responsible for increased wet deposition of BC while leaving the atmospheric NO_X unaffected, resulting in blurring correlations between the two parameters during the winter.

We have added a few words to indicate that the bimodal pattern is stronger for the NO_X concentrations compared to the BC_{FF} concentrations.

We have checked our data again and found no reason why the calculations here should be invalid.

2. Page 11, line 25: If NOx is being oxidized in transport to the site, then shouldn't the CMFF and NOx show the highest correlation during winter when there is less photochemistry compared to the other seasons? Why is there such a better correlation in spring compared to the other seasons?

This is a very good question and hard to explain. As we answered on the former comment, one can speculate that increased wet deposition during winter resulted in a scavenging effect on BC while leaving the atmospheric NO_X unaffected. Consequently, the correlations between BC and NO_X during winter may have been weakened.

Studying the precipitation of the other seasons we find that the spring had the lowest precipitation, hence possibly explaining the improved correlation between BC_{FF} and NO_X during this period ($R^2=0.41$; $p<0.001$). However, the precipitation during spring is not significantly different from the precipitation during fall and summer (seasons with much lower R^2 value between BC_{FF} and NO_X, $R^2=0.07$; $p=0.021$ and $R^2=0.09$; $p=0.009$, respectively). Hence, precipitation may only partially explain the increased correlation during spring.

3. Page 12, lines 1-3: I find it surprising that the CMwb was better correlated with NOx than CMFF. You explain this by stating that both NOx and CMwb have a seasonal dependence, but why would NOx and CMwb have the same seasonal dependence? Have you examined the correlation between CMwb and NOx to see if there is a change for the seasons?

NO_X is mainly emitted from traffic, which is a rather stable emitter throughout the year. Furthermore, NO_X has a longer lifetime during the cold/dark period of the year due to a lower rate of atmospheric photo-oxidation. Hence, NO_X concentrations can be expected to be elevated (due to longer lifetime) during winter, and lower during summer. The same pattern applies for CM_{WB} but for a different reason. Residents heat their homes through WB during winter, an activity that is almost absent during summer. We have clarified this in the text.

There are no changes in the correlation between CM_{WB} and NO_X, all seasons show significant correlations.

4. Page 12, line 17. In Fig S6, why there is a very large spike in the concentration of levoglucosan in late March that is not observed in AAE (fig 2)? This sharp spike in levoglucosan suggests a biomass burning event, and I would have thought you would observe a corresponding increase in AAE if wood burning aerosols have a high AAE? Investigating the cause of the spike may help guide the choice of AAE for wood burning at the site.

The levoglucosan peak is derived from a 72h quartz filter with a stop-date of 2015-03-19. Hence, the filter represents ambient air during 16-18th of March 2015. This is indeed a pollution episode. The OC and EC concentrations are also elevated as displayed in Fig. 1a. Air mass trajectory analysis revealed that southeasterly (SE) air masses totally dominated (92 %) during this three day period. As pointed out in section 3.5, air masses from SE are associated to higher levels of aerosol loading. Higher aerosol concentrations from the SE are further supported by the study by Kristensson et al. (2008).

During this three day period we actually had somewhat elevated AAE (although it is hard to see in Fig. 2.). The mean AAE during this three day period was 1.44 (±0.03 standard deviation), which is higher compared to the average AAE for the whole month of March 2015 (mean=1.37±0.09). However, since the measured $F^{14}C$ from the same filter showed a value of 0.86 there are some obvious contribution from fossil fuel combustion. Hence, we would not regard this pollution episode as being totally dominated by wood burning.

Nevertheless, there is a discrepancy in apportioned wood burning between the aethalometer model and the radiocarbon + levoglucosan method during this three day period. The aethalometer model apportions 54 % of the TC to wood burning while the radiocarbon + levoglucosan method apportions 90 % of the TC into wood burning. However, entangling the causes for this discrepancy is difficult. For instance, combustion of lignite has been shown to emit large quantities of levoglucosan, although it is a fossil source (Fabbri et al., 2008). Further, 55 % of the heat and power generation in Poland (located in the SE direction of Vavihill) are generated from lignite combustion (Burmistrz et al., 2016). Hence, deriving any source specific AAEs from this pollution episode should be conducted with great caution.

5. Section 3.5: did you use annual means for your comparison of the aethalometer and radiocarbon and levoglucosan apportionment? Did you see any changes in agreement between the two methods for the seasons, e.g. was there better agreement in summer or winter?

In section 3.4 we are comparing mainly annual means between the two source apportionment methods. As displayed in Fig. 6, we are comparing the methods on a seasonal basis. We re-analyzed possible differences on a seasonal basis through analysis of variance (ANOVA). There was a significant difference between the fossil fuel apportionments between the two methods for all seasons. There were no significant differences in apportionment of wood burning and biogenic carbonaceous aerosol between the two methods in any of the seasons.

We have clarified in section 3.4 that these comparisons discuss annual means.

6. Page13, line 15: In the aethalometer model, to calculate C1 and C2 only winter data was used as it was assumed that there would be negligible CMbio. However, the results from the radiocarbon and levoglucosan model suggest that biogenic carbon was not negligible during winter. I think that you should therefore include some discussion on how the presence of biogenic carbon in winter affected the source apportionment by the aethaolometer model.

As described in our answer to the first question, we have performed a sensitivity analysis where we increased or decreased the carbon in Eq. 10-11, while not changing the b_{abs} parameters. This would be analogous to change the mass of non-light absorbing carbon. We have written a detailed discussion regarding this in section 3.4

7. Page 13, line 31: Why did you fix CMbio to -0.103 ug m-3 and not zero as you expect no CMBIO in winter?

In this case we are comparing our method (i.e. letting CM_{Bio} vary outside the linear regressions) to the model proposed by Sandradewi et al. (2008) where they suggested solving a bilinear regression model with an allowed intercept. Hence, in order to adopt the Sandradewi method, we need to fix our intercept.

8. Section 3.6: My understanding is that in the proposed aethalometer model, the influence of biogenic carbon needs to be minimized in order to calculate C1 and C2. In addition to only using winter data, could you not also select data for the calculation by wind direction? My reading of this section is that there are geographically distinct areas around the sampling site, and that filtering by wind direction you could further decrease in the biogenic influence (e.g. removing data when the wind is from a forested area or from the NE?) in the data.

This is a good idea suggested by the reviewer. In our study we have the lowest amount of incoming NE air mass during winter (i.e. 10 % of the air masses were from this direction). Hence, we believe that the selected winter data in our study exhibit favorable conditions in order to minimize biogenic carbonaceous aerosol.

We have added a sentence in section 3.5 describing the low abundance of NE air masses during winter.

9. Page 14, line 19-20: Why would SW air masses have high NOx but not be associated with carbonaceous aerosols, when traffic emissions are a significant source of both?

This is indeed very hard to explain. One explanation might be that the SW air masses are associated to increased precipitation (R^2=0.19; p<0.01). This correlation was particularly high during winter (R^2=0.41; p<0.01), a time when NO_X

can be expected to have increased lifetime due to low photochemical rates. Hence, it is possible that the increased SW-precipitation increased the wet deposition of carbonaceous aerosol particles while leaving the NO_X unaffected.

We have added a sentence to offer this explanation in section 3.5.

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Interactive comment on “Carbonaceous aerosol source apportionment using the aethalometer model – Evaluation by radiocarbon and levoglucosan analysis at a rural background site in southern Sweden” by Johan Martinsson et al.

Anonymous Referee #2

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General comments

The authors present an evaluation of the aethalometer model for carbonaceous particle source apportionment using radiocarbon and levoglucosan measurements, and quantify wood burning (WB) and fossil fuel combustion (FF) aerosol for a year-long dataset from a rural station in southern Sweden. The model is modified to allow for apportioned non-light absorbing biogenic aerosol to vary in time, improving the aethalometer-based source apportionment compared to radiocarbon and levoglucosan data. This is an interesting and solid study. The manuscript is very well written (with a few grammatical errors here and there, I suggest having it checked by a native English speaker), and the analysis is sound. I therefore recommend publication in ACP after the following comments have been addressed:

Specific comments

P. 4, l. 13: How efficient are the active carbon denuders? Please add information on that and the expected background. Is there any information on the evaporation of semi-volatiles from the particles after disturbance of the gas-particle equilibrium due to the denuders?

Genberg et al. (2011) conducted a full year source apportionment study at Vavihill 2008-2009. They conducted tests on the installed denuders and found 90-95% denuder efficiency (Genberg et al. 2011).

Further, when denuders were installed, Genberg et al. (2011) observed that obtained field blanks contained a carbon content similar to that of the sampled back filters, indicating that the possible negative artefact (due to disturbance of the gas-particle equilibrium) was low. Hence, Genberg et al. (2011) did not consider nor corrected for this artefact. In our study, we did not obtain any field blanks, however we have adopted the same approach as Genberg et al. (2011) since we are performing a similar study at the same measurement site with the same sampling setup, i.e. we have not corrected for this artefact.

We have added information on the efficiency of the denuders and the presumably low negative artefact caused by the denuders in section 2.1.

P. 6, l. 1 – 4: Why were the AAE values not calculated based on the actual data, or at least calculated and compared to literature data? Assuming an AAEFF of 1, and plotting/fitting babs vs wavelength (either averaged, or time-dependent, more appropriate here) can be used to derive AAEWB.

We do not see how we can calculate an AAE_{WB} using the method suggested by the reviewer. To be able to derive AAE_{WB} we need to know AAE values from the wood burning, i.e. through emission inventories. Our actual measured data shows the *babs* from a mixture of different aerosol sources. Hence, we cannot see how we could select any AAE_{WB} based on these source mixtures of *babs*.

We instead obtained our source specific AAE values from emission inventories as displayed in Table 1. The mean AAE_{WB} are in line with selected AAE_{WB} values in previous aethalometer model source apportionment studies by Sandradewi et al.

(2008) and Massabo et al. (2015). Further, our selected AAE_{WB} value (1.81) is rather close to the recently suggested AAE_{WB} (1.68) by Zotter et al. (2016).

P. 6, l. 11-12: If site specific sigma_abs were calculated based on linear regression of babs against EC, doesn't that imply an overestimation of sigma_abs, as light-absorbing OC is not included in EC? Please clarify.

This is true. We have added two sentences in order to clarify this.

P. 6, l.13: CM could also be SOA from WB and FF; should be mentioned here.

We have added this information.

P. 12, l. 2-3: This statement should be supported by references and more explanations.

We have developed and clarified this statement with some explanations.

P. 12, l. 29: Is the year-long time series correlated, or the diel evolution? I am assuming you are talking about the correlation of the time series. Apart from the non-optimal apportionment, a reason could also be, similar to the correlation of NOx and CMwb, a similar trend, but a different cause. CMFF is higher in winter than in summer, and so is NOx – potentially traffic emissions become more important in winter as well, or meteorological conditions favor the build-up of pollution episodes?

The correlation refers to the year-long time series since the levoglucosan data is in low time resolution (i.e. 72 h). This has been clarified.

This relation is hard to explain. It seems like the traffic emissions (judging from CM_{FF} and NO_X data) are relatively more important during winter compared to summer, at least in relation to TC. In absolute concentration, CM_{FF} shows highest values during the fall and similar values during the other seasons (Table 4).

However, studying the relation on a seasonal basis we can see that a large portion of the correlation is explained by high correlations during winter and spring (R^2=0.77; p<0.001 and R^2=0.62; p<0.001, respectively) as compared to summer and fall (R^2=0.04; p=0.3 and R^2=0.35; p=0.001, respectively). Hence, one can speculate that the stronger correlation during winter and spring are associated to increased wood burning where some of the generated aerosols are absorbing light with a spectral dependence, AAE, close to 1, thus being falsely apportioned as fossil fuel combustion aerosol. It is also possible that lignite combustion aerosols from continental Europe, containing levoglucosan and exhibiting a spectral dependence of an AAE close to 1, may show higher abundance during these seasons, however we have no data supporting this speculation.

P. 13, l. 15: CMbio was assumed to be 0 for calculations of C1 and C2. Could this be a reason for the overestimation of CMFF?

We have added a new discussion paragraph were we performed a sensitivity analysis of the impact of non-light absorbing carbon on the aethalometer model results. It is very likely that the overestimation in CMFF can be explained by presence of non-light absorbing carbon (possibly biogenic carbon).

Technical comments

P. 7, l. 14: typo in chloride (also in subsequent use of trimethylsilyl chloride) P. 7, l.16: typo, should be dichloromethane.

This has been corrected.

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Carbonaceous aerosol source apportionment using the aethalometer model-Evaluation by radiocarbon and levoglucosan analysis at a rural background site in southern Sweden

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Abstract. With the present demand on fast and inexpensive aerosol source apportionment methods, the aethalometer model was evaluated for a full seasonal cycle (June 2014-June 2015) at a rural atmospheric measurement station in southern Sweden by using radiocarbon and levoglucosan measurements. By utilizing differences in absorption of UV and IR, the aethalometer model apportions carbon mass into wood burning (WB) and fossil fuel combustion (FF) aerosol. In this study, a small modification in the model in conjunction with carbon measurements from thermal-optical analysis allowed apportioned non-light absorbing biogenic aerosol to vary in time. The absorption differences between WB and FF can be quantified by the absorption Ångström exponent (AAE). In this study AAE_{WB} was set to 1.81 and AAE_{FF} to 1.0. Our observations show that the AAE was elevated during winter (1.36±0.07) compared to summer (1.12±0.07). Quantified WB aerosol showed good agreement with levoglucosan concentrations, both in terms of correlation (R^2=0.70) and in comparison to reference emission inventories. WB aerosol showed strong seasonal variation with high concentrations during winter (0.65 $\mu g\ m^{-3}$, 56 % of total carbon) and low concentrations during summer (0.07 $\mu g\ m^{-3}$, 6 % of total carbon). FF aerosol showed less seasonal dependence, however black carbon (BC) FF showed clear diurnal patterns corresponding to traffic rush hour peaks. The presumed non-light absorbing biogenic carbonaceous aerosol concentration was high during summer (1.04 $\mu g\ m^{-3}$, 72 % of total carbon) and low during winter (0.13 $\mu g\ m^{-3}$, 8 % of total carbon). Aethalometer model results were further compared to radiocarbon and levoglucosan source apportionment results. The comparison showed good agreement for apportioned mass of WB and biogenic carbonaceous aerosol but discrepancies were found for FF aerosol mass. The aethalometer model overestimated FF aerosol mass by a factor of 1.3 compared to radiocarbon and levoglucosan source apportionment. A performed sensitivity analysis suggests that this discrepancy can be explained by interference of non-light absorbing biogenic carbon during winter. In summary, the aethalometer model offers a cost-effective, yet robust high time resolution source apportionment at rural background stations compared to a radiocarbon and levoglucosan alternative.

1 Introduction

Carbonaceous aerosol, i.e. the fraction of the aerosol containing carbon, is approximately contributing with 25 % to the mass of particulate matter with smaller diameter than 10 µm (PM_{10}) in Europe (Fuzzi et al., 2015) and is presently estimated to be one of the most important climate forcers (IPCC, 2013). However, the magnitude of the carbonaceous aerosol impact on climate is still associated with significant uncertainty (IPCC, 2013). The carbonaceous aerosol originates mainly from three sources; wood burning, fossil fuel combustion and biogenic emissions. Black carbon (BC) or soot is formed from incomplete combustion of fossil fuels and biofuels. BC has a graphitic carbon structure and is known to efficiently absorb incoming solar radiation (Bond et al., 2013). This absorption leads to molecular vibration and rotation which causes emission of longwave radiation, heating the atmosphere. On the other hand, the organic aerosol (OA) is known to mainly scatter incoming sunlight, thereby cooling the climate. Recently, the strongly ultraviolet-absorbing brown carbon (BrC) has gained interest in the scientific community (Laskin et al., 2015;Martinsson et al., 2015;Saleh et al., 2013;Saleh et al., 2014). BrC is emitted in large quantities from wood burning and has been proposed to affect lower tropospheric photochemistry by reducing ultraviolet (UV) radiation (Jacobson, 1999). Although BrC is a much less effective light absorber than BC, deposition of BrC on bright surfaces such as snow or ice may cause significant changes in albedo (Doherty et al., 2010).

Carbonaceous aerosols have also been linked to serious health effects, mainly through inhalation (Grahame et al., 2014;Laden et al., 2006;Pope and Dockery, 2006). Carbonaceous aerosols derived from wood burning have been shown to be hazardous to humans (Barregard et al., 2006;Eriksson et al., 2014;Jalava et al., 2010;Naeher et al., 2007;Sehlstedt et al., 2010;Unosson et al., 2013). Additionally, diesel and gasoline vehicles emit large quantities of BC and associated compounds (e.g. polycyclic aromatic hydrocarbons, PAH) which have been suggested as one of the most health-damaging particle types (Benbrahim-Tallaa et al., 2012;Hoek et al., 2002;Salvi et al., 1999).

One of the re-emerging air pollutants in Europe is particles from residential wood burning (van der Gon et al., 2015). Wood burning is increasing with approximately 3.5 % per year in Europe due to its potential CO_2-neutral effect on climate, while the fossil energy consumption is decreasing by 2 % per year (EEA, 2015). Particle emissions from residential wood burning are usually elevated during winter. It has been estimated that 45-65 % of the total ambient carbonaceous aerosol mass (TC) in Europe is associated with wood burning during this period of the year (Gilardoni et al., 2011;Szidat et al., 2006). Due to the severe climate and health effects from different particle sources, and the importance of wood burning in particular, it is crucial to develop and evaluate source apportionment methods of the carbonaceous aerosols. An accurate source apportionment enables justified mitigation of particle emissions that affect health and climate, as well as a possibility to evaluate emission inventories and chemical transport models.

Levoglucosan is an anhydrosugar formed during pyrolysis of cellulose at temperatures above 300 °C (Simoneit, 2002). Due to its specificity for cellulose combustion, it has been widely used as a molecular tracer for wood burning in source apportionment studies (Gelencser et al., 2007;Genberg et al., 2011;Yttri et al., 2011a;Yttri et al., 2011b). However, there are some drawbacks of using levoglucosan for this purpose. Several studies have shown that levoglucosan may not be stable in the troposphere, it may react with OH both in the gas-phase (Hennigan et al., 2010;May et al., 2012) and aqueous phase (Hoffmann et al., 2010;Zhao et al., 2014) leading to relatively short estimated atmospheric life-times of 1-5 days, depending on the season and atmospheric conditions. The importance of the degradation of levoglucosan in the ambient atmospheric aerosol is still not clarified (Yttri et al., 2015). Also, the relative levoglucosan contribution to the carbonaceous aerosol mass is dependent on combustion conditions (Hedberg and Johansson, 2006). Levoglucosan is most commonly measured on aerosol-laden filters. Filter sampling is generally associated with low time resolution which makes it difficult to study rapid variations of this source marker.

More recently, the aethalometer model (Sandradewi et al., 2008a), employing multi-wavelength light absorbing measurement techniques with high time resolution, has been used for a number source apportionment studies (Favez et al., 2009;Favez et al., 2010;Herich et al., 2011;Sandradewi et al., 2008a), as an alternative to the methods based on chemical analysis of filter samples. This method relies on the assumption that particles generated from wood burning are relatively more light-absorbing in the UV than infrared (IR) compared to particles from traffic and other fossil fuel combustion (Kirchstetter et al., 2004). The difference in light absorption can be quantified using the absorption Ångström exponent (AAE) which is a measure of the spectral absorption dependence (Kirchstetter et al., 2004). Wood burning emissions are assumed to have an AAE between 1.5-2.5 while traffic and fossil fuel combustion derived particles exhibits an AAE around 1.0 (Kirchstetter et al., 2004). Despite the great benefits the light-absorption based source apportionment can offer, with its high time resolution and low costs, the relations between the highly source specific levoglucosan and light absorption measurement derived aethalometer model parameters have so far not been thoroughly investigated. Some studies have found good correlation between levoglucosan and AAE, or calculated BC from wood burning (BC_{WB}), using the aethalometer model (Fuller et al., 2014;Herich et al., 2011;Lack et al., 2013). On the other hand, recently published studies claim that the aerosol spectral dependence is more affected by combustion conditions than the type of fuel being combusted (Garg et al., 2016;Martinsson et al., 2015). Garg et al. (2016) found that the gaseous tracer for biomass burning, acetonitrile, correlated well with AAE during smoldering combustion but poorly during flaming combustion, and further that AAE varied greatly throughout combustion of the same fuel type. Calvo et al. (2015) measured levoglucosan in a wood stove with controlled combustion and a traditional fireplace; they found elevated concentrations of levoglucosan during the fuel addition followed by a rapid decrease in concentration in the flaming phase. Hence, it is possible that observed correlations between AAE and levoglucosan may only be valid for the smoldering combustion, which may limit the use of both levoglucosan and AAE as universal tracers of biomass burning.

The aethalometer model has so far mainly been applied during winter in highly polluted urban environments (Favez et al., 2009;Favez et al., 2010;Fuller et al., 2014;Harrison et al., 2013;Sandradewi et al., 2008a). There is thus a lack of knowledge regarding the performance of the aethalometer model during summer, and in less polluted rural environments. For instance, it is not known how the aethalometer model will cope with the usually dominating and presumably non-light absorbing biogenic secondary organic aerosol (SOA) during summer.

This study was initiated with the aim to compare a light-absorption source apportionment technique, the aethalometer model (Sandradewi et al., 2008a), to traditional filter-based chemical and physical analysis source apportionment using radiocarbon and levoglucosan measurements for a whole year at a rural measurement station in southern Sweden.

2 Methods

2.1 Measurement site and sampling

Sampling of atmospheric aerosols was conducted at the aerosols, clouds and trace gases research infrastructure (ACTRIS) and European monitoring and evaluation programme (EMEP) rural background station Vavihill, located in southern Sweden (56°01' N, 13°09' E, 172 meters above sea level). The surrounding landscape consists of coniferous and deciduous forests, farmland and pastures. The measurement station is placed on a pasture that is visited by grazing cattle during spring, summer and fall. The closest large cities are Helsingborg, Malmö and Copenhagen which are located at distances of 20, 50 and 65 km in the west to southwest direction, respectively. Aerosols were sampled with a PM_{10}-inlet on pre-heated (900 °C for 4 h in air) 47 mm quartz filters (Pallflex 2500QAT-UP) using a sampling time of 72 h at a flow rate of 38 liters per minute (lpm) with an automatic Leckel SEQ47/50 sampler. The sampling line consisted of active carbon denuders followed by two quartz filters in series (i.e. front and back filters) with the purpose of correcting for any sampling artefacts caused by volatile organic compounds (VOCs). The installed denuders have shown an efficiency of 90-95 % in a denuder test conducted at Vavihill 2008-2009 (Genberg et al., 2011). However, sampling through active carbon denuders may change the gas-particle equilibrium at the filter, leading to evaporation of semi-volatile compounds from the filter. Genberg et al. (2011) observed that field blanks had similar carbon concentration as the back filters, and consequently concluded that this negative artefact was small. Hence, no correction was considered in the present study. After sampling, filters were put in petri dishes, wrapped in aluminium foil and stored in a freezer at -18 °C until analysis. The total measurement period lasted from June 2014 until June 2015 and included in total 123 filter samples. The measurement period was divided into seasons with 3 months intervals, summer=June-August, fall=September-November, winter=December-February and spring=March-May.

2.2 OC/EC analysis

Elemental carbon (EC), organic carbon (OC) and total carbon (TC) were measured through thermal-optical analysis (TOA) with a DRI Carbon analyzer (Model 2001). The EUSAAR_2 analytic protocol was used for the analysis (Cavalli et al., 2010). In short, OC from a 0.5 cm^2 filter punch is evolved in four different temperature steps in an inert helium atmosphere at a maximum temperature of 570 °C. A 633 nm He/Ne-laser is irradiating the filter and the light transmission through the filter is measured during the increase of temperature. When the measured light transmission reaches its initial base-line value the remaining carbon is considered to be EC. EC is evolved in an oxidizing atmosphere (2 % O_2) during high temperatures (500-850 °C). All carbon is oxidized and evolved from the filter as CO_2, which is further converted to methane and finally quantified with a flame ionization detector (FID). TC is the sum of OC and EC. Cavalli et al. (2016) estimated the combined random uncertainties from inter-laboratory comparisons between 2008-2011 to be 17 % relative standard deviations (RSD) for Vavihill TC measurements.

2.3 Light absorption measurements and the aethalometer model

Aerosol light absorption was measured with an aethalometer (AE33, Magee Scientific) (Drinovec et al., 2015). The aethalometer utilizes an airflow through a filter where particles are deposited. The filter deposition spot is irradiated with seven LEDs of different wavelengths (370, 470, 520, 590, 660, 880, 950 nm) and the attenuation is calculated per unit of time. In this campaign the aethalometer was operating with a flow of 5 liters per minute through a PM_{10} inlet at a time resolution of 1 minute. Two main measurement artefacts are associated with filter-based light absorption techniques; the shadowing effect and the filter matrix scattering effect (Weingartner et al., 2003). The AE33 aethalometer handles these artefacts in two ways: attenuation enhancement due to filter matrix scattering is compensated by a factor 1.57, and the shadowing effect is treated by measuring the attenuation at two filter deposition spots with different depositions rates (Drinovec et al., 2015).

The output data of the aethalometer are absorption coefficients, $b_{abs}(\lambda)$, in the units of m^{-1}. $b_{abs}(\lambda)$ can be converted into BC mass concentration units ($g\ m^{-3}$) by division of the mass absorption coefficient (MAC), $\sigma_{abs}(\lambda)$ ($m^2\ g^{-1}$) according to Eq (1):

$$BC(\lambda) = \frac{b_{abs}(\lambda)}{\sigma_{abs}(\lambda)} \tag{1}$$

In the aethalometer model (Sandradewi et al., 2008a), the entire aerosol light absorption is assumed to come from fossil fuel combustion aerosol (FF) or wood burning aerosol (WB):

$$b_{abs}(\lambda) = b_{absFF}(\lambda) + b_{absWB}(\lambda) \tag{2}$$

$$\frac{b_{absFF}(370\text{nm})}{b_{absFF}(950\text{nm})} = \left(\frac{370}{950}\right)^{-AAE_{FF}} \tag{3}$$

$$\frac{b_{absWB}(370\text{nm})}{b_{absWB}(950\text{nm})} = \left(\frac{370}{950}\right)^{-AAE_{WB}} \tag{4}$$

By combining Eq. (2-4), it is now possible to calculate the light absorption that is caused by WB and FF in 370 and 950 nm (Mohr et al., 2013;Zotter et al., 2016), respectively:

$$b_{absFF}(950nm) = \frac{b_{abs(370nm)} - b_{abs(950nm)} \cdot \left(\frac{370}{950}\right)^{-AAE_{WB}}}{\left(\frac{370}{950}\right)^{-AAE_{FF}} - \left(\frac{370}{950}\right)^{-AAE_{WB}}} \tag{5}$$

$$b_{absWB}(370nm) = \frac{b_{abs}(370nm) - \left(\frac{370}{950}\right)^{-AAE_{FF}} \cdot b_{abs}(950nm)}{1 - \frac{\left(\frac{370}{950}\right)^{-AAE_{FF}}}{\left(\frac{370}{950}\right)^{-AAE_{WB}}}} \tag{6}$$

In Eq. (3-6) the AAE is the source specific spectral dependence. In the aethalometer model, the selection of source specific AAEs (AAE_{FF} and AAE_{WB}) are crucial for accurate source contribution estimation. Traditionally, is has been assumed that pure black carbon is dominating fossil fuel combustion emission, leading to an AAE_{FF}=1. Wood burning emissions have previously been assumed to have an AAE around 2 (Kirchstetter et al., 2004). However, recent studies have shown that it is the combustion conditions rather than the fuel itself that determines the organic content in the aerosol, and consequently the AAE (Garg et al., 2016;Martinsson et al., 2015). Martinsson et al. (2015) found that flaming combustion in a modern conventional wood stove emitted aerosol with highly agglomerated soot structure and an AAE of 1.3. Garg et al. (2016) determined the combustion efficiency by analysing emission gas data and reached similar conclusions. We estimated AAE_{FF} and AAE_{WB} based on literature data (Table 1). From Table 1 a mean $AAE_{FF}=1.0$ (SD=0.1) and mean $AAE_{WB}=1.81$ (SD=0.52) was chosen in this study. The value of $AAE_{WB}=1.81$ is close to the values chosen by Massabo et al. (2015) and Sandradewi et al. (2008a), i.e. 1.81 and 1.86, respectively.

By using Eq. (5-6) it is possible to calculate the light absorption due to FF ($b_{absFF}(\lambda)$) or WB ($b_{absWB}(\lambda)$). These light absorption coefficients can then be divided with the site specific MAC (Table 2) in order to calculate the BC mass concentration from each source (Eq. 7-8):

$$BC_{FF} = \frac{b_{absFF}(950\text{nm})}{\sigma_{abs}(950\text{nm})} \tag{7}$$

$$BC_{WB} = \frac{b_{absWB}(370\text{nm})}{\sigma_{abs}(370\text{nm})} \tag{8}$$

$\sigma_{abs}(\lambda)$ is in this case the site-specific mass absorption coefficients for the respective wavelengths which can be found in Table 2. Site specific $\sigma_{abs}(\lambda)$ was determined by linear regression of $b_{abs}(\lambda)$ against elemental carbon (EC) concentration in PM_{10}. However, it should be noted that OC also may absorb light, which can result in an overestimated site specific $\sigma_{abs}(\lambda)$ by using the regression between $b_{abs}(\lambda)$ and EC. However, EC is believed to be a much stronger light absorber than light absorbing OC (Bond and Bergstrom, 2006;Laskin et al., 2015), therefore this overestimation is believed to be small. It is also possible to calculate the carbonaceous aerosol mass (CM, i.e. the sum of primary and secondary aerosol) from FF and WB, together with non-light absorbing secondary aerosol. The latter is presumably mostly derived from biogenic sources, hence the acronym CM_{Bio}:

$$TC = CM_{FF} + CM_{WB} + CM_{Bio} = C_1 \cdot b_{absFF}(950\text{nm}) + C_2 \cdot b_{absWB}(370\text{nm}) + CM_{Bio} \tag{9}$$

In Eq. (9), C_1 and C_2 are the slopes from the linear regression of measured total carbonaceous matter (TC) and the light absorption due to FF ($b_{absFF}(950\text{nm})$) and WB ($b_{absWB}(370\text{nm})$), respectively. Previous work has set CM_{Bio} as the intercept when solving the multilinear equation, however this is highly unrealistic since biogenic primary and secondary aerosol formation is seasonal dependent and should vary accordingly (Guenther et al., 1995). We propose an alternative method where CM_{Bio} is allowed to vary outside the suggested regressions (Eq. 10-12). If Eq. (9) is rewritten, a linear regression can be used in order to calculate C_1 and C_2:

$$\frac{TC}{b_{absWB}(370nm)} = C_1 \cdot \frac{b_{absFF}(950nm)}{b_{absWB}(370nm)} + C_2 + \frac{CM_{Bio}}{b_{absWB}(370nm)} \tag{10}$$

$$\frac{TC}{b_{absFF}(950nm)} = C_2 \cdot \frac{b_{absWB}(370nm)}{b_{absFF}(950nm)} + C_1 + \frac{CM_{Bio}}{b_{absFF}(950nm)} \tag{11}$$

For Eq. (10), C_1 can be calculated as the slope of the regression line by setting $TC/b_{absWB}(370\text{nm})$ as the dependent variable and $b_{absFF}(950\text{nm})/b_{absWB}(370\text{nm})$ as the independent. A similar approach can be applied to Eq. (11) to calculate C_2. By selecting only winter data for calculation of C_1 and C_2 the interference of CM_{Bio} is minimized and the division of CM_{Bio} by one of the light absorption parameters is forcing CM_{Bio} towards zero. Hence, the intercept of the linear regression line should be close to C_2 when calculating the slope as C_1 in Eq. 10, and vice versa for Eq. 11. The linear fits used to derive C_1 and C_2 contained one suspected outlier each. These outliers were confirmed by Grubbs test (Grubbs, 1950) for both dependent and independent variables with 95% confidence and hence removed. The linear fits without outliers are displayed in Fig. S1 and S2. Finally, CM_{Bio} is allowed to vary outside the linear regressions:

$$CM_{Bio} = TC - CM_{FF} - CM_{WB} \tag{12}$$

Since CM_{Bio} is assumed to be the residual carbonaceous matter, i.e. the carbonaceous matter that does not absorb light, this parameter may have a negative value during winter when the sum of CM_{FF} and CM_{WB} exceeds TC.

C_1 was calculated to be 214 467 µg m^{-2} with an intercept of 133 794. C_2 was estimated to 113 881 µg m^{-2} with an intercept of 273 603. Hence, C_1 (from Eq. 10) was deviating 22 % from the intercept in the calculation of C_2 (Eq. 11), while C_2 (from Eq. 11) was deviating 15 % from the intercept in the calculation of C_1 (Eq. 10).

Herich et al. (2011) found high standard errors in their modelled C_1 and C_2 parameters (± 30 %). This was the main reason for Herich et al. (2011) to exclude the CM-approach and proceed with the BC approach presented in Eq. (7-8). In comparison to Herich et al. (2011), we found similar standard error for C_1 (31 %) but lower for C_2 (18 %). We have therefore chosen to proceed with the CM-approach.

2.4 Levoglucosan analysis

1,6-Anhydro-beta-D-glucose (levoglucosan) analysis was performed using the method of Wu et al. (2008) with some modifications. Levoglucosan was purchased from Sigma Aldrich (St. Louise, USA). Hexane from Scharlau (Spain), 1-phenydodecane, 97 % from Acros Organics (Geel, Belgium) and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1 % trimethylsilyl chloride (TMCl) was purchased from Sigma (St. Louise, USA). Filter punches were divided into small pieces using a surgical blade and placed in a 50 ml conical flask. Extraction was carried out by sonication using three aliquots of 15 ml, 10 ml and 10 ml of dichloromethane and methanol (1:3) for 45 minutes, 30 minutes and 15 minutes respectively. Extract from each step was filtered and pooled together in a 50 ml beaker using a 0.45 µm polypropylene membrane syringe filter. The total extract was concentrated to dryness under a gentle stream of nitrogen at 60 °C. The final volume of the extract was made up to 1 ml with dichloromethane.

50 µl of each extract was placed in gas chromatography (GC) vials with 300 µl glass inserts and evaporated to dryness under a gentle stream of nitrogen at 60 °C. 15 µl of 1-phenydodecane (97 % Acros Organics, internal standard) solution prepared in hexane (1 µg ml^{-1}) and 10 µl of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1 % trimethylsilyl chloride (TMCl) were added to the vials (Sigma-Aldrich). The vials were sealed using screw caps with Teflon septa. Samples were derivatized in an oven at 80 °C for 1 h. Solvent blanks and calibration curve were run for each batch of eight samples. Samples were analyzed immediately after derivatization.

An Agilent 6890 series GC with 5973 MS (Agilent Technologies, Palo Alto, USA) was used for the analysis. An Agilent HP-5ms column (30 m x 0.25 mm x 0.25 µm film thickness) was used. Injection volume was 2 µl, splitless, with injector temperature of 280 °C. The temperature program was as follows; initial temperature 60 °C for 3 minutes then the temperature was raised to 190 °C at a rate of 10 °C min^{-1} and then it was finally raised to 300 °C at a rate of 30 °C min^{-1}. Transfer line, ion source and quadruple temperatures were 280 °C, 250 °C and 180 °C, respectively. The MS was operated in electron ionization mode. Scan mode was used to identify levoglucosan (99 % pure, Sigma-Aldrich) and 1-phenyldodecane with m/z 217 and 246 respectively. The exact masses used for calibration curves and aerosol samples were determined by SIM mode as m/z 217.3 and 246.3, respectively. The measurement uncertainty in SD of the GC-MS measurements was estimated to be ±1 % of the levoglucosan peak areas.

2.5 ^{14}C analysis

The ^{14}C/^{12}C ratio in the sampled particles was measured with accelerator mass spectrometry (AMS) (Hellborg and Skog, 2008) by using the 250 kV single-stage AMS at Lund University (Skog, 2007;Skog et al., 2010). Prior to the analysis, the carbon in the particle filter sample was transformed to graphite according to the procedure described in Genberg et al. (2010). In brief, a filter sample corresponding to approximately 50 µg carbon was mixed with CuO and combusted in a vacuum. Evolved CO_2 was purified cryogenically, mixed with H_2 and heated to 600 °C in the presence of an iron catalyst. In the latter reaction the CO_2 was reduced into graphite. The results are presented as fraction modern carbon, F^{14}C (Reimer et al., 2004). A F^{14}C value of 1 represents the 1950 concentration of ^{14}C excluding human influences. The true atmospheric ^{14}C content has however been altered due to two effects, known as the bomb effect (Rafter and Fergusson, 1957) and the Suess effect (Suess, 1955). The bomb effect, which is referring to atmospheric testing of thermonuclear weapons in the 1940-1960s, has had a positive effect on the F^{14}C values, due to neutron-induced reactions forming ^{14}C. The Suess effect is the result of emission of CO_2 from anthropogenic fossil fuel combustion, leading to the ongoing increase of the atmospheric CO_2 concentration. Since fossil fuels are ^{14}C-free, the Suess effect generates decreased F^{14}C values of atmospheric carbon (Baxter and Walton, 1970). Estimated measurement uncertainties expressed as SD, are typically ±1 % of measurement values.

Prior to the F^{14}C measurements, 104 out of 123 filter samples were pooled with a neighbouring sample due to limited amount of filter material. In the pooled samples, filter material corresponding to 25 µg C were punched out from each of the two filter samples, resulting in the desirable mass of 50 µg C. Two pooled samples (19th-25th December 2014 and 17th-23rd February 2015) were omitted due to failure in the graphitization process and consequently lack of filter material.

Evaluation of the aethalometer model results was performed using mainly F^{14}C data and the source apportionment approach by Bonvalot et al. (2016). The ambient carbonaceous aerosol can be assumed to be composed of one fossil and one non-fossil fraction. Determination of the non-fossil fraction (f_{NF}) is performed by normalizing the measured F^{14}C (F^{14}C$_S$) by a non-fossil reference value (F^{14}C$_{NF,ref}$):

$$f_{NF} = \frac{F^{14}C_S}{F^{14}C_{NF,ref}} \tag{13}$$

A previous source apportionment study at Vavihill suggests that winter samples are highly influenced by wood burning but low levels of other modern carbon sources, i.e. biogenic primary and secondary aerosol (Genberg et al., 2011). Biomass used for wood burning has usually had a growth period of decades, implying that the integrated average $F^{14}C$ for wood burning is higher than the atmospheric $F^{14}C$ at the time of sampling. As in previous studies, we also assume that the biomass used in wood burning has an average $F^{14}C_{WB}$ of 1.10 (Szidat et al., 2006;Bonvalot et al., 2016). Hence, we use $F^{14}C_{NF,ref}$=1.10 during winter.

Summer carbonaceous aerosol mass at Vavihill has been found to be dominated by biogenic primary and secondary organic aerosol (Genberg et al., 2011;Yttri et al., 2011a). Hence, the summer time carbonaceous aerosol should have a $F^{14}C$ close to the atmospheric value at the sampling time, i.e. $F^{14}C_{Bio}$=1.04. Thus, summer time $F^{14}C_{NF,ref}$ was set to 1.04. Spring and fall are characterized by highly mixed sources of modern carbon. It can be expected that both wood burning and biogenic emissions contribute significantly to the carbonaceous mass during these seasons. We therefore chose the mean of winter and summer $F^{14}C_{NF,ref}$ to represent the spring and fall samples, i.e. 1.07. The total carbon can be assumed to be derived from three possible sources:

$$TC = TC_{NF} + TC_{FF} = TC_{WB} + TC_{Bio} + TC_{FF} \tag{14}$$

In Eq (14), sample TC is divided into non-fossil (NF) and fossil fractions (FF). NF can be further subdivided into wood burning (WB) and biogenic carbon (Bio). From Eq. (14) it is now possible to set up the ^{14}C mass balance equation:

$$TC \cdot F^{14}C_s = TC_{WB} \cdot F^{14}C_{WB} + TC_{Bio} \cdot F^{14}C_{Bio} + TC_{FF} \cdot F^{14}C_{FF} \tag{15}$$

In Eq. (15) $F^{14}C_S$ is the sample $F^{14}C$. $F^{14}C_{WB}$, $F^{14}C_{Bio}$ and $F^{14}C_{FF}$ are the reference $F^{14}C$ value for each of the respective sources. Since $F^{14}C_{FF}$ is equal to zero, this gives:

$$TC \cdot F^{14}C_s = TC_{WB} \cdot F^{14}C_{WB} + TC_{Bio} \cdot F^{14}C_{Bio} \tag{16}$$

TC non-fossil (TC_{NF}) can be calculated by Eq. (17):

$$TC_{NF} = TC \cdot f_{NF} \tag{17}$$

Total carbon from wood burning (TC_{WB}) can then be calculated by Eq. (18):

$$TC_{WB} = a \cdot [levoglucosan] \tag{18}$$

Here, a is the slope from the linear fit between TC_{NF} and levoglucosan for winter samples (Fig. S3), [levoglucosan] is the sample levoglucosan concentration. Only winter samples are used and the linear fit is forced through origin with the purpose of minimizing the effect of biogenic carbon on TC_{NF}. Hence, we assume that all non-fossil carbon is derived from wood burning during winter. However, it should be noted that combustion of fossil lignite (i.e. brown coal), can emit large quantities of levoglucosan and be confused with wood combustion (Fabbri et al., 2008). It is now possible to calculate the total carbon from biogenic sources:

$$TC_{Bio} = \frac{F^{14}C_S \cdot TC - TC_{WB} \cdot F^{14}C_{WB}}{F^{14}C_{Bio}} \tag{19}$$

In Eq. (19), $F^{14}C_S$ is the sample $F^{14}C$, $F^{14}C_{WB}$=1.10 and $F^{14}C_{Bio}$=1.04 (Bonvalot et al., 2016). Finally, it is possible to derive TC_{FF}:

$$TC_{FF} = TC - TC_{WB} - TC_{Bio} \tag{20}$$

2.6 HYSPLIT

The Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxier and Hess, 1998;Stein et al., 2015) was used to study the history of the air mass carrying the particles sampled on the filters and measured by the aethalometer. Gridded meteorological data from the Centre of Environmental Predictions (NCEP) Global Data Assimilation System (GDAS) were used as input to trajectory model. Back-trajectories were calculated at an hourly frequency 120 h backward in time and the trajectories started 100 m above ground at the Vavihill measurement site. For each filter sample, 72 trajectories were used since the sampling time was 72 h. Four regions of origin (Table 3) were defined and for each sample it was investigated how much time the air-mass had spent over each of the regions of origin. Also, the accumulated precipitation along each trajectory during the last 24 h before arrival at Vavihill was used to evaluate the effect of precipitation on aerosol particle concentration. For each sample, the accumulated precipitation along each of the 72 the trajectories were summarized.

2.7 Auxiliary measurements

NO_X was continuously monitored with a time resolution of 1 h with a CLD 700 AL chemiluminescence analyzer (Eco Physics, Duernten, Switzerland). The detection limit was 1 ppb. Mass concentration of PM_{10} was monitored with a tapered element oscillating microbalance (TEOM, 8500 FDMS, ThermoFisher Scientific). The time resolution was 1 h and detection limit 0.1 μg m^{-3}.

3 Results and discussion

3.1 Variations and features in carbon concentrations

Carbonaceous aerosol constitutes on average 13 % of the total PM_{10} during the measurement period. Figure 1a-b displays the temporal variation of particulate carbon throughout the measurement period. OC is elevated during summer (mean=1.29 μg m^{-3}) and fall (mean=1.86 μg m^{-3}) and then decrease during winter (mean=0.96 μg m^{-3}) and spring (mean=1.19 μg m^{-3}). EC peaked during fall (mean=0.32 μg m^{-3}) while the concentrations during winter (mean=0.19 μg m^{-3}), spring (mean=0.21 μg m^{-3}), and summer (mean=0.14 μg m^{-3}) were significantly lower ($p<0.05$, Fig. 1b).

A discrepancy in winter concentrations of carbonaceous compounds was found between this study (2014-2015) and a previous Vavihill source apportionment study (2008-2009). Genberg et al. (2011) found elevated concentrations of OC during winter (2.19 μg m^{-3}, $p<0.1$) and approximately twice the amount of EC during winter compared to summer (0.30 μg m^{-3} vs. 0.14 μg m^{-3}, $p<0.001$). EC is typically elevated during the cold period of the year, when residents burn wood for heating. In the present study we found no significant differences in OC or EC between summer and winter. Figure 1a reveals a decrease in carbonaceous aerosol mass concentration during winter, from the beginning of December 2014 to mid-February 2015. In fact, by comparing the measurement campaign TC during the winter 2014-2015 with the average TC during earlier winters we found that the TC concentration during the winter 2014-2015 was 35 % lower than the average winter of 2008-2013 ($p=0.024$, Fig. S4). By using HYSPLIT we find that the incoming air masses to Vavihill during the winter of this measurement campaign were influenced by approximately 45 % more precipitation than the average winter of 2000-2013 ($p=0.002$, Fig. S5). Furthermore, we found a weak but significant negative relationship between precipitation and TC ($R^2=0.1$; $p<0.05$). Wet deposition losses are thus likely to be at least a partial explanation of lower winter-time concentrations of carbonaceous aerosol in this study.

3.2 Variations in light absorption measurements and aethalometer model derived parameters

Figure 2 shows the AAE throughout the whole measurement campaign (June 2014–June 2015). In general, there was a strong negative relationship between AAE and ambient temperature ($R^2=0.74$; $p<0.001$). During summer the AAE remains low in the range of 1.0-1.2 (mean=1.12; standard deviation=0.07). An increase in AAE follows during the fall (mean=1.23; SD=0.1) and stays at 1.2-1.5 (mean=1.36; SD=0.07) throughout the winter period. In the spring, the AAE remains high (mean=1.31; SD=0.09), but is decreasing towards 1.1-1.2 at the end of the season. There is a significant difference in AAE between all seasons ($p<0.01$), except between winter and spring ($p=0.055$). The observed seasonal pattern is in accordance with earlier studies by Sandradewi et al. (2008b) and Herich et al. (2011) who found elevated AAE of 1.3-1.6 during winter and a decreased AAE of around 1.0 during summer.

Elevated AAE during the cold period of the year is most likely caused by increased use of wood burning for residential heating, this has been confirmed in several studies (Genberg et al., 2011;Herich et al., 2011;Sandradewi et al., 2008b). Since the measured aerosol light absorption most likely is a mixture of fossil and wood burning the selection of AAEs for the aethalometer model calculations are supported by the observed seasonal pattern, i.e. the observed AAE vary between AAE_{FF} and AAE_{WB}.

Figure 3 shows the diurnal variation of AAE (370-950 nm), BC_{FF}, BC_{WB} and NO_X between summer and winter and between weekdays and weekends. There is a minimum in AAE at 7-10 AM (local time, Fig. 3a-b), this coincide with morning traffic rush hours. Sandradewi et al. (2008b) found similar results during winter with a minimum in AAE around 8 AM. This result is confirmed by data presented in Fig. 3d, which shows the calculated BC_{FF} (950nm) from the aethalometer model. It is clear that there is a peak at 8-10 AM and at 5-7 PM in the BC_{FF} emissions. This pattern is validated by NO_X concentrations showing similar diurnal pattern as BC_{FF} (Fig. 3g-h), although the diurnal variation is stronger for the NO_X concentrations. Rissler et al. (2014) found similar peaks in NO_X and BC from a busy road in Copenhagen. A major source of NO_X is vehicle combustion engines and NO_X can thus be expected to correlate with BC_{FF}. Due to the rural location of Vavihill measurement station, it may take 2-3 h for the traffic emissions to reach the station if they originate from the major cities in the region, this can explain why the NO_X (and BC_{FF}) peaks occur somewhat later at Vavihill than expected traffic rush hours. Studying the long-term pattern between BC_{FF} and NO_X, there is a weak but significant correlation throughout the whole measurement campaign ($R^2=0.09$; $p<0.001$). However, since NO_X is efficiently oxidized by OH-radicals and ozone during periods with high UV-radiation it is more suitable to compare these on a seasonal basis. Significant but very weak correlations between

BC_{FF} and NO_X were found during fall (R^2=0.07; p=0.021), winter (R^2=0.2; p<0.001), spring (R^2=0.41; p<0.001) and summer (R^2=0.09; p=0.009). The CM_{FF} parameter shows similar pattern as BC_{FF} to NO_X.

The BC_{WB} concentration has a different diurnal pattern than BC_{FF}. In general, there is a peak in the BC_{WB} concentration from 7 PM to 3 AM (Fig. 3f), which indicates that most residents warm their houses by wood burning during the evenings and nights. Previous studies have found a similar diurnal pattern for wood burning derived emissions (Favez et al., 2010;Harrison et al., 2012;Harrison et al., 2013;Kristensson et al., 2013;Wang et al., 2011).

NO_X is not thought to be emitted in large quantities from wood burning, still NO_X and CM_{WB} concentrations are correlated during the whole measurement period (R^2=0.31; p<0.01). This can be explained by the fact that both parameters are strongly seasonal dependent, but for different reasons. NO_X is mainly emitted from traffic, a source with usually low seasonal dependence. However, since NO_X is susceptible to photo-oxidation, its lifetime will be decreased during summer and increased during winter. Hence, observed NO_X concentrations may be lower during summer and elevated during winter. CM_{WB} concentrations will be elevated during winter when residents heat their homes and mostly absent during summer. Hence, the correlation is strong but causality is most likely absent between them.

The seasonal patterns of other aethalometer model derived parameters are presented in Table 4 and Fig. 4. It is clear that the wood burning derived carbonaceous aerosol, CM_{WB}, follows a seasonal cycle with high concentrations during fall (mean=0.49 µg m^{-3}), winter (mean=0.65 µg m^{-3}) and spring (mean=0.51 µg m^{-3}), and low levels during summer (mean=0.07 µg m^{-3}). The CM_{WB} peaks with 5 % contribution to PM_{10} during winter, in summer the CM_{WB} contribution is low (0.6 %). The CM_{WB} contribution to TC peaks in winter with 56 % and is reduced to 6 % during summer. Hence, it is likely that the largest part of wood burning is conducted with the purpose of residential heating, as in contrast to decorative burning which can be expected independently of outdoor temperature.

The fossil fuel derived parameter, CM_{FF}, shows a less distinct seasonal pattern than CM_{WB}, most probably because the main source, traffic, has a much smaller seasonal variation than wood burning. CM_{FF} contributed 2-4 % to PM_{10} during the year (21-35 % contribution to TC) with a maximum during spring and a minimum during summer. Finally, the biogenic aerosol carbon concentrations are substantial during summer (9 % of PM_{10}; 72 % of TC) and low during winter (0.9 % of PM_{10}; 8 % of TC).

3.3 Comparison: Levoglucosan to aethalometer model

Levoglucosan concentrations displayed an annual variation with elevated concentrations during the cold period of the year (Fig. S6). Mean concentrations during fall, winter and spring were 0.061 (SD±0.082), 0.086 (SD±0.073) and 0.063 (SD±0.115) µg m^{-3}, respectively. The summertime mean levoglucosan concentration was 0.014 (SD±0.0142) µg m^{-3}. There was a significant difference between winter and summer (p=0.03). Measured concentration levels and seasonal patterns were similar to those found by Genberg et al. (2011) at the same measurement site. The aethalometer model derived carbonaceous matter from wood burning, CM_{WB}, correlated well with levoglucosan (Fig. 5, R^2=0.7; p<0.001). The correlation was strongest during winter (R^2=0.82) and spring (R^2=0.81) and lower during fall (R^2=0.37) and summer (R^2=0.30). Mean measured levoglucosan per unit of BC_{WB} was estimated to 0.64 (standard deviation=0.73). Previous wood stove measurements report mean levoglucosan to EC ratio of 0.82 (Iinuma et al., 2007;Schmidl et al., 2008). Thus, the estimated ratios presented in this study are in line with emission inventories from wood stoves. The measured ratios in comparison to references imply that the atmospheric decomposition of levoglucosan is in general slow, at least during the cold seasons. Another possibility is that the wood burning sources are located fairly close to the sampling site.

Further, CM_{FF} is also correlated with levoglucosan throughout the whole year ($R^2=0.39$; $p<0.001$). This finding is in contrast to Herich et al. (2011) who found no correlation between BC_{FF} and levoglucosan in the alpine regions of Switzerland. One explanation might be inaccurate apportionment where the wood burning aerosol exhibits an AAE close to 1, and thus being apportioned as fossil fuel aerosol. This hypothesis is supported by the study of Martinsson et al. (2015), but whether this phenomenon would be more common and pronounced in Swiss alpine regions in comparison to southern Sweden is unknown.

3.4 Aethalometer model evaluation by radiocarbon and levoglucosan source apportionment

We used $F^{14}C$ and levoglucosan data (Fig. S6-7) applied to the method proposed by Bonvalot et al. (2016) to evaluate the aethalometer model parameters. In Eq. (18), a was set to 8.32 based on results from linear regression between winter values of TC_{NF} and levoglucosan. The apportioned fossil fuel carbon fraction from the $F^{14}C$ and levoglucosan method (TC_{FF}) is estimated to 20 % of TC throughout the year (Fig. 6), this is in good agreement with the previous studies from Vavihill measurement station (Genberg et al., 2011;Yttri et al., 2011a). However, there was a significant difference in fossil carbon apportioned between the two methods ($p=0.04$). Throughout the year, the aethalometer model overestimates the fossil carbon by a factor 1.3 compared to $F^{14}C$ and levoglucosan source apportionment. Further, TC_{FF} displays a better agreement with NO_X than the aethalometer model derived CM_{FF} ($R^2=0.15$; $p<0.001$ vs. $R^2=0.06$; $p=0.007$), indicating a more accurate apportionment of fossil carbon using $F^{14}C$.

Apportioned wood burning, TC_{WB}, showed a clear intra-annual variability with high carbon contribution during winter (60 %) and low during summer (9 %), this is similar to the aethalometer model, CM_{WB}, results. For the whole year, there was no significant difference in apportioned wood burning carbonaceous aerosol between the two methods ($p=0.8$).

The biogenic carbon fraction, TC_{Bio}, is dominating TC during summer (75 %), but is not negligible during winter (13 %, Fig. 6) in the radiocarbon and levoglucosan model. Apportioned biogenic carbon was in good agreement between the methods, i.e. no significant differences between the methods were observed for the whole year data ($p=0.32$).

Thus, with respect to apportioned wood burning and biogenic carbonaceous aerosol, the aethalometer model setup presented in this paper shows good agreement with the radiocarbon and levoglucosan model. However, it is interesting to investigate two other possible setups of the model, for a possibly more accurate aethalometer model source apportionment of the fossil carbon: A) to include the removed outliers in the linear regressions used to derive C_1 and C_2; B) to solve Eq. 9 with a bilinear fit, as originally proposed by Sandradewi et al. (2008a).

A) Including removed outliers would result in C_1 and C_2 parameters of 371 047 µg m^{-2} and 88 188 µg m^{-2}, respectively. The statistics for both linear regressions would improve, the R^2 for C_1 would for instance increase from 0.29 to 0.67. However, increasing the C_1 parameter by a factor of 1.7 (from 214 467 to 371 047 µg m^{-2}) would result in large discrepancies compared to the $F^{14}C$ and levoglucosan method. In general, for the whole measurement campaign, the fossil fuel contribution by the aethalometer model would be overestimated by a factor 2.4 while the biogenic mass contribution would be underestimated by a factor 1.7 compared to radiocarbon and levoglucosan source apportionment. The CM_{WB} contribution to TC would be underestimated by a factor 1.3 compared to TC_{WB}.

B) When we derived the C_1 and C_2 parameters by solving Eq. 9 as a multilinear fit (letting CM_{Bio} be a fixed intercept) C_1 and C_2 were determined to 497 279 µg m^{-2} and 68 859 µg m^{-2}, respectively. CM_{Bio} was fixed to -0.103 µg m^{-3}. Hence, the multilinear solution provides a C_1 parameter that is approximately 2.2 times larger than the C_1 obtained by the current linear regression of Eq. 10, and a C_2 parameter that is 1.7 times smaller than the C_2 obtained by Eq. 11. The multilinear aethalometer model solution should ideally be compared to radiocarbon and levoglucosan source apportionment results derived from Eq. 18 were *a* was derived from a linear fit of winter data with an allowed intercept, i.e. biogenic carbon is allowed in TC_{NF}. *a* is then determined to 7.16 with an intercept of 0.17. This approach will lead to an overestimation of CM_{FF} by a factor 3.2 compared to TC_{FF} and an underestimation of CM_{WB} by a factor 1.5 compared to TC_{WB}. Thus, a bilinear solution to Eq. 9 would increase the discrepancy between the aethalometer model and the radiocarbon and levoglucosan source apportionment method.

Furthermore, we performed a sensitivity analysis with the aim of studying the impact of increased or decreased biogenic carbon during winter on the derived C_1 and C_2 parameters and the resulting source apportionment. In Eq. 10 and 11 we increased and decreased the TC by +5 % and -5 %, respectively, without changing any of the b_{abs} parameters. Thus, the induced change in TC will be analogous to changes in biogenic carbon concentration, assuming that this fraction is non-light absorbing. A 5 % change in TC led to a corresponding 5 % change in the derived C_1 and C_2 parameters. Hence, increasing the non-light absorbing TC would result in increased apportionment of TC into fossil fuel and wood burning, this would in turn result in a decreased apportionment to biogenic carbon. Increased concentrations of non-light absorbing carbon by 5 % during winter would result in an even larger annual significant overestimation of fossil fuel carbon by the aethalometer model (a factor 1.4 higher, p=0.007) in comparison to the $F^{14}C$ and levoglucosan source apportionment. However, this 5 % increase would not result in a significantly different aethalometer model apportionment of wood burning and biogenic carbon in comparison to the $F^{14}C$ and levoglucosan method. On the other hand, a 5 % decrease of non-light absorbing carbon would lead to better agreement between the aethalometer model and the $F^{14}C$ and levoglucosan method. For the whole year, there would be no significant difference in apportioned fossil fuel carbon by the two methods (p=0.137). Also, apportioned wood burning and biogenic carbon would not show any significant differences between the methods. Thus, the presence of non-light absorbing carbon might explain the observed significant difference in apportioned fossil fuel carbon (Fig. 6). We conclude that the model is sensitive to non-light absorbing carbon and that this fraction needs to be minimized in order for the model to function correctly.

3.5 Air mass trajectory analysis

For the whole measurement period, air masses arriving from SW dominated and contributed with 35 % of the incoming air masses. The remaining contributions of the NW, SE and NE sectors were 32, 17 and 16 %, respectively. Air masses arriving from SE were dominating during the fall (31 %) and were more polluted than air masses from other directions. CM_{FF}, CM_{WB}, levoglucosan and PM_{10} all increased with increasing fraction of incoming SE winds ($p<0.01$). The elevated PM levels from this area can be explained by a large fraction of densely populated land and with air dominated by high pressure systems inhibiting vertical mixing with cleaner air.

Increasing fraction of NE air masses correlated with increasing amount of biogenic aerosol (CM_{Bio}, $p<0.01$), while other types of PM were low. $F^{14}C$ also increased with NE fraction ($p=0.03$), supporting the impact of biogenic sources from this direction. This relation seems geographically sound, due to the relatively large and sparsely populated land area. Further, since the abundance of incoming NE air masses was low during winter (10 %), the possible disturbance of biogenic carbon in the aethalometer model should have been minimized.

The NW direction from Vavihill is dominated by the North Atlantic, North Sea and Norwegian Sea which are displayed in the results; all carbonaceous PM species tend to decrease with increasing fraction of incoming air mass from NW ($p<0.01$). Air masses arriving from this region can thus be considered relatively clean, this direction dominated during the summer (43 %). Finally, SW air masses tend to carry NO_X, but no carbonaceous PM species correlates with this air mass direction. Increased fraction of SW air masses correlates to increased precipitation ($p<0.01$), hence it is possible that SW-related precipitation decreases carbonaceous PM through wet deposition while leaving the NO_X unaffected.

These results are in line with the findings of Kristensson et al. (2008) who found that air masses from north were in general cleaner than air masses from continental Europe.

3.6 Source apportionment uncertainty estimation by the propagation of errors

Many source apportionment studies omit comprehensive uncertainty estimations. This can have severe impacts for decision and policymaking based on the studies. In the present study, an attempt to approximate measurement and linear estimation uncertainty on the calculated fractions of fossil fuel (CM_{FF}), wood burning (CM_{WB}) and biogenic (CM_{Bio}) carbonaceous aerosol was conducted by the recommendations of Henry et al. (1984). The approach of propagation of errors was used and the most obvious uncertainties were estimated and summarized. Aethalometer measurements have been suggested to give an uncertainty of 5 % to absorption coefficients (Hansen, 2005). However, recent work by Zanatta et al. (2016) proposes an uncertainty of 35 % to aethalometer derived absorption coefficients. We select the more conservative uncertainty of 35 % for this analysis. AAE_{WB} and AAE_{FF} are associated with uncertainties of 30 % and 10 %, respectively (Table 1). It should be noticed that previous studies support our selection of AAEs (Massabo et al., 2015;Sandradewi et al., 2008b). The measured values of OC, EC and TC are associated with an uncertainty of 17 % (Cavalli et al., 2016). Finally, the estimation of the C_1 and C_2 parameters were associated with uncertainties of 31 % and 18 %, respectively. Considering that the fraction of fossil fuel combustion aerosol is based on aethalometer measurements (absorption coefficients), AAE_{FF}, TOA (OC, EC, TC) and C_1, this parameter get a total uncertainty of 41 %. Similarly, for the fraction wood burning aerosol, we base the total uncertainty on aethalometer measurements, AAE_{WB}, TOA and C_2. The overall uncertainty is then estimated to 42 %. Despite the relatively high estimated uncertainty, it is worth noting that the CM_{WB} agreement with levoglucosan was satisfactory (Fig. 5). Finally, we base the biogenic aerosol (CM_{Bio}) uncertainty on aethalometer measurements, AAE_{FF}, AAE_{WB}, C_1, C_2 and TOA. The biogenic carbonaceous aerosol fraction then reaches a total uncertainty of 50 %.

4 Conclusions

The aethalometer model offers fast, inexpensive apportionment of the carbonaceous aerosol. The accuracy and robustness of the model principle has previously been questioned. In this study we propose a small modification to the aethalometer model which enables apportioned non-absorbing carbon, here assumed to be biogenic carbon, to vary. Propagation of errors showed that fossil, wood burning and biogenic carbonaceous aerosol quantification by the aethalometer model may be highly uncertain. Nevertheless, we show that the model works well for a whole year source apportionment for quantifying wood burning and variable biogenic carbonaceous aerosol at a rural site in southern Sweden, as there was a good agreement between aethalometer model and the radiocarbon and levoglucosan source apportionment. The aethalometer model overestimated the fossil carbonaceous aerosol compared to the radiocarbon and levoglucosan method, which may be explained by possible interference of non-light absorbing biogenic carbon during winter. However, relating aerosol light absorption to carbon mass concentration by a bilinear solution or including statistically determined outliers resulted in even larger discrepancies between the two methods. Future studies are needed to investigate the repeatability of our proposed modified aethalometer model.

5 Data availability

All data are accessible through the supporting information.

Author contributions

Johan Martinsson designed the study and analysed all data. Hafiz Abdul Azeem conducted levoglucosan analysis. Moa Sporre generated the HYSPLIT results. Erik Ahlberg and Emilie Öström were involved in the aerosol sampling. Adam Kristensson, Erik Swietlicki, Kristina Eriksson Stenström and Robert Bergström assisted in the writing process.

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Table 1: Values of AAE_{FF} and AAE_{WB} derived from reference emission inventories.

AAE_{FF}	Spectral region	AAE_{WB}	Spectral region	References
1	470-660nm	2.1	470-660nm	(Clarke et al., 2007)
		1.45	UV-IR	(Day et al., 2006)
		1.4	UV-IR	(Garg et al., 2016)
0.9	UV-IR	2.5	UV-IR	(Kirchstetter et al., 2004)
		1.9	UV-IR	(Kirchstetter and Thatcher, 2012)
		1.75	UV-IR	(Lewis et al., 2008)
		1.3	UV-IR	(Martinsson et al., 2015)
		1.3	467-660nm	(Roden et al., 2006)
		1.6	UV-IR	(Saleh et al., 2013)
		2.8	UV-IR	(Sandradewi et al., 2008b)
1.1	450-700nm			(Schnaiter et al., 2003)

Table 2: Site specific mass absorption coefficients (MAC) from the Vavihill measurement station. Values were obtained by linear regression analysis of measured absorption coefficients and elemental carbon (EC) concentrations. The slope is equivalent to $\sigma_{abs}(\lambda)$. Uncertainties are represented by standard errors (N=123).

λ (nm)	$\sigma_{abs}(\lambda)$ (m^2 g^{-1})
370	41.21 ± 1.00
470	29.06 ± 0.96
520	24.78 ± 0.80
590	21.29 ± 0.68
660	17.57 ± 0.55
880	12.64 ± 0.39
950	11.93 ± 0.37

Table 3: Definition of wind directions of incoming air masses.

Direction	Degrees (°)
Northeast (NE)	0-90
Southeast (SE)	90-180
Southwest (SW)	180-270
Northwest (NW)	270-360

Table 4: Seasonal mean concentrations and contributions to PM_{10} and TC of aethalometer model derived parameters. Uncertainties are given in standard deviations.

	Concentration ($\mu g\ m^{-3}$)			Contribution to PM_{10} (%)			Contribution to TC (%)		
Season	**CM_{WB}**	**CM_{FF}**	**CM_{Bio}**	**CM_{WB}**	**CM_{FF}**	**CM_{Bio}**	**CM_{WB}**	**CM_{FF}**	**CM_{Bio}**
Summer	0.07±0.05	0.31±0.19	1.04±0.59	0.6±0.4	2.7±1.1	9.0±2.8	6.1±4.0	21.5±6.9	72.4±6.5
Fall	0.49±0.46	0.62±0.36	1.06±0.68	2.6±1.9	3.7±1.1	6.8±3.4	22.2±14.9	28.4±8.0	49.3±19.8
Winter	0.65±0.53	0.37±0.25	0.13±0.21	5.4±3.5	3.1±1.3	0.9±1.6	56.5±13.3	35.5±9.4	8.0±14.4
Spring	0.51±0.69	0.35±0.30	0.54±0.32	4.9±3.5	3.9±2.1	8.9±9.6	32.3±17.9	25.6±9.0	42.1±22.5

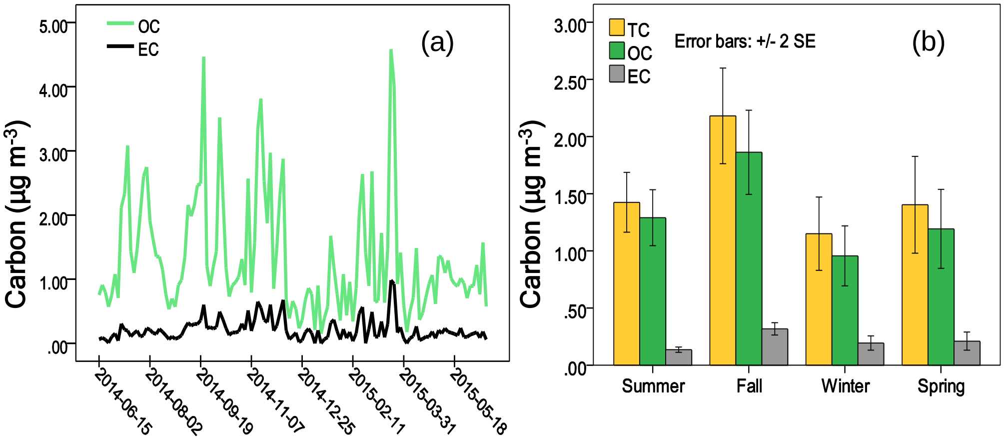

Figure 1: Temporal variations in OC, EC and TC. (a) Shows the temporal variation of OC and EC with a time resolution of 72 h (N=123). (b) Displays the average concentration of TC, OC and EC divided into seasons; summer (N=32), fall (N=30), winter (N=30) and spring (N=31). Error bars display ±2 standard errors (SE).

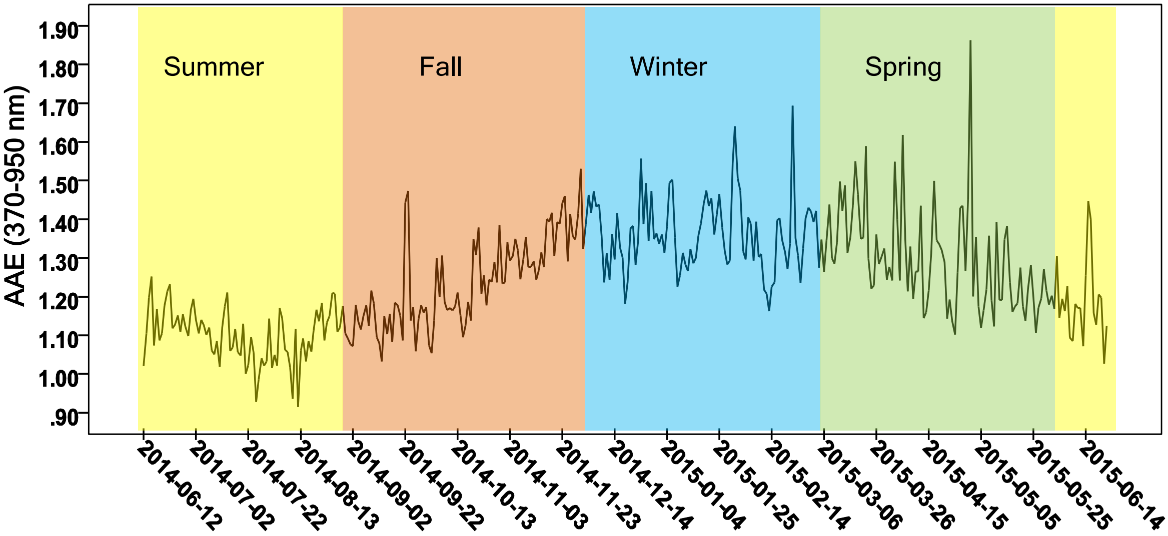

Figure 2: Annual variations in AAE (370-950nm) at the Vavihill measurement station. Colours represent different seasons of the year. N=369.

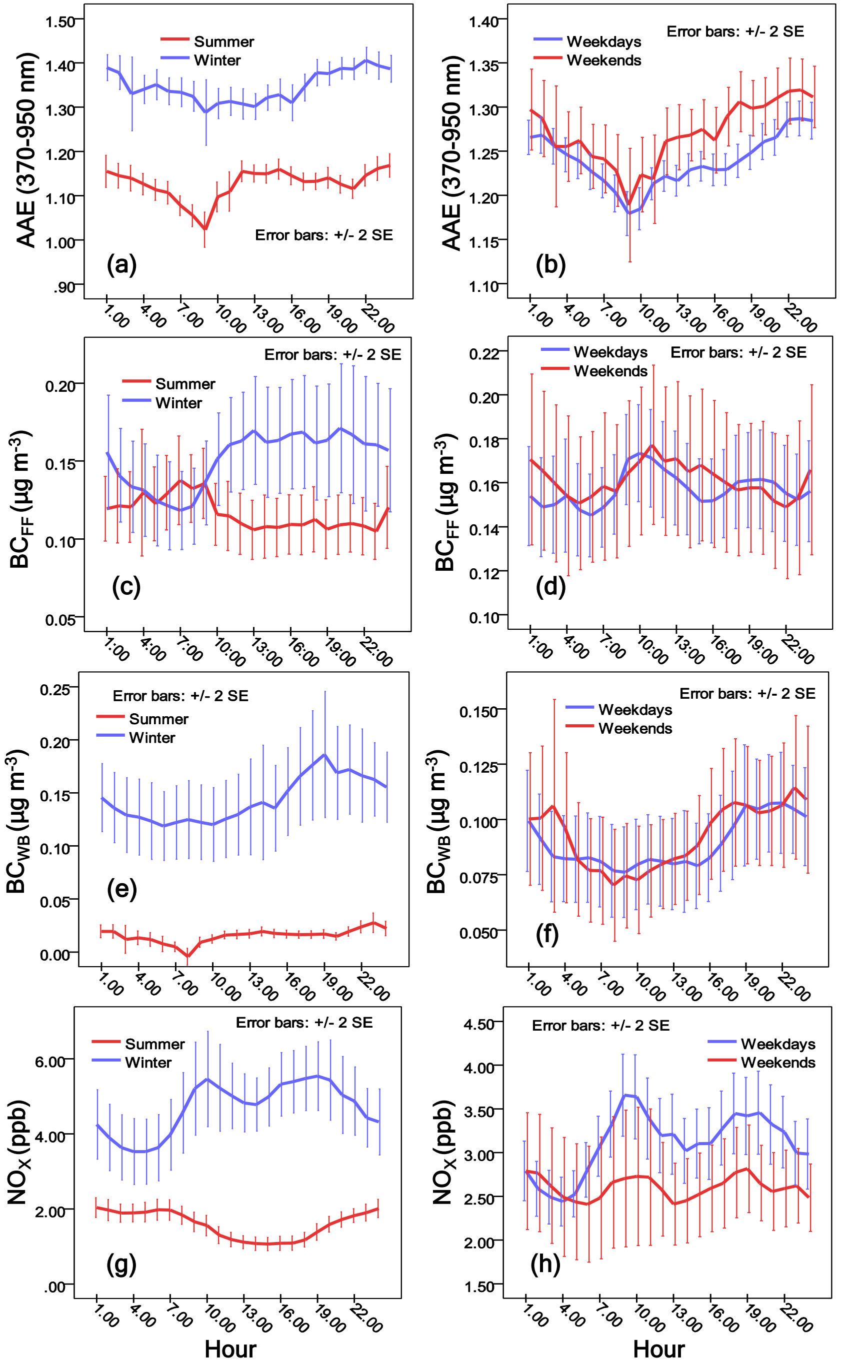

Figure 3: Diurnal variations of AAE (370-950 nm, a-b), BC_{FF} (950 nm, c-d), BC_{WB} (370 nm, e-f) and NO_X (g-h) at the Vavihill measurement station. Figures (a), (c), (e) and (g) represents diurnal differences between summer and winter while Fig. (b), (d), (f), and (h) represents diurnal differences between weekdays (Monday-Friday) and weekends (Saturday-Sunday, including national holidays). Uncertainties are given as 2 times the standard error (SE). 5

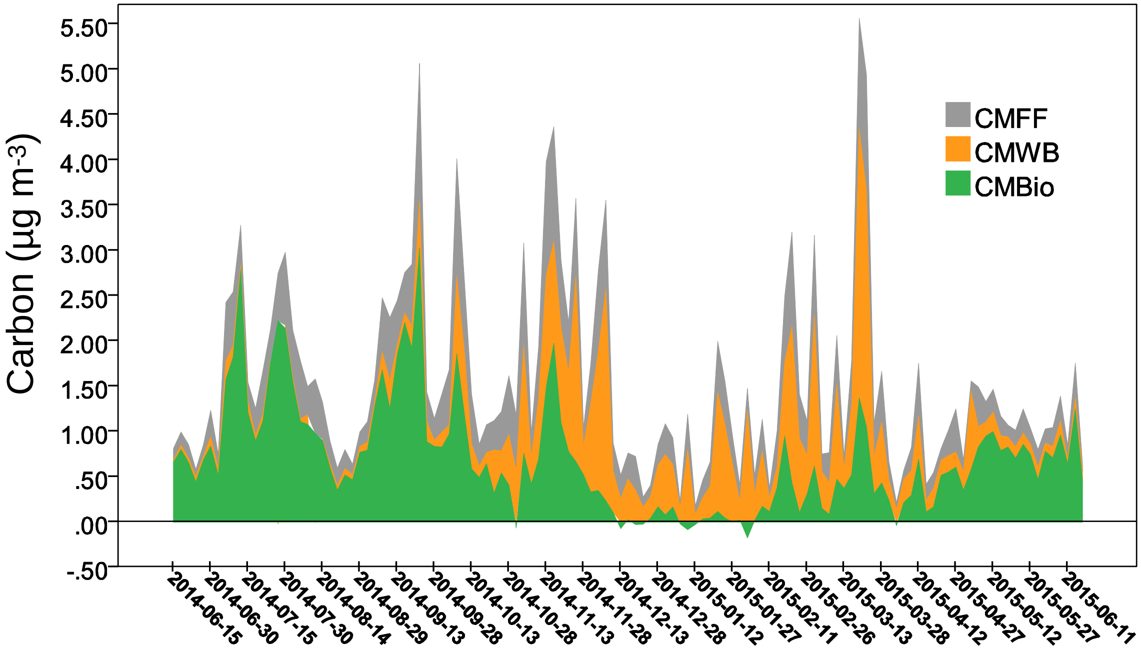

Figure 4: Aethalometer model source apportionment of total carbon from the Vavihill measurement station, June 2014–June 2015. N=123.

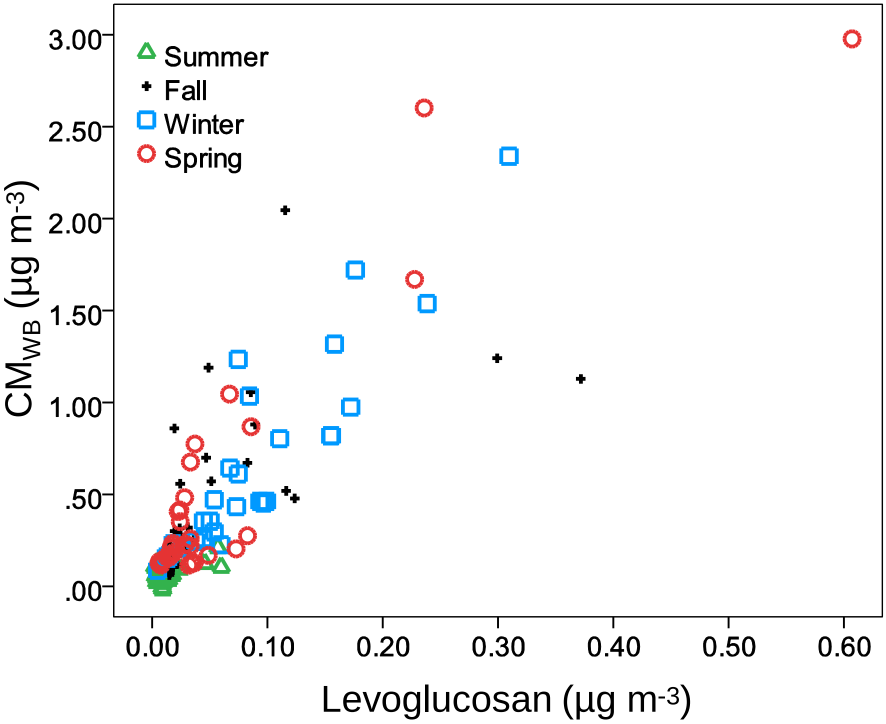

Figure 5: Comparison between CM_{WB} and levoglucosan. R^2=0.70, N=122.

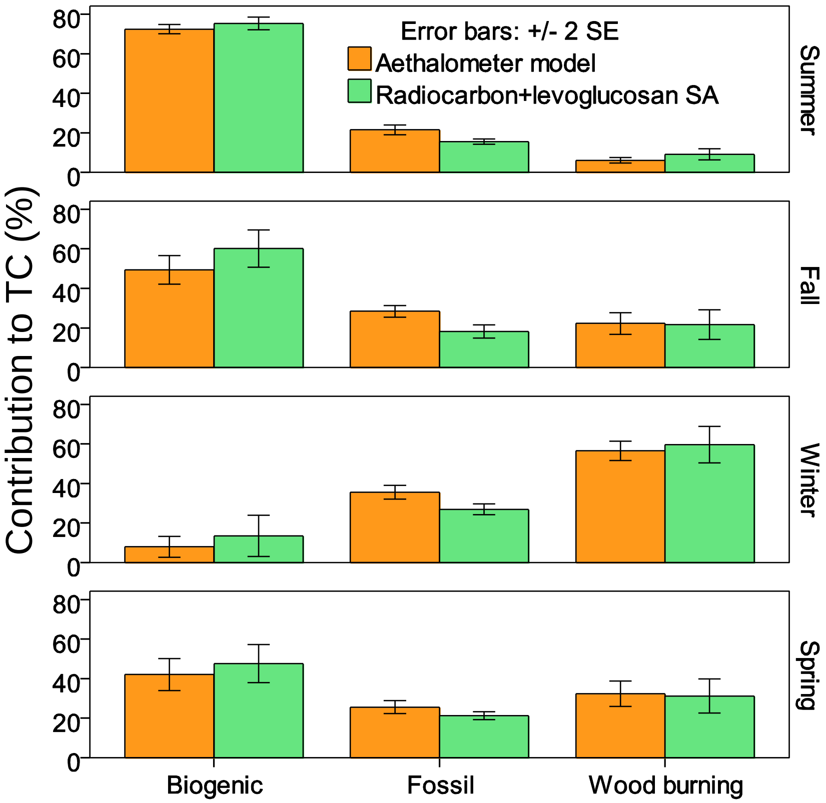

Figure 6: Seasonal comparison of source contribution to total carbon (TC) between the aethalometer model and radiocarbon + levoglucosan source apportionment (SA). Error bars display 2 times standard error of the mean (SE).