



## Evaluation of $\delta^{13}\text{C}$ in Carbonaceous Aerosol Source Apportionment at a Rural Measurement Site

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### ABSTRACT

The stable isotope of carbon,  $^{13}\text{C}$ , has been used in several studies for source characterization of carbonaceous aerosol since there are specific signatures for different sources. In rural areas, the influence of different sources is complex and the application of  $\delta^{13}\text{C}$  for source characterization of the total carbonaceous aerosol (TC) can therefore be difficult, especially the separation between biomass burning and biogenic sources. We measured  $\delta^{13}\text{C}$  from 25 filter samples collected during one year at a rural background site in southern Sweden. Throughout the year, the measured  $\delta^{13}\text{C}$  showed low variability ( $-26.73$  to  $-25.64\%$ ). We found that the measured  $\delta^{13}\text{C}$  did not correlate with other commonly used source apportionment tracers ( $^{14}\text{C}$ , levoglucosan).  $\delta^{13}\text{C}$  values showed lower variability during the cold months compared to the summer, and this narrowing of the  $\delta^{13}\text{C}$  values together with elevated levoglucosan concentrations may indicate contribution from sources with lower  $\delta^{13}\text{C}$  variation, such as biomass or fossil fuel combustion. Comparison of two Monte Carlo based source apportionment models showed no significant difference in results when  $\delta^{13}\text{C}$  was incorporated in the model. The insignificant change of redistributed fraction of carbon between the sources was mainly a consequence of relatively narrow range of  $\delta^{13}\text{C}$  values and was complicated by an unaccounted kinetic isotopic effect and overlapping  $\delta^{13}\text{C}$  end-member values for biomass burning and biogenic sources.

**Keywords:** End-member distributions; Biomass burning; Biogenic aerosol.

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### INTRODUCTION

Atmospheric particulate matter (PM) can have a negative effect on human health (Dockery *et al.*, 1993; Pope *et al.*, 1995; Abbey *et al.*, 1999; Brook *et al.*, 2010). For example, incomplete combustion of biomass or fossil fuels may produce polycyclic aromatic hydrocarbons (PAH's), which are highly carcinogenic (IARC, 2010; Eriksson *et al.*, 2014). Anthropogenic particulate emissions also affect climate. These effects can be direct, such as increased scattering or absorption of incoming solar radiation, or indirect by increasing light scattering caused by altered cloud properties (Twomey, 1974; Albrecht, 1989). Black carbon (BC), and more recently brown carbon (BrC), have been shown to absorb light, thereby contributing to climate warming (Bond

*et al.*, 2013; Laskin *et al.*, 2015). In contrast, sulphate and nitrate compounds mainly scatter light and thereby contribute to climate cooling (IPCC, 2013). The climate radiative forcing by carbonaceous atmospheric aerosols is believed to have the highest uncertainty of all climate forcers (IPCC, 2013).

Carbonaceous aerosols, a significant contributor to PM, originate from both natural and anthropogenic sources. Natural sources include volcanos, forest fires, and biogenic emissions from plants. Biogenic emissions can be divided into biogenic primary organic aerosol (BPOA), containing pollen and fungal spores, and biogenic secondary organic aerosol (BSOA), which are formed by gas-particle partitioning where various biogenic gases are partitioned into particle phase. Among the anthropogenic sources, fossil fuel and biomass combustion are two of the major ones (Dusek *et al.*, 2014). Since many particle-types have specific origins, source apportionment of atmospheric aerosols can be used to reduce the overall uncertainty of the climate effects. An improved apportionment could also make it easier to develop abatement strategies regarding the health aspects of aerosols.

The relative abundance of stable carbon isotopes

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(expressed as  $\delta^{13}\text{C}$ ) has been widely used to characterize the sources of atmospheric aerosol (Chesselet *et al.*, 1981; Cachier *et al.*, 1985; Cachier, 1989; Widory, 2006; Cao *et al.*, 2011; Kawashima and Haneishi, 2012). Common sources of aerosols have specific isotopic signatures, but variation in  $\delta^{13}\text{C}$  in aerosols from different sources can depend on many factors. The isotopic signature of the aerosol can be the same as the source, but oxidation and aging of the aerosols lead to isotopic changes. Compounds formed from oxidation processes are in general more depleted in the heavier isotopes (Sakugawa and Kaplan, 1995; Wang and Kawamura, 2006). This phenomenon is called the kinetic isotopic effect (KIE). It has been shown that  $\delta^{13}\text{C}$  of the organic carbon (OC) fraction of the aerosol can be affected by atmospheric processing (Kirillova *et al.*, 2013).

Cachier (1989) found that aerosols in the northern hemisphere were more depleted in  $\delta^{13}\text{C}$  ( $\sim -26\%$ ) than southern hemisphere aerosols ( $-23$  to  $-17\%$ ). This phenomenon was explained by a larger contribution of combustion emissions, such as industrial processes and vegetation fires in the northern hemisphere while the southern hemisphere was dominated by marine and/or natural vegetation/soil emissions. However, it should be noted that an alternative explanation for the hemisphere  $\delta^{13}\text{C}$  differences was recently suggested, involving marine primary production and sea spray aerosol (Ceburnis *et al.*, 2016). For aerosol generated through different fossil combustion sources, the  $\delta^{13}\text{C}$  range from  $-26$  to  $-20\%$  for gasoline,  $-28$  to  $-24\%$  for diesel,  $-27$  to  $-23\%$  for natural gas (methane) and  $-25$  to  $-21\%$  for coal (Widory *et al.*, 2004; Widory, 2006; Cao *et al.*, 2011; Kawashima and Haneishi, 2012). However, differences in  $\delta^{13}\text{C}$  between the hemispheres may also be explained by differences in metabolic pathways among plants (i.e.,  $\text{C}_3$ - and  $\text{C}_4$ -plants), where  $\text{C}_4$ -plants is thought to dominate the southern hemisphere (Taiz, 2015).  $\text{C}_3$ - and  $\text{C}_4$ -plants differ in the carbon assimilation pathway, which results in different  $\delta^{13}\text{C}$  values.  $\text{C}_3$ -plants are in the range of  $-35$  to  $-24\%$  while  $\text{C}_4$ -plants range from  $-20$  to  $-11\%$  (Turekian *et al.*, 1998; Das *et al.*, 2010; Cao *et al.*, 2011; Kawashima and Haneishi, 2012). Thus, combustion and biogenic emissions of these different groups of plants generate aerosols with different  $\delta^{13}\text{C}$ -signatures. Thereby, the plant source can be traceable, with respect to metabolic pathway. Isotope fractionation between biomass fuels and the produced combustion aerosol may occur, however the present research in this area display straggly results. Fractionation may be limited to a maximum of 0.5% higher  $\delta^{13}\text{C}$  for  $\text{C}_3$ -plants generated combustion aerosols (Turekian *et al.*, 1998), however, other studies have seen larger absolute fractionation in the original biomass material of  $-1.3$  to  $-4.7\%$  (Czimeczik *et al.*, 2002; Turney *et al.*, 2006; Garbaras *et al.*, 2015).

Several of the major sources of carbonaceous aerosol show an overlap in  $\delta^{13}\text{C}$  values. There is a considerable overlap of  $\delta^{13}\text{C}$ -signatures within the sources of fossil fuel combustion, although liquid fuels are somewhat more depleted than solids. The fossil fuel sources in turn overlap with the  $\delta^{13}\text{C}$  values of  $\text{C}_3$ -plants, which are consistent with biomass burning, BPOA and BSOA. The case of

overlapping  $\delta^{13}\text{C}$  values for different sources can be difficult to handle when it comes to source characterization of the aerosol. Inspired by the work by Martinelli *et al.* (2002), Gorka *et al.* (2009) conducted a simple two-component source apportionment using  $\delta^{13}\text{C}$  in an urban area in Poland. They assumed that the ambient carbonaceous aerosol was only influenced by coal combustion or  $\text{C}_3$ -plants and used mean values of  $\delta^{13}\text{C}$  of these sources in order to calculate the contribution from each source during the seasons. However, the carbonaceous aerosol is most often influenced by a larger number of sources, meaning that more extensive source apportionment models are needed. Andersson *et al.* (2015) measured dual carbon isotopes ( $^{14}\text{C}$  and  $^{13}\text{C}$ ) of elemental carbon (EC) in order to apportion combustion sources in China. By utilizing the difference in  $\delta^{13}\text{C}$  between solid fossil fuels, liquid fossil fuels and biomass burning (i.e.,  $\text{C}_3$ -plants) they successfully apportioned the combustion carbonaceous aerosol (EC).

Quantifying the sources with  $\delta^{13}\text{C}$  on the total carbon (TC) is more difficult due to the chemically reactive organic carbon (OC). While EC is more or less inert, the  $\delta^{13}\text{C}$  in OC may change significantly due to photochemical processing in the atmosphere (Kirillova *et al.*, 2013; Kirillova *et al.*, 2014). Also, EC only originates from combustion, implying that fewer possible sources are available for EC apportionment. However, OC may originate from a large number of sources such as combustion and various biogenic sources (microbial and plants). Hence, the  $\delta^{13}\text{C}$  source values for OC are much less constrained compared to EC. Thus, lack of separation of OC and EC prior to  $\delta^{13}\text{C}$  analysis may obstruct successful source apportionments.

In source characterization and apportionment, the combination of using measurements of OC, EC,  $^{14}\text{C}$  and levoglucosan has shown to be successful in several studies where the three most common sources of carbonaceous aerosol are investigated: biogenic, fossil fuel combustion and biomass combustion (Genberg *et al.*, 2011; Yttri *et al.*, 2011a, b). In the present study we analyzed particles collected on filters at a rural monitoring site in southern Sweden in order to investigate if  $\delta^{13}\text{C}$  can contribute to a refined source apportionment of the total carbonaceous aerosol (TC). Aerosols collected on filters were analyzed for  $\delta^{13}\text{C}$ , this data was complemented with data for levoglucosan, radiocarbon, OC and EC from the same filters. Data for OC, EC, radiocarbon and levoglucosan analysis have been published in a previous study (Genberg *et al.*, 2011). However, the above mentioned measurements techniques consume filter material which resulted in that a total continuous measurement period of a whole year was not achievable (i.e., for some filter samples the filter material was not enough for all analyzes).  $\delta^{13}\text{C}$  was also measured on sawdust from common tree species in southern Sweden with the aim to enhance the differences in  $\delta^{13}\text{C}$  distributions between all  $\text{C}_3$ -plants (i.e., trees), responsible for biogenic aerosol emissions, and common tree species for biomass combustion. A Markov Chain Monte Carlo (MCMC) based source apportionment model was used with the aim of estimating and comparing source contribution using  $\delta^{13}\text{C}$ .

## METHODS

### Site Description and Sampling

Aerosol sampling was conducted on the ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure network) and EMEP (European Monitoring and Evaluation Programme) background station Vavihill in southern Sweden (56°01' N, 13°09' E, 172 m.a.s.l.) (Fig. 1). The station is located on a pasture that is occasionally visited by grazing cattle. The surrounding land is mainly deciduous forest. The closest large pollution sources are Copenhagen, Malmö and Helsingborg, which are located southwest and west of the station at a distance of 50, 45 and 25 km, respectively. Earlier studies have shown that air masses from the south carry a significant contribution of particles, while northerly air masses are less polluted (Kristensson *et al.*, 2008).

Prior to sample collection, all filters were pre-heated for 4 hours at 900°C to volatilize volatile organic compounds (VOC) and were then stored in a –18°C freezer until sampling. Particles were collected from May 2008 to April 2009 on a weekly basis (168 h) with a flow of 38 l min<sup>-1</sup> on 47 mm quartz-fiber filters (N = 25, Pallflex 2500QAT-UP) using a PM<sub>10</sub> inlet and a Leckel SEQ 47/50 sampler. Filters were placed in petri dishes, wrapped in aluminum foil and stored in a refrigerator at +5°C until analysis. Filter sampling can occasionally suffer from positive artifacts during the sampling due to VOCs entering the particle phase and thus deposit on the filter. In the present study this issue was handled by installing preheated carbon denuders in the sampling inlet to absorb VOCs and thus prevent these compounds from reaching the filters. However, carbon denuders can create a negative sampling artefact since removal of organic gases may change the gas-particle equilibrium and thus potentially volatilize particles collected on the filter. This negative sampling artefact can be treated by supporting each front filter by a back filter which is

used to add measured analytes of the back filter to the front filter. However, back filter loadings were close to the loading of field blanks, indicating that the negative artefact was low. Hence, no correction of the negative artefact was performed. These procedures are according to the recommendations of the European infrastructure network ACTRIS (Cavalli *et al.*, 2016). The sampling was divided into four seasons as shown in Table 1.

Sawdust from various tree species was sampled from two sites in southern Sweden (Table 2), Köpinge (56°10'N, 13°27' E) and Bihult (56°54'N, 15°14'E). The sawdust was sampled by sawing a section of a log of wood. Sawdust was collected in aluminum foil and stored in a refrigerator until analysis. The saw used was non-motor driven in order to avoid contamination of fossil fuels.

### δ<sup>13</sup>C Analysis

Filter material corresponding to 10–40 µg C was punched out and enclosed in tin capsules (Thermo Scientific). An amount of 100–300 µg sawdust was also placed in tin capsules and 3–5 replicates were made for each tree species and location. δ<sup>13</sup>C was measured using an elemental analyzer connected to isotope ratio mass spectrometry (Flash 2000 Organic Elemental Analyzer coupled to Thermo Scientific DELTA V™ Advantage Isotope Ratio Mass Spectrometer). Isotopic composition is expressed relative to the international standard V-PDB as:

$$\delta^{13}\text{C}_{\text{sample}} (\text{‰}) = \left( \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} - 1 \right) \cdot 1000 \quad (1)$$

Analyses were corrected for drift using glycine. Sucrose-IAEA-CH-6 and acetanilide were used as standards. Typical

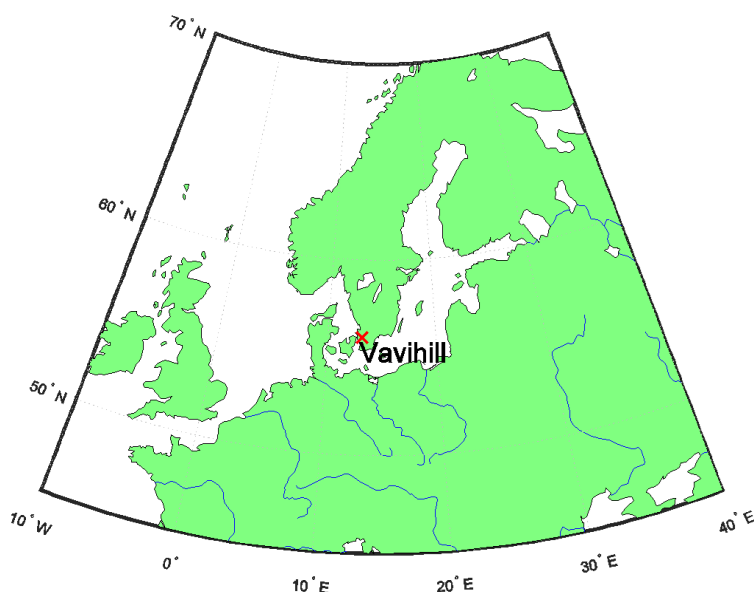


Fig. 1. Location of Vavihill measurement station.

**Table 1.** Definitions of seasons in the current study.

Season	Period	Number of filters
Summer 2008	3 May–25 September	10
Fall 2008	25 September–19 December	7
Winter 2008/2009	19 December–4 March	4
Spring 2009	4 March–22 April	4

**Table 2.** Sampled sawdust from tree species and location.

Bihult		Köpinge	
Scientific name	Common name	Scientific name	Common name
<i>Acer platanoides</i>	Norway Maple	<i>Alnus glutinosa</i>	Alder
<i>Betula pendula</i>	Birch	<i>Betula pendula</i>	Birch
<i>Corylus avellana</i>	Hazel	<i>Picea abies</i>	Norway Spruce
<i>Fagus sylvatica</i>	Beech	<i>Pinus sylvestris</i>	Scots Pine
<i>Juniperus communis</i>	Common Juniper	<i>Populus tremula</i>	Aspen
<i>Larix decidua</i>	European Larch	<i>Quercus robur</i>	Pedunculate Oak
<i>Picea abies</i>	Norway Spruce		
<i>Pinus sylvestris</i>	Scots Pine		
<i>Prunus avium</i>	Wild cherry		
<i>Quercus robur</i>	Pedunculate Oak		
<i>Sorbus aucuparia</i>	Rowan		

maximum measurement uncertainty expressed as standard deviation (SD) is  $\pm 0.2\%$ .

#### OC/EC Analysis

OC/EC analysis was conducted on a 0.5 cm<sup>2</sup> punch of the original filter using a DRI Model 2001 OC/EC Carbon Analyzer (Atmoslytic, Calabasas, CA, USA). The EUSAAR\_2 protocol was used for separation of OC and EC (Cavalli *et al.*, 2010). In the EUSAAR\_2 protocol the filter punch is heated in four steps up to 650°C in pure helium to evolve OC. To evolve EC, the temperature is first decreased to 500°C then oxygen (2%) is added, followed by an increase in temperature to 850°C in four steps. To distinguish the signals of OC and EC a He/Ne laser beam (633 nm) is continuously attenuated through the filter. The transmission of the laser is monitored and when the transmission reaches its initial value, the carbon left on the filter is determined as EC. The measurement uncertainty expressed as SD was estimated to  $\pm 0.03 \mu\text{g m}^{-3}$  for TC, OC and EC.

#### <sup>14</sup>C and Levoglucosan Analysis

The <sup>14</sup>C/<sup>12</sup>C ratio in collected particles was analyzed with accelerator mass spectrometry (AMS) (Hellborg and Skog, 2008) using the 250 kV single-stage AMS at Lund University (Skog, 2007; Skog *et al.*, 2010). Prior to analysis, the carbon in the aerosol sample was transformed into graphite according to the procedure in Genberg *et al.* (2010). In brief, 20–100  $\mu\text{g}$  carbon was mixed with CuO and combusted in vacuum. The evolved CO<sub>2</sub> was purified cryogenically, mixed with H<sub>2</sub> and heated to 600°C in the presence of an iron catalyst. In the subsequent reaction the CO<sub>2</sub> was reduced to graphite. The results are presented as F<sup>14</sup>C, fraction modern carbon (Reimer *et al.*, 2004). A F<sup>14</sup>C value of 1 represents the concentration of <sup>14</sup>C from 1950 if

human influences are not taken into consideration. The real atmospheric <sup>14</sup>C content has however been altered due to two effects, known as the Suess effect and the bomb effect. The Suess effect is the result of emission of CO<sub>2</sub> from fossil fuel combustion, leading to the ongoing increment of the atmospheric CO<sub>2</sub> concentration. Since fossil fuels are <sup>14</sup>C-free, the Suess effect generates lowered F<sup>14</sup>C values of atmospheric carbon (Baxter and Walton, 1970). The bomb effect, referring to atmospheric testing of thermonuclear weapons in the past, has had the opposite effect on the F<sup>14</sup>C values, due to neutron-induced reactions forming <sup>14</sup>C. Measurement uncertainty expressed as SD is estimated to  $\pm 1\%$  of measurement values.

Levoglucosan was analyzed using the method proposed by Zdrahal *et al.* (2002), with modifications as described in detail by Genberg *et al.* (2011). In short, levoglucosan was extracted during sonication in a (3:1) solvent mixture of dichloromethane and methanol. Extracts were concentrated and derivatized prior to gas chromatography-mass spectrometry analysis. Here, levoglucosan with derivatives were separated and quantified with  $m/z = 246$ . The measurement uncertainty expressed as SD was estimated to  $\pm 0.003 \mu\text{g m}^{-3}$ .

#### Trajectory Analysis

The trajectory model HYSPLIT (Draxler and Hess, 1998) was used to investigate the history of the air carrying the particles sampled on the filters. 72 hour back trajectories starting 100 m above ground at Vavihill with hourly frequency were calculated for the duration of each sample. The meteorological data used by the HYSPLIT model comes from the Centre of Environmental Predictions (NCEP) Global Data Assimilation System (GDAS). Trajectories were averaged into wind directions; North = 315–45°, East = 45–135°, South = 135–225° and West = 225–315°.

**Source Apportionment Methods**

A Markov Chain Monte Carlo (MCMC)-based source apportionment model (Andersson *et al.*, 2015; Bosch *et al.*, 2015) was used in order to apportion the TC to the different sources (biogenic, fossil and biomass burning), while accounting for the end-member (source profile of a measured parameter) variability. Measured dual carbon isotopes ( $F^{14}C$  and  $\delta^{13}C$ ) and the relative amount of levoglucosan (levoglucosan-to-EC ratio) together with their associated measurement uncertainty were used as source markers.

Levoglucosan-to-EC ratio was used with the motivation that these data are easy to access from bottom-up inventory studies of wood stoves, usually expressed as an emission factor. As in the present study, several previous Monte Carlo based source apportionment studies have estimated their biomass burning end-member value by using normalized values of levoglucosan derived from emission inventories (Gelencser *et al.*, 2007; Szidat *et al.*, 2009; Genberg *et al.*, 2011; Yttri *et al.*, 2011a). Using levoglucosan normalized to EC instead of OC may prevent a larger degree of significant change to the ratio due to atmospheric processing. Possible interference from SOA and biogenic OC is also reduced. However, combustion of fossil fuels also emits EC, which implies that this source will have a negative effect on the levoglucosan-to-EC ratio, leading to possible underestimation of biomass burning in the source apportionment calculations. This effect may be particularly strong during the warmer period of the year when fossil fuel combustion is expected to be the main source of EC.

The variability of the end-members was represented using normal distributions, where the means and SDs for the different sources and markers were compiled from the literature (Table 3). The calculations were performed in Matlab, using 100,000 iterations for each sample, with data thinning of 10 and burn-in phase of 10,000. The best estimates from the median of each source contribution are presented from the simulations (Tables S4–S5). A detailed description of the model can be found in Andersson *et al.* (2015). Results from the three-component ( $F^{14}C$ ,  $\delta^{13}C$  and levoglucosan/EC) MCMC3 model were then compared to a two-component ( $F^{14}C$  and levoglucosan/EC) MCMC2 model in order to estimate the contribution of  $\delta^{13}C$  to source apportionment.

Birch (*Betula pendula*), pine (*Pinus sylvestris*) and spruce (*Picea abies*) are common tree species used in biomass combustion in Northern Europe (IVL, 2006). In this study these species and their corresponding  $\delta^{13}C$  values were selected to represent the  $\delta^{13}C$  biomass burning distribution. Since we do not have any information regarding isotope fractionation during combustion, we hypothesize that the measured  $\delta^{13}C$  distribution of the total plant material in these tree species correlates to the  $\delta^{13}C$  distribution of biomass burning aerosol found in ambient air. Although, it should be noted that several studies have observed isotope fractionation with a large associated variation (Turekian *et al.*, 1998; Czimeczik *et al.*, 2002; Turney *et al.*, 2006; Garbaras *et al.*, 2015). Thus to clarify, the biomass burning  $\delta^{13}C$  end-member distribution comprises **only** these  $C_3$ -tree species (birch, pine and spruce). To separate biomass burning from

**Table 3.** End-member values in the MCMC2 and MCMC3 model.

	Biomass burning		Biogenic		Fossil fuel	
	Lev/EC	$F^{14}C$	$\delta^{13}C$ (‰)	Lev/EC	$F^{14}C$	$\delta^{13}C$ (‰)
Mean	0.82	1.20	-27.07	0	1.04	-27.17
SD	0.11	0.09	1.79	0	0.01	1.56
Reference	(Iinuma <i>et al.</i> , 2007; Schmidl <i>et al.</i> , 2008)	(Genberg <i>et al.</i> , 2011)	<sup>a</sup>		(Levin <i>et al.</i> , 2008; Genberg <i>et al.</i> , 2011)	<sup>b</sup>

<sup>a</sup> Derived from values in Table S1 of the most common biomass burning species (*Betula pendula*, *Picea abies* and *Pinus sylvestris*).

<sup>b</sup> All tree species in Table S1. Suppose to represent a wide range of  $C_3$ -plants.

<sup>c</sup> Derived from the fossil sources in Fig. 2.

biogenic emissions we regard the  $\delta^{13}\text{C}$  distribution of **all** measured  $\text{C}_3$ -tree species (Table 2, Table S1) as a signature for biogenic emissions. In order to get a comprehensive biogenic  $\delta^{13}\text{C}$  distribution, and to account for long-range transport, the  $\delta^{13}\text{C}$  tree measurements were complemented with literature data from other locations (Table S1).

$\text{F}^{14}\text{C}$  is thought to be somewhat higher in biomass burning aerosol compared to biogenic emissions due to the 1950s bomb-pulse effect (Genberg *et al.*, 2011). Levoglucosan is present in biomass burning aerosol but absent in biogenic aerosol. We used levoglucosan/EC ratio in order apportion biomass burning aerosol (Table 3). Fossil fuel aerosol has a  $\delta^{13}\text{C}$  distribution that is estimated from the literature data presented in Fig. 2.  $\text{F}^{14}\text{C}$  and levoglucosan/EC ratio is zero in fossil fuel aerosols (Table 3).

## RESULTS AND DISCUSSION

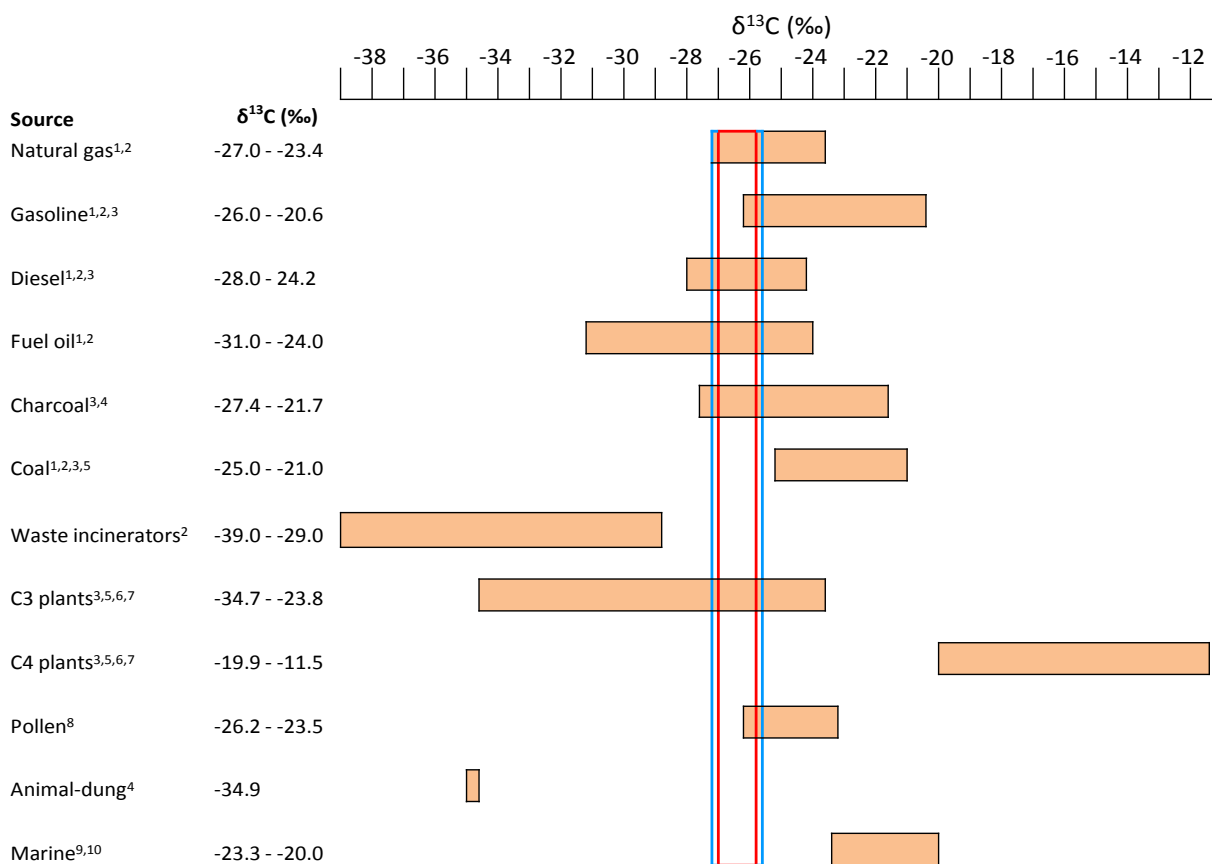
### Tree Species $\delta^{13}\text{C}$ Measurements

Sawdust from different tree species from Bihult and Köpinge were analyzed for  $\delta^{13}\text{C}$  with the aim to investigate possible differences in  $\delta^{13}\text{C}$  between biogenic (all trees, 24 species) and biomass burning trees (birch, pine and spruce). The results are displayed in Table S1 together with literature

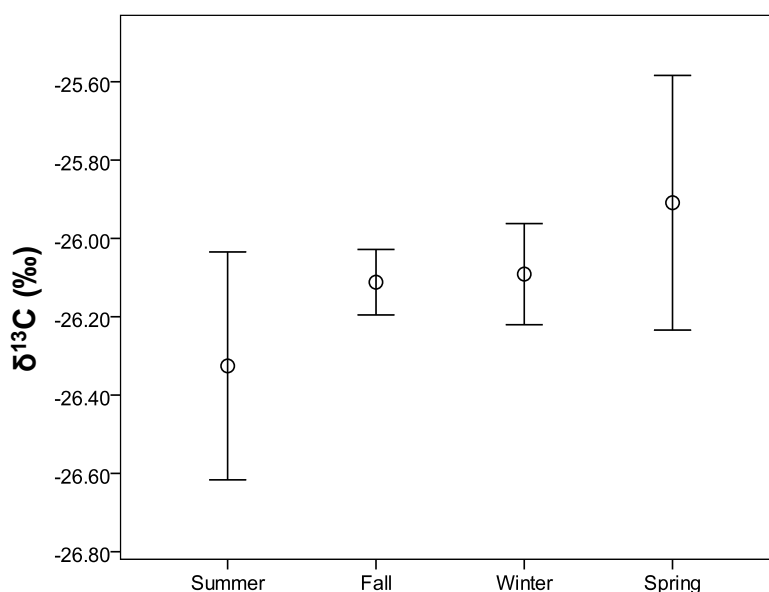
data from other trees at other locations. The overall mean biogenic  $\delta^{13}\text{C}$  (all trees) was  $-27.17\text{‰}$  (SD =  $1.56\text{‰}$ ) and  $\delta^{13}\text{C}$  in the biomass burning trees  $-27.07\text{‰}$  (SD =  $1.79\text{‰}$ ). There was no significant difference between the two end-member distributions ( $p = 0.79$ ). Frequency distributions are presented in Figs. S1 and S2.

### Seasonal Variations in $\delta^{13}\text{C}$ in Aerosol Filters

Results from the  $\delta^{13}\text{C}$  measurements of the aerosol samples are shown in Figs. 2, 3 and Table S3. As shown in Figs. 2 and 3,  $\delta^{13}\text{C}$  for the aerosol samples varied in a narrow range between  $-26.73\text{‰}$  and  $-25.64\text{‰}$  with a mean of  $-26.16\text{‰}$  during the whole sampling period (throughout the whole year the  $\delta^{13}\text{C}$  varies with  $1.09\text{‰}$ ). This range overlaps with several sources such as combustion of fossil fuels like gasoline, diesel, natural gas and fuel oil (Fig. 2). Within this interval we also find charcoal and  $\text{C}_3$ -plants. In comparison to other  $\delta^{13}\text{C}$  measurements conducted on aerosols collected in rural measurement sites, this study shows low variation between the samples (Table S2). It is also shown that the aerosols in this study are on average more depleted in  $\delta^{13}\text{C}$  compared to most of other studies (Table S2). It can be speculated that the relative enrichment of  $\delta^{13}\text{C}$  at other field stations compared to Vavihill may be



**Fig. 2.** Particulate isotopic composition of carbon from various sources (1 = (Widory *et al.*, 2004); 2 = (Widory, 2006); 3 = (Kawashima and Haneishi, 2012); 4 = (Agnihotri *et al.*, 2011); 5 = (Cao *et al.*, 2011); 6 = (Das *et al.*, 2010); 7 = (Turekian *et al.*, 1998); 8 = (Jung and Kawamura, 2011); 9 = (Cachier, 1989); 10 = (Ceburnis *et al.*, 2011)). The red rectangle displays the range of the measured  $\delta^{13}\text{C}$  values in this study. The blue rectangle displays the uncertainty of the measured  $\delta^{13}\text{C}$  values in this study.



**Fig. 3.** Seasonal  $\delta^{13}\text{C}$  values for sampled aerosols during the measurement period at Vavihill measurement station. Circles display means, error bars display one standard deviation.

caused by larger impact of fossil fuel sources (i.e., coal combustion) at these sites. A higher influence of  $\text{C}_4$ -plants at these sites, either as fuel in biomass burning or as biogenic emitters, may also explain the difference. In addition, many of these sites are in the proximity of large marine areas which have shown to have an enrichment effect on  $\delta^{13}\text{C}$  of the ambient aerosol (Cachier, 1989; Ceburnis *et al.*, 2011).

Particles collected during summer were more depleted in  $\delta^{13}\text{C}$  (mean =  $-26.32\text{‰}$ ) than during the other seasons (Fig. 3), however the differences were only significant between summer and spring ( $p = 0.033$ ). Studying Fig. 2, it seems plausible that  $\text{C}_3$ -plants may be responsible for this depletion in  $\delta^{13}\text{C}$  since they in general show a greater depletion in  $^{13}\text{C}$  than other sources. It is well known that many plants have increased emissions of biogenic volatile organic compounds (BVOCs) during summer, which may go into particle phase (BSOA) (Guenther *et al.*, 1995), usually pollen emissions are also high during this time of the year. Both BSOA and pollen will have similar  $\delta^{13}\text{C}$  values as  $\text{C}_3$ -plants which are completely dominating the wild flora in Sweden (Sage, 1999). Summer samples also showed the largest spread of  $\delta^{13}\text{C}$  values, ranging from  $-26.73$  to  $-25.86\text{‰}$  (Fig. 3). However, this can be explained by the relatively longer season compared to the others. Genberg *et al.* (2011) estimated that 80% of the summer carbonaceous aerosol in southern Sweden had a biogenic origin. Hence, the variability in  $\delta^{13}\text{C}$  during summer might also be explained by a variation of  $\delta^{13}\text{C}$ -signatures within the  $\text{C}_3$ -plants.

The highest  $\delta^{13}\text{C}$  values were measured during spring (mean =  $-25.91\text{‰}$ ) and winter (mean =  $-26.09\text{‰}$ ), which may reflect the relatively larger impact of fossil fuel combustion (Figs. 2 and 3). A previous study by Genberg *et al.* (2011) found that the contribution from fossil sources peaked during winter, accounting for 30% of the TC. Further, residential wood combustion is usually a large source of the carbonaceous aerosol during winter (Genberg

*et al.*, 2011), hence if biomass burning aerosol is affected by positive isotope fractionation due to combustion of biomass, this may also explain elevated  $\delta^{13}\text{C}$  levels during the cold period of the year.

#### Comparison of $\delta^{13}\text{C}$ with OC, EC, $\text{F}^{14}\text{C}$ and Levoglucosan

As previously mentioned, the combination of OC, EC,  $^{14}\text{C}$  and levoglucosan has been successful in several source apportionment studies on the three most common sources of aerosols in Scandinavia: biogenic, fossil fuel combustion and biomass combustion (Genberg *et al.*, 2011; Yttri *et al.*, 2011a, b). In the present study, these parameters (Table S3) were compared to  $\delta^{13}\text{C}$  in order to evaluate possible significant correlations (i.e., if  $\delta^{13}\text{C}$  can give any useful additional information regarding the above mentioned sources).

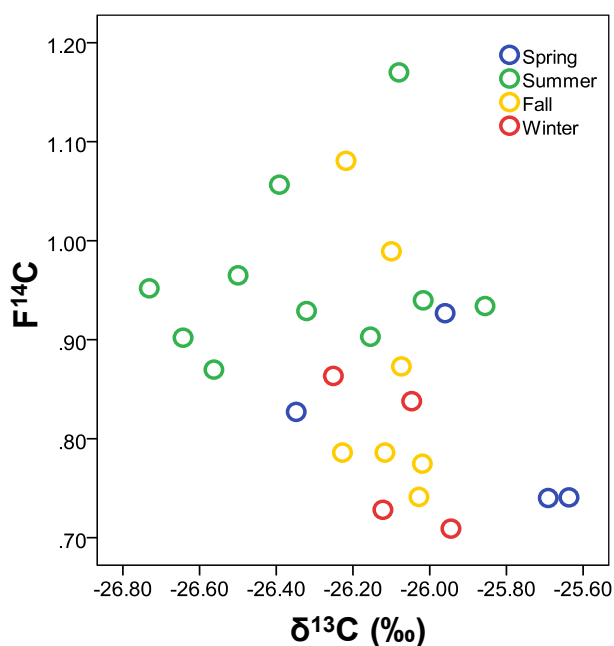
Table 4 shows the Pearson correlation coefficients ( $r$ ) in a correlation matrix. It is evident that  $\delta^{13}\text{C}$  correlates poorly ( $-0.365 < r < 0.251$ ) with the other parameters. A very weak trend was found when correlating  $\delta^{13}\text{C}$  to  $\text{F}^{14}\text{C}$  ( $r = -0.365$ ,  $p = 0.073$ , Fig. 4). This is a negative relationship showing that  $\delta^{13}\text{C}$  tends to increase when  $\text{F}^{14}\text{C}$  decrease. Kawashima and Haneishi (2012) measured  $\delta^{13}\text{C}$  in EC in Japan and found elevated  $\delta^{13}\text{C}$  values during winter ( $-24.5$  to  $-23.1\text{‰}$ ). They hypothesized that this increase could be due to long range transport of coal combustion aerosols. Szidat (2004) also found a slight increase in  $\delta^{13}\text{C}$  in Zurich urban aerosols at winter compared to summer (summer:  $-27.4$  to  $-26.5\text{‰}$  vs. winter:  $-26.7$  to  $-26.0\text{‰}$ ).

The relationships between  $\delta^{13}\text{C}$  and the other parameters (levoglucosan, OC and EC) show low  $r$  values ( $0.111 < r < 0.251$ , Table 4). Thus, by the means of Pearson correlation coefficients,  $\delta^{13}\text{C}$  does not contribute to any additional information regarding biomass combustion (levoglucosan), general combustion (EC) or organic aerosol (OC). A low  $\text{F}^{14}\text{C}$  corresponds in general to high levoglucosan concentrations

**Table 4.** Pearson correlation matrix for measured parameters from collected aerosols (N = 25).

Variables	1	2	3	4
1 $\delta^{13}\text{C}$				
2 $\text{F}^{14}\text{C}$	–0.365			
3 Levoglucosan	0.218	–0.458*		
4 OC	0.111	–0.28	0.586**	
5 EC	0.251	–0.439*	0.720**	0.643**

\* $P < 0.05$ ; \*\* $P < 0.01$ .



**Fig. 4.** Relationship between measured  $\text{F}^{14}\text{C}$  and  $\delta^{13}\text{C}$  for aerosol samples at Vaviihill measurement station.

( $r = -0.458$ ,  $p < 0.05$ ) (i.e., high impact of fossil fuel and biomass burning). We expect to have elevated contributions of biomass burning during winter and low contributions during summer. On the other hand, fossil fuel combustion can be expected to show low seasonal variability as the main source, traffic, is not seasonal dependent. Furthermore, the biogenic contribution to carbonaceous aerosol is usually low during winter, which also may explain the relatively larger fossil contribution (i.e., lower  $\text{F}^{14}\text{C}$ ) during winter (Genberg *et al.*, 2011; Martinsson *et al.*, 2017). Levoglucosan versus OC shows a relatively strong relationship ( $r = 0.586$ ,  $p < 0.01$ ). This is not surprising since levoglucosan is an organic molecule, hence a fraction of OC. During winter levoglucosan can contribute to a considerable fraction to OC (Oros and Simoneit, 2001a, b), 4% in this study. A stronger relationship is found between levoglucosan and EC ( $r = 0.72$ ,  $p < 0.01$ ), which can be explained by the fact that they are both biomass combustion products. A negative correlation is found between  $\text{F}^{14}\text{C}$  and EC ( $r = -0.439$ ,  $p < 0.05$ ), where low  $\text{F}^{14}\text{C}$  values are accompanied with high EC concentration as a result of fossil fuel combustion. Finally, OC and EC are highly correlated ( $r = 0.643$ ,  $p < 0.01$ ), which is mainly due to biomass burning and fossil fuel combustion where both OC and EC are emitted

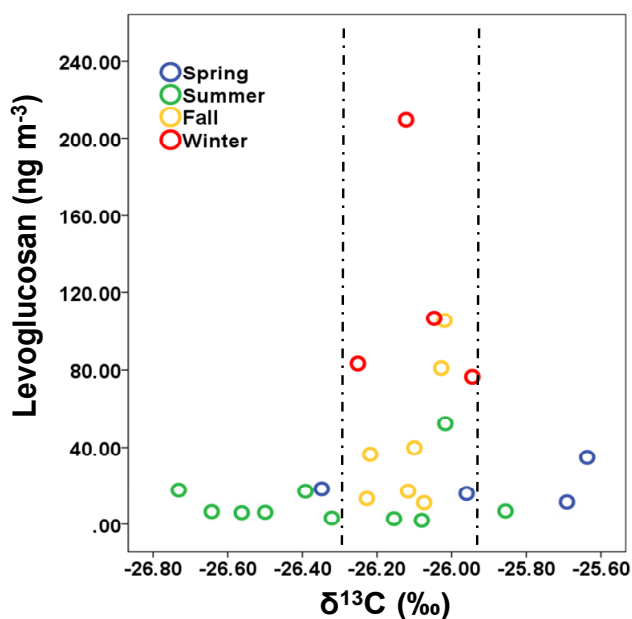
in large quantities.

A difference in the distribution of  $\delta^{13}\text{C}$  values between the seasons was observed. During summer and spring (N = 14) the  $\delta^{13}\text{C}$  varied between  $-26.73$  and  $-25.64\text{‰}$ , thereby covering the range of minimum to maximum values of  $\delta^{13}\text{C}$  for the whole year. However, the  $\delta^{13}\text{C}$  values of winter and fall (N = 11) were within a narrower range ( $-26.25$  to  $-25.94\text{‰}$ ). The explanation for this pattern might be that during summer and spring, a period that is believed to be dominated by aerosols of biogenic origin, a diversity of  $\text{C}_3$ -plants releases pollen and VOCs that are prone to form BSOA, which would be reflected in a large variation in  $\delta^{13}\text{C}$ . Gorka *et al.* (2009) characterized pollen and fungal spores in Poland during two winters and two summers and found that the diversity of pollen and fungal spores was considerably larger during summer compared to winter. In addition, biomass burning for residential heating is one of the dominating sources of carbonaceous aerosol during winter and fall. Mainly birch, pine and spruce is used for wood combustion for residential heating in Sweden (IVL, 2006). This very limited number of tree species for biomass combustion fuels may be reflected in a narrower  $\delta^{13}\text{C}$  range in the aerosols. Fig. 5 shows the relationship between levoglucosan and  $\delta^{13}\text{C}$ . The aerosols collected during winter and fall have the highest levoglucosan concentrations ( $11.24$ – $209.35 \text{ ng m}^{-3}$ ), and they have (as shown by the lines in Fig. 5) a narrower  $\delta^{13}\text{C}$ -range than summer and spring samples. However, when comparing this range ( $-26.25$  to  $-25.94\text{‰}$ ) to the biomass burning  $\delta^{13}\text{C}$  end-member distribution (Fig. S2), it is shown that the measured  $\delta^{13}\text{C}$  range is around 1‰ higher compared to the distribution (mean =  $-27.07\text{‰}$ ). This difference might be explained by possible isotope fractionation during biomass burning together with increased impact of fossil fuels during the cold season, both resulting in  $\delta^{13}\text{C}$  enrichment. Another issue is the uncertainty of the  $\delta^{13}\text{C}$  measurements. In this study the  $\delta^{13}\text{C}$  measurement uncertainty was estimated to be  $\pm 0.2\text{‰}$ , thus the argued narrow  $\delta^{13}\text{C}$ -range as a potential tracer for biomass combustion might not be valid with the estimated uncertainty taken into account. Considering this fact, more studies are needed to determine whether this is a valid relationship.

#### Source Apportionment and Model Comparison

A one year carbonaceous aerosol source apportionment using  $\delta^{13}\text{C}$ ,  $\text{F}^{14}\text{C}$  and levoglucosan (MCMC3) is shown in Fig. 6 (MCMC2, without  $\delta^{13}\text{C}$ , is shown in Fig. S5). During summer the emissions from biogenic sources are dominating (68%) over the others (biomass burning = 21%,





**Fig. 5.** Relationship between measured levoglucosan and  $\delta^{13}\text{C}$  for aerosol samples at Vavihill measurement station. The ranges of  $\delta^{13}\text{C}$  for winter and fall seasons are indicated by the two dotted lines.

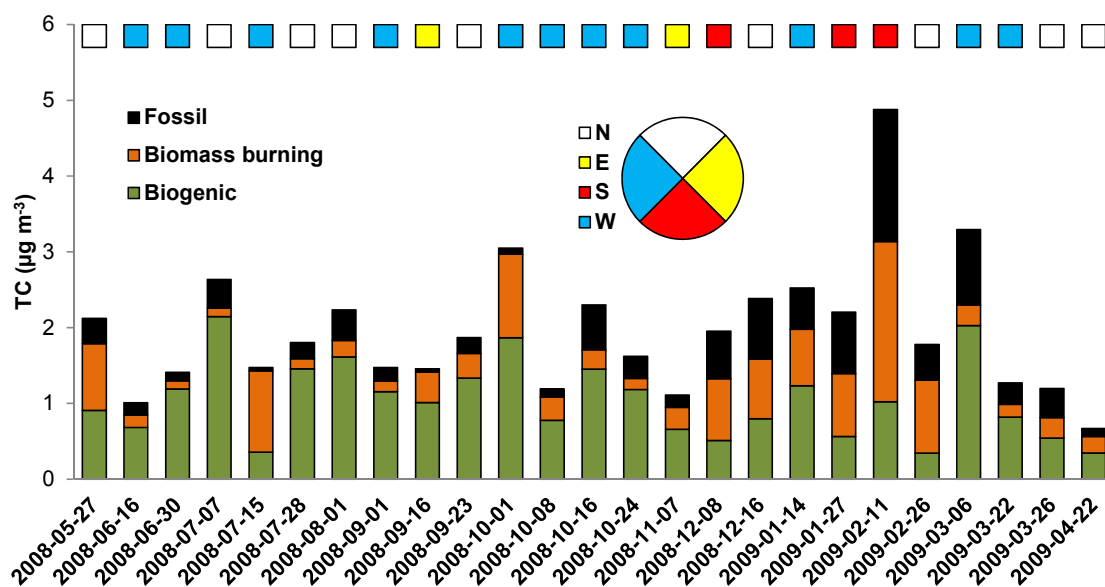
fossil = 11%). However, during the colder seasons of fall and winter the biogenic emissions are decreased to 54 and 29%, respectively, in favor of biomass burning (26 and 41%, respectively) and fossil fuel combustion (19 and 30%, respectively). These results are in line with the earlier study by Genberg *et al.* (2011) who also found biogenic dominance (82%) during summer and increased impact of biomass burning (45%) and fossil fuel (35%) and during winter. The seasonal source apportionment with (MCMC3) and without (MCMC2)  $\delta^{13}\text{C}$  is displayed in Figs. S4 and S5,

respectively. Source apportionment for each filter sample with uncertainty expressed as SD is presented in Tables S4 and S5.

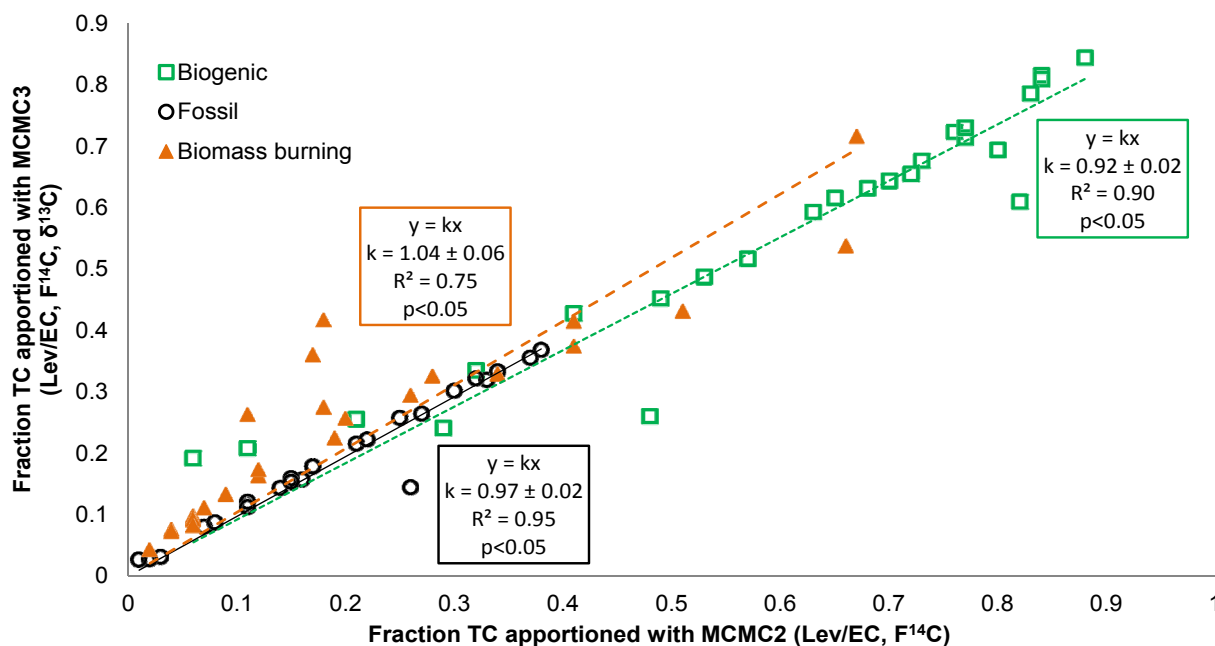
Trajectory analysis showed that in 80% of the collected samples (N = 20) the air masses originated from north (N = 9) or west (N = 11) (Fig. 6). In these directions, biogenic emissions were significantly higher than other sources ( $p < 0.05$ ). There was no significant difference in total TC between wind directions. Highest TC concentration during this campaign was noted on February 11. This sample contained aerosol collected from air masses with southern origin and had the highest contribution of both fossil (36%) and biomass burning (43%).

Inclusion of  $\delta^{13}\text{C}$  lowered the apportioned fraction of biogenic carbonaceous aerosol by 8% (slope =  $0.92 \pm 0.02$ ) and increased apportioned fraction of biomass burning carbonaceous aerosol by 4% (slope =  $1.04 \pm 0.06$ ) (Fig. 7). The explanation can be found by comparing the  $\delta^{13}\text{C}$  end-member values for these sources with measured  $\delta^{13}\text{C}$ , the measured aerosol  $\delta^{13}\text{C}$  are closer to the end-member-value of biomass burning ( $-27.07\text{‰}$ ) than biogenic ( $-27.17\text{‰}$ ), which leads to an increased estimation of biomass burning and a decrease in biogenic. However, the large overlap between the biogenic and biomass burning  $\delta^{13}\text{C}$  end-member distributions ( $-27.17 \pm 1.56$  and  $-27.07 \pm 1.79\text{‰}$ , respectively, Table 3, Figs. S1–S2) prevents any quantitative distinction between these sources.

The fossil fraction is decreased by 3% (slope =  $0.97 \pm 0.02$ ) by inclusion of  $\delta^{13}\text{C}$  in the model. This small difference may be explained by the fact that the measured  $\delta^{13}\text{C}$  are relatively far from the fossil  $\delta^{13}\text{C}$  end-member compared to the  $\delta^{13}\text{C}$  end-members of biomass burning and biogenic emissions. This small difference may also have been caused by the outlier showed in Fig. 7. Exclusion of this data point leads to a fossil fuel apportionment that is equal in the two models (i.e., 1:1).



**Fig. 6.** Apportionment of TC for all samples at Vavihill measurement station using the MCMC3 model with  $\delta^{13}\text{C}$ , Lev/EC and  $\text{F}^{14}\text{C}$ . Wind direction from trajectory analysis is showed by the top colored squares.



**Fig. 7.** Comparison in fraction TC apportioned between MCMC2 and MCMC3. Fitted lines are forced through origin.  $k$  denotes the slope and is followed by an associated standard error of the slope.

Fraction apportioned carbon from the MCMC2 and MCMC3 was further compared by analysis of variance (ANOVA). The ANOVA displayed no significant difference in apportioned carbon between the two models for any of the sources. Hence, since there was no significant difference, the relative large uncertainties of the slopes in relation to the small difference from the 1:1 regression lines (Fig. 7), together with totally overlapping  $\delta^{13}\text{C}$  end-member distributions of biogenic and biomass burning, we conclude that inclusion of  $\delta^{13}\text{C}$  in the source apportionment model does not lead to any improvement in separation of carbonaceous aerosol sources.

#### Uncertainties

$\delta^{13}\text{C}$  of the OC can be affected by atmospheric processing, it has been shown that the water-soluble OC may be enriched by 3–4‰ (Kirillova *et al.*, 2013). Thus, the  $\delta^{13}\text{C}$  emitted from the source may change significantly. This type of KIE has not been taken into account in this study. In future studies it would be favorable to measure  $\delta^{13}\text{C}$  on the EC fraction since EC is more inert to chemical transformation (i.e., KIE), than OC. This has been done in previous studies and shown promising results in apportionment of the combustion aerosol (Andersson *et al.*, 2015).

In this study we have not considered possible isotope fractionation that most probably occurs in the combustion process from original biomass material to biomass combustion aerosol. It is likely that this combustion derived isotope fractionation can influence the model comparison since the observed  $\delta^{13}\text{C}$  values showed low variability throughout the year, but were within the isotope fractionation range discovered in previous studies (Turekian *et al.*, 1998; Czimczik *et al.*, 2002; Turney *et al.*, 2006; Garbaras *et al.*, 2015).

The complexity is high in the  $\delta^{13}\text{C}$  end-members of biomass burning and biogenic carbonaceous aerosol emissions. Here, we based the end-members on literature data complemented with measurements of  $\delta^{13}\text{C}$  on  $\text{C}_3$ -tree species. We also assumed that all biogenic emissions and biomass burning originated from  $\text{C}_3$ -plants. In other environments (i.e., warmer and drier), where  $\text{C}_4$ -plants are more common the end-member values for both sources will be different and possibly more complex. Plant species used in biomass burning would determine the success of source separation. If biomass burning is dominated by fuels from  $\text{C}_3$ -plants, but biogenic emissions are mainly from  $\text{C}_4$ -plants, then the end-member values will be significantly different and make separation easier. However, if both biomass burning and biogenic emissions originate from  $\text{C}_4$ -plants there will be a scenario like the one described in this study: the end-member values will be highly overlapping.

Finally, the relatively low variability in measured  $\delta^{13}\text{C}$  over the whole measurement campaign (–26.73‰ to –25.64‰) together with a relatively high  $\delta^{13}\text{C}$  measurement uncertainty of  $\pm 0.2\text{‰}$  (SD) complicates many of the interpretations and leads to an increased uncertainty on the effect of  $\delta^{13}\text{C}$  on source apportionment models. Hence, the authors encourage continued work on this matter in order to make more substantiated claims and interpretations.

#### CONCLUSIONS

In this study the potential of  $\delta^{13}\text{C}$  as an improvement for source apportionment studies of the whole carbonaceous aerosol (TC) has been investigated. Measured  $\delta^{13}\text{C}$  distribution show overlap between all sources investigated in this study (fossil, biomass burning and biogenic). Overlapping distributions are especially pronounced between

un-combusted biomass used for biomass burning and biogenic sources. However, by selecting the most common tree species used for biomass burning, a small, but insignificant, difference between biomass burning and biogenic source distributions can be achieved.

In comparison to other rural measurement stations, Vavihill aerosol samples were more depleted in  $\delta^{13}\text{C}$ . This depletion can be explained by low fossil fuel contribution (i.e., coal and oil combustion) together with a high biogenic aerosol contribution from  $\text{C}_3$ -plants at Vavihill. The source apportionment results, using  $\delta^{13}\text{C}$ , showed large contribution of biogenic emissions during summer and higher contribution of biomass burning and fossil fuel combustion during fall and winter. Trajectory analysis showed that air masses from the north and west were dominating and had low anthropogenic influence. High levoglucosan concentrations during fall, winter and spring were accompanied by a narrow distribution of  $\delta^{13}\text{C}$ , possibly indicating emissions from fewer tree species (biomass burning) compared to summer (biogenic). The source apportionment model comparison showed that inclusion of  $\delta^{13}\text{C}$  in the model led to no significant change in the apportioned fraction TC, compared to omitting  $\delta^{13}\text{C}$  in the model. Overlapping end-member distributions complicates any kind of quantitative distinction between the sources.

In cases of low  $\delta^{13}\text{C}$  variability, unaccounted or untreated KIE and the occurrence of overlapping end-member distributions,  $\delta^{13}\text{C}$  only can act as a minor (if any) improvement in source apportionments of the total carbonaceous aerosol (TC). High uncertainties in  $\delta^{13}\text{C}$  source apportionment are associated to changes in isotopic composition due to KIE in the atmosphere, especially for the OC, but also from possible isotope fractionation between wood and wood combustion aerosol. In order to optimize the usage of  $\delta^{13}\text{C}$  it is desirable in future studies to measure  $\delta^{13}\text{C}$  on separate carbon fractions (OC and EC).

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The measurement station described in this study is positioned on private land. The owner of the land has given permission for this measurement activity. No specific permissions are required for these locations/activities. There are no regulations in the Swedish law that prohibits measurement as the one conducted in this study. The field studies did not involve endangered or protected species.

## SUPPLEMENTARY MATERIAL

A table with literature and measured values of  $\delta^{13}\text{C}$  in different tree species. A table of measured  $\delta^{13}\text{C}$  at other rural background stations. A complete data set of measured parameters from this study. Table format results from the MCMC calculations. Frequency distribution figures of end-member  $\delta^{13}\text{C}$  for biomass burning and biogenic carbon.

Figures displaying source apportionment results per season and source apportionment results of all samples using the MCMC2 model.

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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