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δ^{13}C – A useful tool of source characterization of the carbonaceous aerosol at rural measurement sites?

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Introduction

The ambient air contains various amounts of particles, aerosols. These can be of anthropogenic or natural origin. The carbonaceous fraction of the atmospheric aerosol has considerable effects on climate and human health. This fraction can be divided into organic carbon (OC) and elemental carbon (EC). EC or black carbon (BC) is formed during incomplete combustion and is strongly light absorbing and thus warms the climate. OC is emitted from various sources (fossil fuel combustion, biomass combustion and biogenic emissions) and was formerly believed to scatter solar radiation and thereby to have a cooling effect on the climate. However, recent studies [1] have shown that fractions of OC can be strongly light. Due to the different climate effects of OC and EC, and of different types of OC, large uncertainties are associated with the net effect of carbonaceous aerosols on the climate. If the sources of the atmospheric aerosols are known, both qualitatively and quantitatively, the uncertainty of the climate effect of carbonaceous aerosols can be lowered.

There are many techniques that are used to characterize the sources of atmospheric carbonaceous aerosols. Two of the most common are radiocarbon (^{14}C) and levoglucosan [5]. These are tracers for biomass combustion and fossil fuel combustion, respectively. Stable carbon isotopes have widely been used to characterize the sources of atmospheric aerosol since the 1980’s [2,3,4]. In principle, depending on the sources of particles they have specific isotopic signatures.

Several studies has been carried out were δ^{13}C has been measured in various environments [6,7,8,9]. When measuring δ^{13}C next to the source the measured δ^{13}C value reflects the δ^{13}C value of the source. For example, if δ^{13}C are measured in aerosols on a highly trafficated highway, the δ^{13}C value will most probably reflect the δ^{13}C signature of gasoline or diesel. However, many aerosol measurement stations are rural and thus influenced by a large number of various anthropogenic and biogenic activities. A problem is that many aerosol sources overlap in δ^{13}C signatures (Figure 1). The case of overlapping values of δ^{13}C for different sources can be difficult to handle when applying source characterization of the aerosol. One way to treat these difficulties is to measure δ^{13}C on specific fractions of the carbonaceous aerosol. For instance, separate the OC from the EC and measure δ^{13}C on both fractions, separately. However, at present, there are no robust standardized methods for separating OC from EC. Due to the lack of a robust separation method it is still desirable to measure δ^{13}C on the total carbon (TC). The applicability of δ^{13}C for source apportionment studies can thus be questioned at these rural sites.

Filters containing atmospheric aerosols were analyzed for levoglucosan and radiocarbon. Remaining filter material (TC) was analyzed for δ^{13}C for comparison with the above mentioned tracers to see if the δ^{13}C value is susceptible for influences of biomass and fossil fuel combustion and to evaluate if δ^{13}C contributes to an improved source characterization at a rural sampling site.
Methods

Sampling was conducted on the EUSAAR and EMEP background station Vavihill in southern Sweden (56°01’ N, 13°09’ E, 172 m.a.s.l.). The station is located on a pasture which is occasionally visited by grazing cattle. The surrounding land is mainly deciduous forest. The closest large pollution sources are the cities of Copenhagen, Malmö and Helsingborg which are located west and southwest of the station with distances of 50, 45 and 25 km, respectively.

Particles were collected weekly (168 h) from May 2008 to April 2009 on 47 mm quartz-fiber filters (n=25). After sampling, filters were placed in petri dishes, wrapped in aluminum foil and stored in a refrigerator at +5°C until analysis.

OC/EC analysis was conducted on a 0.5 cm² punch of the original filter using a DRI Model 2001 OC/EC Carbon Analyzer (Atmoslytic, Calabasas, CA, USA).

Stable isotopes of carbon were measured on a filter punch using an elemental analyzer connected to isotope ratio mass spectrometry (EA-IRMS) at the newly installed IRMS facility at the Department of Biology, Lund University.

Results and Discussion

Figure 1. Data for particulate δ¹³C from various sources from the litterature. ¹[6]; ²[7]; ³[8]; ⁴[9]; ⁵[10]; ⁶[11]; ⁷[12]; ⁸[13]. The yellow area illustrate the measured δ¹³C range in this study.

Figure 1 and 2 shows that the δ¹³C varied between -26.73 ‰ and -25.54 ‰ with a mean of -26.16 ‰ during the sampling period. These values overlap with several sources, such as combustion of fossil fuels like gasoline, diesel, natural gas and fuel oil (figure 1). Within this interval we also find charcoal, C₃ plants and pollen. It is thus difficult to conclude any sources from such a narrow interval that overlap with the values for several potential sources.

Table 1 shows that the δ¹³C correlates poorly (0.012<R²<0.133) with all the other measured parameters. The largest R²-value (0.133) for δ¹³C is found when compared to f¹⁴C. This is a negative relationship showing that δ¹³C tends to increase when f¹⁴C decrease. A low f¹⁴C indicates influence of fossil fuel combustion. From figure 2 we conclude that higher δ¹³C values also tend to correspond with fossil fuel combustion. Thus, in this data set, δ¹³C might act as a weak tracer for fossil fuel combustion.

Table 1

<table>
<thead>
<tr>
<th>Source</th>
<th>δ¹³C(‰)</th>
<th>Source</th>
<th>δ¹³C(‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>-27.0</td>
<td>Waste incinerators</td>
<td>-30.0</td>
</tr>
<tr>
<td>Gasoline</td>
<td>-26.0</td>
<td>C₄ plants</td>
<td>-19.9</td>
</tr>
<tr>
<td>Diesel</td>
<td>-28.0</td>
<td>C₃ plants</td>
<td>-34.7</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>-31.0</td>
<td>Pollen</td>
<td>-26.2</td>
</tr>
<tr>
<td>Charcoal</td>
<td>-27.4</td>
<td>Animal-dung</td>
<td>-34.9</td>
</tr>
</tbody>
</table>
The relationship between δ\textsuperscript{13}C and the other parameters (levoglucosan, OC and EC) show very low R\textsuperscript{2}-values (0.012<R\textsuperscript{2}<0.063). Thus, δ\textsuperscript{13}C does not contribute with any information regarding biomass combustion (levoglucosan), general combustion (EC) or organic aerosol (OC).

![Figure 2. δ\textsuperscript{13}C values for aerosols when the measurement periods were divided into seasons.](image)

Table 1. R\textsuperscript{2}-values for measured parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>δ\textsuperscript{13}C</th>
<th>δ\textsuperscript{14}C</th>
<th>Levoglucosan</th>
<th>OC</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan</td>
<td>0.047</td>
<td>0.079</td>
<td>0.344</td>
<td>0.193</td>
<td>0.518</td>
</tr>
<tr>
<td>OC</td>
<td>0.063</td>
<td>0.193</td>
<td>0.518</td>
<td>0.413</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The overlap between sources with respect to δ\textsuperscript{13}C signatures together with the poor correlation to other strong source tracers (\textsuperscript{14}C and levoglucosan) makes source identification and characterization of the rural aerosol TC fraction difficult using this method. Future work will aim to measure δ\textsuperscript{13}C on the separated fractions of TC (OC and EC) for improved source characterization of the carbonaceous aerosol.

References
