The contribution of fossil sources to the organic aerosol in the Netherlands

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HIGHLIGHTS

- First measurements of ^{14}C in organic carbon (OC) in the Netherlands.
- Modern sources dominate OC both at the urban and coastal site.
- Significantly higher $F^{14}C(OC)$ at the coastal site than at the urban site.
- Clear signature of pollution long-range transport in $F^{14}C(OC)$ at the coastal site.

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ABSTRACT

We measured the radiocarbon (^{14}C) content of organic carbon (OC) samples from two locations in the Netherlands, the urban location of Amsterdam and the coastal location of Petten. PM10 samples were collected in Amsterdam and total suspended particles were collected in Petten using high volume samplers. The $^{14}C/^{12}C$ fraction in the samples is reported as fraction modern ($F^{14}C$). It can be used to roughly estimate the contribution of fossil sources to OC, since $F^{14}C$ of fossil fuels is 0, whereas biogenic and wood burning sources are characterized by $F^{14}C$ values close to 1. At the coastal location organic carbon has higher $F^{14}C$ values (0.83 ± 0.04 standard uncertainty) than at the urban location (0.68 ± 0.05). A fraction modern of 0.68 is in the range of $F^{14}C$ values published for OC of other European urban areas ($0.68-0.81$). The coastal $F^{14}C$ of 0.83 agrees well with measurements at the coastal location of Mace Head, even though in Mace Head measurements were made on particles smaller than 1.5 μm (PM1.5). A $F^{14}C$ of 0.83 is on the lower end of $F^{14}C(OC)$ values estimated for continental background sites in Europe. Fossil sources might be contributing slightly more to organic carbon in the Netherlands than in other European regions. However, a bigger data set is needed to substantiate this finding. On average, fossil fuel combustion is responsible for approximately 40% of the organic carbon in Amsterdam and approximately 20% at the coastal location. At the coastal location, $F^{14}C$ was clearly lower than average when polluted air masses reached the measurement site, whereas in the urban area, air mass history did not have a strong influence on $F^{14}C$.

1. Introduction

Organic matter constitutes a significant aerosol fraction over Europe (Putaud et al., 2010) and contains many toxins, allergens, and other harmful substances. The source apportionment of organic aerosol has therefore become an important goal in aerosol science (Mauderly and Chow, 2008). One method for source apportionment that has become increasingly popular is the measurement of the radioactive carbon isotope ^{14}C of the carbonaceous aerosol (e.g. Currie, 2000; Szidat et al., 2006).

^{14}C is produced at a relatively stable rate in the upper atmosphere through reactions initiated by cosmic rays. In the atmosphere, this cosmogenic ^{14}C ultimately forms $^{14}CO_2$, which enters the biosphere, and via photosynthesis and respiration fluxes an approximate ^{14}C equilibrium with the atmosphere is achieved. The living biosphere has therefore a characteristic ratio of $^{14}C/^{12}C$,

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which is closely linked to atmospheric $^{14}CO_2$ levels. After the death of an organism the uptake of $^{14}CO_2$ stops and ^{14}C starts to decay with a half-life 5730 years (Godwin, 1962).

The ^{14}C content of a sample is expressed as a $^{14}C/^{12}C$ ratio and reported relative to a standard of oxalic acid, whose activity is related to the activity of atmospheric CO_2 and thus of the biosphere under natural circumstances in the year 1950. Following the nomenclature of Reimer et al. (2004), we report our ^{14}C data as fraction modern ($F^{14}C$)

$$F^{14}C = \frac{\frac{^{14}C}{^{12}C}(\text{sample})}{\frac{^{14}C}{^{12}C}(1950)}.$$

The $^{14}C/^{12}C$ ratio of the sample and the standard are both background corrected and normalized for fractionation to $\delta^{13}C = -25\text{‰}$, and the standard is not corrected for decay since the year 1950.

Under natural equilibrium conditions a sample from the natural contemporary biosphere would have $F^{14}C = 1$. The situation is complicated due to two anthropogenic effects that influence the $^{14}C/^{12}C$ ratio of atmospheric CO_2, and thus of the biosphere. After 1950, nuclear bomb testing significantly increased the ^{14}C levels in the atmosphere, such that $F^{14}C$ of atmospheric CO_2 almost doubled in the Northern Hemisphere. $F^{14}C$ decreased again after the ban of above-ground bomb tests, since ^{14}C is taken up by the oceans and the terrestrial biosphere. The second anthropogenic effect on the ^{14}C activity of atmospheric CO_2 is the increasing emission of fossil-fuel derived CO_2, which does not contain any ^{14}C. The present-day value of atmospheric CO_2 is around 1.04 (Levin et al., 2010).

Measuring the ^{14}C content of an aerosol sample gives a relatively clear-cut way of finding the carbon fraction that arises from fossil sources, since in fossil fuels ^{14}C has decayed and $F^{14}C = 0$. The $F^{14}C$ of the other two major aerosol sources, namely biomass burning and secondary organic aerosol (SOA) formation from biogenic precursor gases is close to $F^{14}C$ of contemporary biomass. More precisely, SOA from biogenic precursor gases, as well as minor sources such as primary biogenic particles, cigarette smoke and cooking emissions, are expected to have $F^{14}C$ around 1.04, since they arise from living or recent biomass. The $F^{14}C$ of organic carbon from wood combustion is higher, because a significant fraction of the wood was fixed during the bomb peak in $^{14}CO_2$. Estimates of $F^{14}C$ are commonly based on tree growth models (Lewis et al., 2004; Mohn et al., 2008) and range from 1.08 to 1.30 (Szidat et al., 2006, 2009; Minguillon et al., 2011; El Haddad et al., 2011; Genberg et al., 2011; Gilardoni et al., 2011) depending on assumptions of the age of the wood, and to a lesser extent on its origin.

Most ^{14}C measurements have been conducted on the total carbonaceous fraction of PM10 or PM2.5 (e.g., Currie, 2000 and references therein; Fushimi et al., 2011; Gelencser et al., 2007; Schichtel et al., 2008; Glasius et al., 2011). However, the elemental and organic carbon fractions have different formation mechanisms and differ strongly in their radiocarbon content. Elemental carbon (EC) is formed by combustion processes and is usually dominated by fossil sources, unless there are strong biomass burning sources nearby (Szidat et al., 2007). Organic carbon (OC) on the other hand has a high contribution of secondary material, which is dominated by natural sources (e.g. Kanakidou et al., 2005; Goldstein et al., 2009), and therefore contains a higher fraction of modern carbon. Analyzing radiocarbon from OC and EC separately gives more conclusive information on the sources of carbonaceous aerosol (e.g., Szidat et al., 2006; Szidat et al. 2004a,b; Heal et al., 2011; Szidat et al., 2009; Bernardoni et al., 2012; Zhang et al., 2012).

The objective of this study is to derive the fossil fraction of OC at a coastal and at an urban background site in the Netherlands. The Netherlands is a densely populated country with high PM levels compared to other western European countries. The carbonaceous aerosol comprises 15–22% of PM10 and 18–30% of PM2.5 across various rural and urban stations. 60–90% of the total carbon resides in the fine PM2.5 fraction of the aerosol (Weijers et al., 2011). A source apportionment study (Mooibroek et al., 2011) using positive matrix factorization (PMF) receptor modeling shows that about half of the OC in the Netherlands is associated with secondary inorganic species, pointing to a secondary origin for the OC. Another major contribution comes from a mixed industrial activities/incineration source that is apparent also in rural locations, far from industrial centers and the authors therefore speculate that also domestic wood combustion contributes to this factor.

2. Experimental methods

2.1. Sampling and sampling sites

The measurements reported in this work result from a pilot study for applying radiocarbon measurements to aerosols in the Netherlands, funded by the Dutch Ministry of Infrastructure and Environment (I&M). Filter samples originate from two locations: the urban location of Amsterdam and the coastal location of Petten. The urban filter samples were provided by the Municipal Health Service of Amsterdam (GGD) and collected from January to June 2006 at the Amsterdam Overtoom station. The site is approximately 60 m from a busy road but separated by a 5-story building from the road and can therefore be considered an urban background site. The coastal filter samples were collected at the ECN site in Petten near the Coast of the North Sea, 50 km North-West of Amsterdam from July to September 2009.

At both sites filter samples were collected with high volume samplers (Graseby Andersen) on Whatman QMA quartz fiber filters (No, 1851865). At the coastal site total suspended particles (TSP) were sampled, whereas PM10 was collected at the urban site. The flow rate was 600 m^3 day^{-1} for the coastal samples (Petten) and 1630 m^3 day^{-1} for the urban samples (Amsterdam). The coastal filter samples were stored at 10 °C, wrapped in aluminum foil. The urban filter samples were stored at 20 °C according to European legislature for weighing chambers (EN 12341). Due to the routine sampling protocols following European standard procedures the filters were not pre-heated in the respective laboratories immediately prior to sampling to remove adsorbed organic material. Ten Brink et al. (2009) tested the possibility of using routine PM samples for carbon analysis and found that the adsorbed organic material on QMA quartz fiber filters taken out of the box is roughly 1–2 µg carbon per cm^2 of filter material. For short sampling times this constitutes a non-negligible fraction of the organic carbon sample and has to be corrected for.

2.2. Extraction of OC for radiocarbon analysis

For radiocarbon analysis the organic carbon in the filter sample is converted to CO_2 by combustion in O_2 and separated from other interfering gases. Fig. 1 shows the experimental setup which is similar to the THEODORE (two-step heating system for the EC/OC determination of radiocarbon in the environment) setup described by Szidat et al. (2004c). Briefly, the system consists of two subsystems, a combustion tube, where the CO_2 is formed, and the CO_2 collection line. The combustion tube is made of quartz glass and surrounded by three ovens, the first at a temperature of 340 °C, the other two at 650 °C and the last oven is filled with a platinum