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Wet deposition of fossil and non-fossil derived particulate carbon: Insights from radiocarbon measurement

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HIGHLIGHTS

- Radiocarbon content in particulate OC and EC extracted from rainwater was measured.
- Fossil and non-fossil contribution to rainwater OC and EC was qualified.
- Particulate organic carbon in precipitation is dominated by non-fossil sources.
- EC sources are shared by fossil-fuel combustion and biomass burning.
- Fossil emissions account for approximately 20% of particulate carbon in wet deposition.

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ABSTRACT

Radiocarbon (^{14}C) measurements of both organic carbon (OC) and elemental carbon (EC) allow a more detailed source apportionment, leading to a full and unambiguous distinction and quantification of the contributions from non-fossil and fossil sources. A thermal-optical method with a commercial OC/EC analyzer to isolate water-insoluble OC (WIOC) and EC for their subsequent ^{14}C measurement was applied for the first time to filtered precipitation samples collected at a costal site in Portugal and at a continental site in Switzerland. Our results show that WIOC in precipitation is dominated by non-fossil sources such as biogenic and biomass-burning emissions regardless of rain origins and seasons, whereas EC sources are shared by fossil-fuel combustion and biomass burning. In addition, monthly variation of WIOC in Switzerland was characterized by higher abundance in warm than in cold seasons, highlighting the importance of biogenic emissions to particulate carbon in rainwater. Samples with high particulate carbon concentrations in Portugal were found to be associated with increased biogenic input. Despite the importance of non-fossil sources, fossil emissions account for approximately 20% of particulate carbon in wet deposition for our study, which is in line with fossil contribution in bulk rainwater dissolved organic carbon as well as aerosol WIOC and EC estimated by the ^{14}C approach from other studies.

1. Introduction

Carbonaceous particles (total carbon, TC) are of great importance due to effects on human health and earth's climate (Pöschl, 2005; IPCC, 2013). Particulate carbon in precipitation has been investigated in various locations across the globe, including sites in urban, rural, mountain, coastal and marine areas. Wet deposition is

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known to be a key scavenging (removing) process of carbonaceous particles (Fig. 1). Much of this research has been focused on the abundance of different carbon fractions (elemental carbon, EC, and water-insoluble organic carbon, WIOC), their spatial distribution, incorporation of particles in hydrometeors and wet deposition fluxes (Cadle et al., 1980; Ducret and Cachier, 1992; Chylek et al., 1999; Cerqueira et al., 2010). In contrast, rather less attention has been paid to the identification of sources (e.g. fossil and non-fossil emissions) and the assessment of their relative contribution to particulate carbon.

Radiocarbon (^{14}C) measurements have been widely used to distinguish contemporary and fossil carbon in ambient air aerosol samples in either bulk TC (Szidat et al., 2013; Zotter et al., 2014b) or in different carbonaceous fractions (Szidat et al., 2009; Zhang et al., 2014a, 2014b). Source attribution is based on a simple model which assumes that emissions from biogenic processes or biomass combustion are labelled with the ambient $^{14}C/^{12}C$ ratio and emissions from fossil-fuel combustion contain no ^{14}C because of the large age of this material (Currie, 2000).

To the best of our knowledge this approach has never been used in source apportionment studies of WIOC and EC in precipitation samples (rain and snow), although it was applied in some cases to deposited snow of ice core research (Jenk et al., 2006; Cao et al., 2013) as well as total organic carbon (TOC) and dissolved organic carbon (DOC) in rain (Raymond, 2005; Avery et al., 2006, 2013). One of the most challenging problems of the method lies in lower concentration of particulate organic carbon (POC) compared to DOC and offline separation methods for ^{14}C measurements in water-insoluble total carbon (WITC) and, especially, different carbon fractions such as EC and WIOC. Thermal-optical analysis (TOA) is one of the most commonly used methods for measuring the OC/EC concentration in aerosol and precipitation samples. In most TOA methods such as NIOSH, IMPROVE and EUSAAR protocols, the filter sample is heated sequentially in an inert (He) and oxidative (He/O_2 mixture) atmosphere (Cavalli et al., 2010). Ideally, OC and EC are released in each step separately. However, part of OC is formed as charring (EC-like material that is refractory and light-absorbing), which occurs in the first step and is mistakenly detected as EC in the second step. Therefore, a laser is used to monitor the filter transmittance throughout analysis to account for the charring contribution. The charring correction is then carried out to quantify OC/EC mass concentration by assigning a split point at the time when the transmittance returns to its initial value during the He/O_2 step (Cavalli et al., 2010). However, the charring correction is not feasible for ^{14}C analysis of OC and EC, since this requires a physical separation of the two fractions and the split point is unknown before measurement. This was recently improved by a thermal-optical method utilizing both the special thermal and optical properties of OC and EC, thereby optimizing both the quantification and isolation of OC and EC (Zhang et al., 2012).

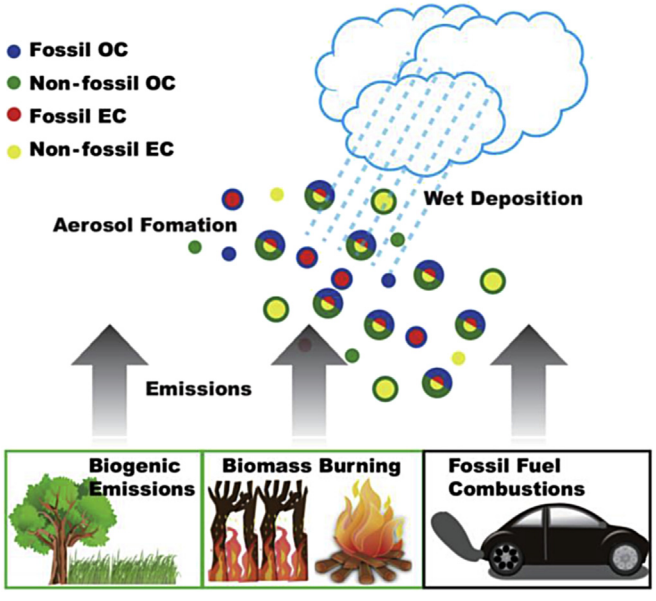

Fig. 1. A simplified sketch showing the sources and wet deposition of carbonaceous particles (organic and elemental carbon).

Aerosol pollution from wood burning has recently been recognized in large-scale areas of Europe including Scandinavia, Portugal and alpine regions, as well as in major European cities such as London, Paris and Berlin despite the importance of fossil-fuel emissions (Szidat et al., 2009; Borrego et al., 2010; Fuller et al., 2013, 2014; Herich et al., 2014; Zotter et al., 2014a). However, current understanding on the impact of fossil versus biomass burning to aerosols is incomplete, since the source of WITC in wet deposition, a major removal process of particulate carbon in the atmosphere (Ducret and Cachier, 1992), are still not well constrained. Therefore, the motivation for the present study was (1) to adapt a method that has been successfully applied for ^{14}C analysis of atmospheric aerosols to the quantification of ^{14}C in particulate carbon extracted from rainwater and (2) to quantify fossil and non-fossil contributions to particulate carbon including OC and EC in precipitation from samples collected in Portugal and Switzerland. This study also provides new insights into the wet deposition of particulate carbon emitted by both fossil and non-fossil sources, and improves our understanding of the role of atmospheric particulate carbon in the models of the global carbon cycle.

2. Experimental

2.1. Measurement sites and analytical method

Investigations were carried out at two different sites, Aveiro in Portugal (40° 38′ 07″N and 8° 39′ 35″E) and Dübendorf (47° 24′ 11″N and 8° 36′ 48″W) in Switzerland. Sampling at Aveiro was conducted at the University of Aveiro campus, located at the south-western rim of the city of Aveiro, western coast of Portugal. The campus is about 7 km from the sea-side and there are no significant pollution sources in the area between it and the ocean. The roof of a small container placed near the campus meteorological station was used as a platform to collect rain samples, at about 4 m above ground level. Sampling at Dübendorf was performed on the premises of EMPA located outside of Dübendorf, a city with 25,000 inhabitants and a suburb of the city of Zurich (400,000 inhabitants). The site therefore is of suburban type located 432 m a.s.l. in the northern part of Switzerland. The rain samples have been collected at 2 m above ground level.

2.2. Sampling method

Rainwater samples in Portugal were collected on an event basis from mid-February until the end of April 2011 with an Eigenbrodt model UNS130/E automatic wet-only collector. The sampler consisted of a glass funnel with an open area of 500 cm^2, connected to a 5 L glass storage bottle, a movable lid and a precipitation sensor to control start and stop of each collection period. Prior to use, all the collector components that could come in contact with samples were cleaned with soap and water, followed by rinsing of them with distilled and deionized water. Rainwater samples at Dübendorf, Switzerland were collected on a daily basis from April 2012 to March 2013 with a Digitel model DRA-92 HK wet-only collector.