Atmospheric Environment 115 (2015) 257–262

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

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.

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form
28 May 2015
Accepted 1 June 2015
Available online 4 June 2015

Keywords:
Radiocarbon
Particulate carbon
Precipitation
Fossil
Non-fossil

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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http://dx.doi.org/10.1016/j.atmosenv.2015.06.005
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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).

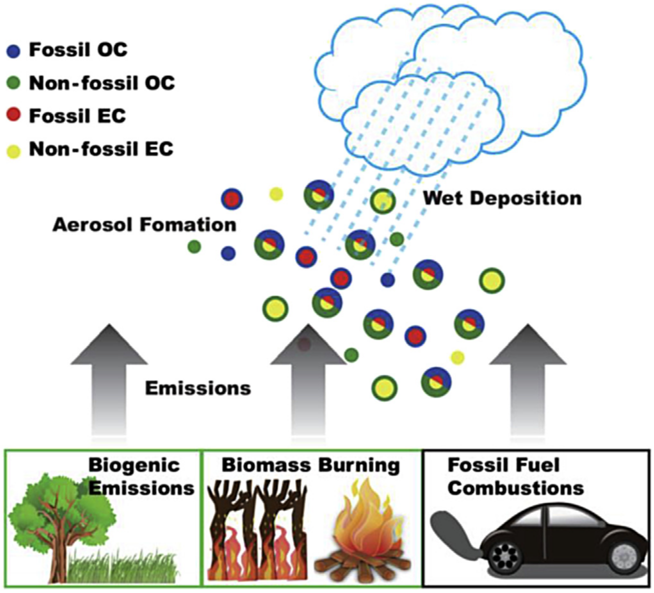

Fig. 1. A simplified sketch showing the sources and wet deposition of carbonaceous particles (organic and elemental carbon).

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.

The sampler consists of a Teflon-coated funnel with an open area of 500 cm^2. The rain samples were collected in storage bottles (polyethylene, 250 mL) which were automatically changed at midnight or when they were full. The funnel and the subsequent Teflon tube have monthly been cleaned with ultrapure water, the storage bottles have been rinsed with ultrapure water before they were used. One field blank at each site was prepared by pouring ultrapure water (50 mL) through the sampling device, collecting the rinsate in a storage bottle and, after staying one day inside the closed collector, processed under the same conditions as samples.

2.3. *Filtration*

The particulate carbon in the rainwater samples were collected on prebaked quartz fibre filter (Pallflex Tissuquartz, 2500QAO-UP) with a diameter of 10–11 mm by filtration using vacuum suction. Prior to the use of containers and the filtration funnel, they were rinsed three times with ~25 mL ultra-pure water with low carbon impurity in order to reduce the blank. A series of three filters were used to collect particles to increase filtration efficiency. The filtration efficiency with a similar approach was reported to be 92 ± 7% using prepared standards of known quantities of soot in water (Hadley et al., 2008). Filtered water volumes were typically in the range of 250–700 mL. For samples from Portugal ($n = 7$), daily rain samples were filtered at the University of Aveiro before sending to the University of Bern for ^{14}C analysis by express mail in a cooled container. For samples from Switzerland ($n = 12$), rain events were pooled per month for filtration, which was conducted at the University of Bern.

2.4. *Determination and separation of different carbonaceous particle fractions*

OC and EC fractions extracted from precipitation samples were isolated by the Swiss_4S protocol for subsequent ^{14}C measurement. This method was first described in Zhang et al. (2012) for analyzing ambient aerosols samples and recently applied for particulate carbon extracted from firn/ice samples by Cao et al. (2013). In brief, WIOC is combusted in pure oxygen at 375 °C for 180 s in step one and subsequently EC is combusted in pure oxygen at 760 °C for 120 s in step four after complete OC removal in pure oxygen at 475 °C for 120 s (step two) and in helium at 650 °C for 180 s (step three). The evolving CO_2 is quantified by a non-dispersive infrared (NDIR) detector, separated from interfering reaction gases, cryo-trapped and sealed in glass ampoules for ^{14}C measurements. By using the Sunset OC/EC analyzer, which monitors the filter optical properties during the combustion with a laser, the quantification of the EC losses before step four is also possible. Therefore, mass concentration of WIOC, EC and WITC can be quantified as well. A good agreement of carbon mass determination by the Swiss_4S and the EUSAAR_2 protocol was previously reported for aerosol samples (Zhang et al., 2012). The extent of charring formation during the thermal treatment can be reduced by using pure oxygen instead of helium, which is evident by the comparison of thermograms applying different protocols (see Supplemental material, Figure S1). However, substantial OC charring still occurs, sometimes larger than 10% of EC mass, which results in a positive bias of the ^{14}C measurement of the EC fraction, as OC and EC often differ in their ^{14}C content (Szidat et al., 2009; Zhang et al., 2013). Since some charred material is very likely removed during step three before the EC step, we assume that 50 ± 15% of the charred OC remains in the EC fraction. Therefore, the fraction of modern (f_M, see Sec 2.4) of EC ($f_{M,EC}$) as corrected for charring ($f_{M,EC,final}$) is as follows:

$$f_{M,EC\ corr} = \left(mC_{EC} {*} f_{M,\ EC} - mC_{charring} {*} f_{M,charring}\right) \Big/ \left(mC_{EC} - mC_{charring}\right),$$

where $f_{M,EC}$ and $f_{M,charring}$ denote the f_M measured and mC_{EC} and $mC_{charring}$ the carbon mass for EC and charred OC, respectively.

$f_{M,charr}$ is assumed to equate to the measured $f_{M,OC}$, as charred OC is part of the OC fraction. The typical uncertainties of source apportionment results arise from analytical uncertainties (i.e. OC/EC mass and ^{14}C measurements), blank/charring correction and the variability of reference $f_{M,nf}$ values (see Sec 2.5) approximately amounted to ±20%, ±20%, ±15% and ±10% for fossil EC, non-fossil EC, fossil OC and non-fossil OC, respectively.

2.5. *^{14}C analysis*

^{14}C analyses of CO_2 produced samples from OC/EC analyzer were measured with the Mini Carbon Dating System (MICADAS) at the Laboratory for the Analysis of Radiocarbon with AMS and at ETH Zurich, both of which using a gas ion source, which allows direct CO_2 injection after dilution with He (Wacker et al., 2013; Szidat et al., 2014). ^{14}C results are usually expressed as fractions of modern (f_M), which were further converted to fraction of non-fossil (f_{NF}) by dividing by f_M reference values for contemporary carbon for the source apportionment of non-fossil and fossil carbon. f_M reference value of OC ($f_{M,ref}$) were estimated as 1.08 ± 0.05 for non-fossil continental sources for both sites according to (Zhang et al., 2014a). For samples influenced by marine sources at the Portugal sampling site, this reference value was estimated as 0.98 ± 0.04 (see Sec 3.1.1. and Figure S2) following the concept of (Ceburnis et al., 2011), which is currently the best available approach for this determination. It should be noted that the uncertainty of source-specific contributions are dependent on the selected f_M reference values. By varying reference f_M by ±0.05, the uncertainty is typically within 5%. A mass-dependent blank correction is applied to the measured f_M values for OC according to an isotopic mass balance approach. The f_M and OC value of the blank was 0.59 ± 0.02 and 1.2 ± 0.8 μgC per filtration, respectively. No blank correction was carried out for ^{14}C measurement of EC as carbon amount of blank EC (0.4 ± 0.4 μgC) was below the detection limit (~2–3 μgC) of the ^{14}C analysis.

3. Results and discussion

3.1. *Particulate OC and EC levels in precipitation*

3.1.1. *Aveiro, Portugal*

Seven rain samples were characterized for their WITC concentrations and the corresponding ^{14}C values. Details about rain events are reported in Table S1 and analytical results are presented in Fig. 2. Backward air mass trajectories arriving at Aveiro during the rain events generated with the HYSPLIT model are shown in Figure S2. According to air mass origins, 7 samples were classified into 2 types: marine (TYPE1: samples AVE1 to AVE5) where the air-mass travelling over the ocean and continental influenced rainwater (TYPE2: samples AVE6 and AVE7) with a mixture of continental and marine influences. The average WITC was 128.4 ± 87.7 μg/L and 272.1 ± 42.3 μg/L for marine and continental influenced rainwater, respectively. The lowest WITC concentrations were found in rain samples AVE1, AVE3 and AVE5, with a mean of 66 ± 12 μg/L. With a similar air mass origin (Figure S2), WITC in sample AVE2 and AVE4 was significantly increased. These two samples were likely influenced by additional local emissions.

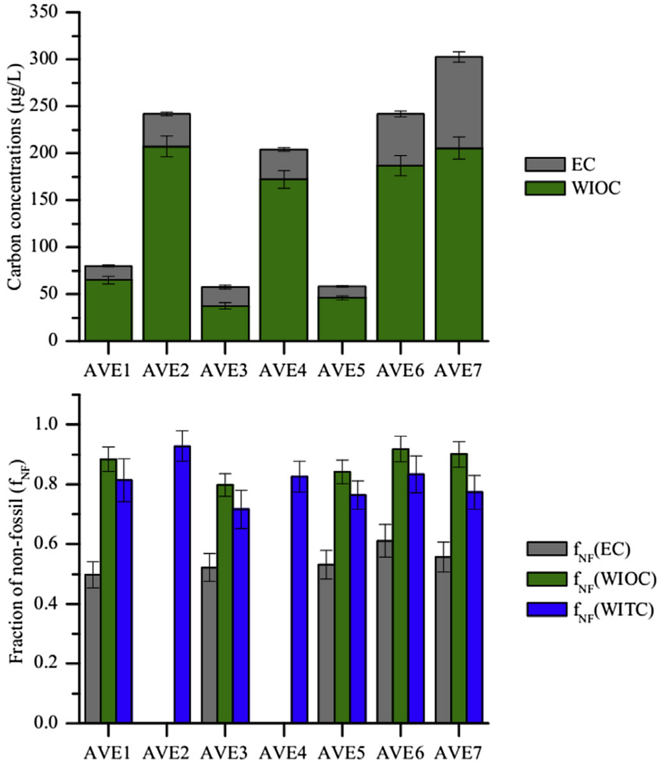

Fig. 2. WIOC and EC concentrations and fraction of non-fossil (f_{NF}) values of WIOC, EC and WITC for rain samples collected at Aveiro, Portugal.

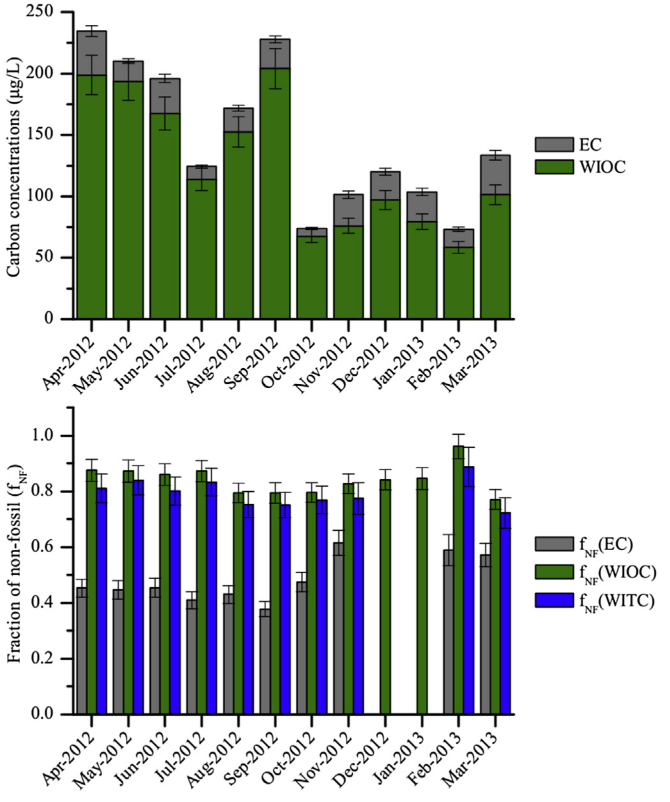

Fig. 3. Monthly WIOC and EC concentrations and fraction of non-fossil (f_{NF}) values of WIOC, EC and WITC for precipitation samples collected at Dübendorf, Switzerland.

Indeed, plant debris (or detritus) was visible after filtration of the sample AVE2, explaining the high WITC concentration. This sample was taken under conditions with elevated wind speed compared to the other samples (Table S1), which might have been the cause of a significant input of plant debris into local air. On the other hand, pollen grains were observed after filtration of sample AVE4. Marine pine (*Pinus pinaster*) is the dominant tree in north-western Portugal and airborne pollen from this species is known to have a seasonal variation with a peak during March (Sousa et al., 2008). Pollen grains of marine pine deposit intensely at this time of the year and are frequently observed as a yellow dust accumulated on outside surfaces. In addition, the average WIOC/EC ratio (5.7) of samples AVE2 and AVE4 were significantly higher than that (3.2) in samples AVE1, AVE3 and AVE5, indicating that the larger TC abundance for samples AVE2 and AVE4 is rather due to biogenic/biomass sources than anthropogenic sources. The higher WITC concentrations detected in TYPE2 were probably due to higher aerosol pollution in continental air-mass origins. Actually, during the rain event of 18–19 of April (sample AVE6), air masses originated from the western coast of Africa and were transported over densely populated areas in coastal Portugal before arriving at the sampling site. Sample AVE7 reflects the influence of two types of transport: whereas air masses arrived from northwest, after crossing France and Spain, during the first half of the sampling period, the second half was dominated by air-mass transport over northern Africa, southern Spain and inland Portugal. However, the source of the continental-influenced samples remains unknown, which we will discuss below (Sec 3.2.1).

3.1.2. Dübendorf, Switzerland

WITC concentration levels in the precipitation samples from Dübendorf ranged from 73 μg/L to 228 μg/L, with an annual average of 147 ± 58 μg/L (Fig. 3). The monthly WIOC concentrations were lower in cold seasons than in warm seasons, associated with larger biogenic emissions in both spring and summer. Although wood burning in winter is a dominant contributor of airborne OC in Switzerland (Zotter et al., 2014a), this may not affect particulate OC fraction in precipitation significantly, as a large fraction of wood-burning OC may be dissolved into the rainwater due to high water solubility and thus mainly exist in the rainwater DOC fraction. Previous studies reported higher levels of DOC in rainwater in warm seasons in other regions, such as coastal New Zealand and North Carolina, USA, as biogenic emissions from vegetation is largely controlled by seasonality (Willey et al., 2000; Kieber et al., 2002). However, this seasonality was not found for EC, as this fraction is only produced by fossil-fuel combustion and biomass burning, but not by biogenic emissions. Actually, monthly EC concentrations showed relatively small variations throughout the year in contrast with the fact that EC abundance in ambient aerosol samples has been reported to be highest in winter due to accumulation during winter-smog episodes and enhanced residential wood burning in Switzerland (Herich et al., 2011). It should be noted that precipitation seldom occurs during winter-smog episodes and most precipitation events in winter are snow events so that different wet scavenging efficiencies between rain and snow events may play a role on wet deposition of EC. Correlation with the amount of precipitation was neither observed for WITC, WIOC, or EC concentrations, and also not for their ^{14}C level, probably because of pooling monthly averaged samples.

3.2. Sources of particulate carbon in precipitation: fossil vs. non-fossil sources

3.2.1. Aveiro, Portugal

In general, both natural and anthropogenic sources including biogenic emissions, biomass burning and fossil-fuel combustion can contribute to rainwater particulate carbon. In this work, the source apportionment of particulate carbon in precipitation was made based on ^{14}C measurements, assuming non-fossil carbon has the same f_M as the contemporary atmosphere and fossil fuel carbon is devoid of ^{14}C. As samples AVE2 and AVE4 were influenced by large primary biogenic particulate matter, ^{14}C measurement has only been performed on bulk WITC, because large primary biogenic particulate matter may significantly affect the WIOC/EC separation. The average non-fossil contribution to WIOC is 84% and 91% for marine and continental influenced rainwater, respectively. The fossil components found in rainwater at this coastal site likely reflect the export of fossil emissions from the North American continent, the input of emissions from ship and aircraft emissions as well as local traffic emissions. ^{14}C measurement of samples with the highest WITC content (samples AVE2 and AVE4) confirm, however, that these two samples are indeed influenced by non-fossil emissions (i.e. primary biogenic emissions). Non-fossil contributions (i.e. biomass burning) to EC were on average 52% ± 2% and 58% ± 2% for TYPE1 and TYPE2, respectively, which was lower than the corresponding non-fossil fraction in OC with average contributions of 84% ± 2% and 90% ± 2%. Biomass burning EC mainly originates from residential wood burning for heating and/or open biomass burning. Wood burning has been reported to be a considerable contributor to EC by many previous studies conducted in Europe (Szidat et al., 2009; Fuller et al., 2014; Zotter et al., 2014a). The MODIS fire counts map (https://firms.modaps.eosdis.nasa.gov/firemap/, Figure S3) during April shows that intensive open biomass-burning activities took place in upwind direction of and/or in surrounding regions of the sampling site, which could be another explanation of the enrichment of non-fossil carbon in both OC and EC fractions of samples AVE6 and AVE7. Therefore, high abundance particulate OC found in continental influenced rainwater is not due to larger urban fossil emissions, but due to enhanced biogenic and biomass-burning emissions according to ^{14}C results in both WIOC and EC fractions.

3.2.2. Dübendorf, Switzerland

On average, non-fossil sources contributed 84 ± 5% to OC on an annual average, which was always higher than non-fossil EC with a mean contribution of 48 ± 7% (Fig. 3). This finding agrees with the fact that OC/EC emissions ratios are higher in biogenic or biomass burning sources than those in fossil fuel emissions (i.e. mainly vehicular emissions in Europe) (Pio et al., 2011). A notable seasonality was not found for relative fossil and non-fossil contributions to OC, whereas non-fossil EC fraction was slightly higher in winter than other seasons due to larger wood burning emission for heating during cold period (Zhang et al., 2013; Zotter et al., 2014a). The high non-fossil fractions in rainwater WIOC are attributed to biogenic and wood burning emissions. Based on a carbon isotope mass balance (i.e. $f_{NF}(\mathrm{WITC})^* \ mC_{WITC} = f_{NF}(\mathrm{OC})^* mC_{OC} + f_{NF}(\mathrm{EC})^* mC_{EC}$), the annual-average non-fossil contribution to WITC was 79 ± 5% with a consistent non-fossil predominance throughout the year, which dominated the wet deposition of atmospheric organic aerosols. Previous studies also found similar ^{14}C values for bulk rain DOC, although there are no studies reporting ^{14}C measurements on POC in rainwater to the best of our knowledge. For example, ^{14}C measurements of rain DOC from two sites in the northeast USA suggest approximately 78% and 85% was non-fossil origin, respectively (Raymond, 2005; Avery et al., 2006).

3.3. Summary and discussions

This paper reports the first successful application of radiocarbon (^{14}C) analysis to water-insoluble particles extracted from precipitation. Based on ^{14}C measurement of particulate OC and EC of rainwater samples at a costal site in Portugal and a continental site in Switzerland, particulate carbon in precipitation is dominated by non-fossil sources, such as biogenic and biomass-burning emissions regardless of season as well as air-mass and rain origins. It should be worth noting that non-fossil contributions in total particulate carbon in precipitation in both studied sites were higher than those reported in airborne aerosol samples. For examples, Gelencsér et al. (2007) showed that non-fossil contribution fraction was on average 73% and 81% of TC in $PM_{2.5}$ aerosol samples collected during summer and winter at Aveiro, Portugal, respectively, (Gelencsér et al., 2007), slightly lower than our finding (averaged to 81%) in rainwater samples. Recently, a yearly cycle of ^{14}C measurement of OC and EC of PM_{10} aerosol samples was investigated at an urban background station in Zurich, Switzerland (Zotter et al., in preparation). Non-fossil contributions to TC is on average 15% lower compared to those extracted from rainwater samples collected at Dübendorf, 6 km north of Zurich. In addition, they found a very clear seasonal cycle for relative non-fossil contribution of EC (ranging from 9 to 50%) in PM_{10} aerosol samples, whereas in the precipitation analysed in this study, less seasonal variation (ranging from 37 to 59%) was observed. We hypothesize that particles emitted from biomass-burning processes may be coated with more hydrophilic compounds such as inorganic substances and oxidized organic aerosols, which may increase the wet removal efficiency of non-fossil particles. By examining aerosol size distributions and BC coating properties sampled in three Canadian boreal biomass burning plumes, Taylor et al. (2014) have also demonstrated that less coated EC particles are less effectively removed by wet deposition (Taylor et al., 2014). Moreover, it should be emphasized that precipitation includes larger particulate matter than PM_{10} aerosol, which may have an influence on the outcome of the ^{14}C source apportionment, as we recently showed for fine and coarse aerosol fractions (Zhang et al., 2013). Further experiments with simultaneous measurements on both aerosol and precipitation samples are required to study wet scavenging processes and mechanisms for carbonaceous particles from both fossil and non-fossil origins.

The findings from our study suggest that wet deposition preferentially removes non-fossil derived carbonaceous particles. Despite of the importance of non-fossil sources, fossil emissions account for approximately 20% of total particulate carbon in wet deposition for our study, which is in line with fossil contribution in bulk rainwater DOC as well as aerosol WIOC and EC estimated by the ^{14}C approach from other studies (Raymond, 2005; Avery et al., 2006; Szidat et al., 2009; Zotter et al., 2014a). Based on literature studies and our observations, a very gross estimation of wet-deposited fossil-derived carbon was also carried out. By assuming 430 Tg C/y is removed from the atmosphere by rainwater DOC (Willey et al., 2000) and multiplying it by the average POC percentages (15%) in TOC (the sum of POC and DOC) from previous studies (Sempere and Kawamura, 1996; Willey et al., 2000) as well as an average fossil contribution (20%) to POC from our current study could approximately yield a net removal of 12.9 Gt fossil-derived C per year in the particulate phase via wet deposition. This gross estimation is within the upper range of bottom-up primary organic aerosols from fossil fuel emissions of 5–15 $\mathrm{TgC\,yr^{-1}}$ (Bond et al., 2004; Hallquist et al., 2009), suggesting that the majority of fossil-derived primary organic aerosols are removed by wet deposition. Therefore, fossil-derived particulate carbon can be transferred between different ecosystem (e.g. from land to ocean or from ocean to land) via wet deposition, and it can play an important role on the Earth's environment and human health via biogeochemical carbon cycle.

Acknowledgements

This study was financially supported by the European Regional Fund Development through the program COMPETE - *Programa Operacional Factores de Competividade* and by the Portuguese Foundation for Science and Technology through the project "Wet deposition of particulate carbon over the Northeast Atlantic region" (PTDC/AMB/66198/2006). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model used in this publication. Also acknowledged is L. Wacker (ETH Zurich) for making available the MICADAS for some of the ^{14}C measurements in this study. Yan-Lin Zhang also acknowledges the "Mobility Fellowship" from Swiss National Science Foundation (152095) and the Startup Foundation for Introducing Talent of NUIST (2015r023).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.06.005.

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