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Solid phase extraction method for the study of black carbon cycling in dissolved organic carbon using radiocarbon

Alysha I. Coppola *, Brett D. Walker, Ellen R.M. Druffel

Department of Earth System Science, 2212 Croul Hall, University of California Irvine, Irvine, CA 92697, United States

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ABSTRACT

Radiocarbon analysis is a powerful tool for understanding the cycling of individual components within carbon pools, such as black carbon (BC) in dissolved organic carbon (DOC). Radiocarbon ($\Delta^{14}C$) measurements of BC in DOC provide insight into one source of aged, recalcitrant DOC. We report a modified solid phase extraction (SPE) method to concentrate 43 ± 6% of DOC (SPE-DOC) from seawater. We used the Benzene Polycarboxylic Acid (BPCA) method to isolate BC from SPE-DOC (SPE-BC) for subsequent ^{14}C analysis. We report SPE-BC $\Delta^{14}C$ values, SPE-BC concentrations, and the relative BPCA distributions from Milli-Q water process blanks, two riverine reference standards, as well as a coastal and an open ocean surface water sample. The composition of BC is less aromatic in the ocean samples than those in the river standards. We find higher BC $\Delta^{14}C$ values in the river standards (+148 to −462‰) than BC in the ocean samples (−592 to −712‰), suggesting that BC ages within oceanic DOC. We report that BC is 4.2 ± 1.0% of SPE-DOC in the open ocean surface sample, or 1.4 ± 0.1 μM C. This work provides the methodological basis by which global BC concentrations, compositions (e.g. relative abundances of BPCA marker compounds) and $\Delta^{14}C$ values can be assessed.

1. Introduction

Black carbon (BC) is formed from incomplete combustion of fossil fuels and biomass. BC plays a strong role in the climate system, as it is considered second to CO_2 as the most important human emission based on its radiative forcing (Bond et al., 2013; Husain et al., 2004; Novakov and Rosen, 2013). BC also is hypothesized to be a long term carbon sink (Masiello and Druffel, 1998; Dai et al., 2005; Kuhlbusch and Crutzen, 1995), because its structure is composed of condensed aromatic rings making it stable and resistant to biological degradation (Goldberg, 1985; Forbes et al., 2006). After a fire, large amounts of charcoal in soils are oxidized and transported to river sheds (Myers-Pigg et al., 2015; Kim et al., 2004; Hockaday et al., 2007; Mannino and Harvey, 2004; Preston and Schmidt, 2006). BC is transported to the ocean by rivers, and is ubiquitous in the water column and sediments (Jaffe et al., 2013; Dittmar and Paeng, 2009; Ziolkowski and Druffel, 2010; Masiello and Druffel, 1998; Coppola et al., 2014; Middelburg et al., 1999).

Once dissolved BC enters the ocean, it contributes to one of Earth's major organic carbon reservoirs, dissolved organic carbon (DOC, passes a 0.2–1.0 μm filter). While most DOC is believed to be produced by phytoplankton in the surface ocean, marine DOC is surprisingly thousands of ^{14}C years old (Williams and Druffel, 1987). The presence of ancient BC in the marine DOC pool may explain this mystery (Ziolkowski and Druffel, 2010; Masiello and Druffel, 1998) and was the motivation for this work. The structural composition and $\Delta^{14}C$ values of SPE-BC provide insight into the composition of recalcitrant DOC, which escapes biological decomposition for thousands of years (Hansell et al., 2012; Ziolkowski and Druffel, 2010; Jiao et al., 2010; Stubbins et al., 2012a).

Ziolkowski and Druffel (2010) reported the first BC $\Delta^{14}C$ measurements in ultrafiltered DOC (UDOC) from river and seawater. They found open ocean BC had a range of ages from 15,680 to 20,100 ^{14}C years, providing evidence for BC stability on $>10^4$ year time scales. BC $\Delta^{14}C$ measurements in UDOC have limitations for evaluating the total DOC pool, because UDOC is only ~25% of DOC and selectively collects high molecular weight compounds (>1000 Da) (Amon and Benner, 1996; Walker et al., 2011; Benner, 2002; Aluwihare et al., 2002; Repeta et al., 2002; Benner et al., 1997). Studies of chemical composition and ^{14}C age of marine organic carbon show that the age of organic carbon increases with smaller sized molecules (Benner and Amon, 2015; Santschi et al., 1995; Walker et al., 2011). Thus, the presumably oldest, low molecular weight BC is not captured in UDOC.

We measured $\Delta^{14}C$ of BC in a greater amount of the DOC pool using SPE, which does not have an inherent size bias. The SPE method concentrates DOC based on chemical composition and retains polar and less-polar DOC compounds. This BC extraction method is an improvement over UDOC, because SPE recovers approximately half of the total DOC

* Corresponding author.
E-mail address: acoppola@uci.edu (A.I. Coppola).

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pool based on the sample type (Louchouarn et al., 2010; Dittmar et al., 2008). Two studies have reported concentrations of BC in SPE-DOC of 0.6–0.8 μM in the Southern Ocean (Dittmar and Paeng, 2009) and 1.0 ± 0.2 μM in surface water at the Bermuda Atlantic Time Series site (Stubbins et al., 2012a).

Our primary motivation is to use the SPE method to measure the ^{14}C age, concentration and structure of BC in ocean water. We use a styrene divinyl benzene copolymer resin to concentrate mostly hydrophilic DOC. We measure the mass and $\Delta^{14}C$ value of SPE-DOC and SPE-BC from a variety of standards and seawater. We assess blanks, reproducibility and the robustness of this SPE-DOC method for $\Delta^{14}C$ analysis. Comparisons of SPE-DOC to total UV-oxidized DOC are used to evaluate whether SPE-DOC $\Delta^{14}C$ values are representative of total DOC $\Delta^{14}C$.

2. Materials and methods

2.1. Sample collection

Coastal seawater DOC samples were collected from Newport Beach Pier (NBP), in Newport Beach, California USA (33°60.70'N, 117°92.89'W) on August 8, 2013 at 1 m depth in 1-gallon glass bottles. Open ocean seawater DOC samples were collected from 20 m depth at Station M located on the northeast Pacific abyssal plain (34°50'N, 123°00'W) on the *R/V* New Horizon in November 2004 using Niskin bottles. NBP samples were filtered through pre-baked 1.0 μm Whatman GFF filters and Station M samples were filtered using Whatman Polycap AS filter capsules (0.2 μm). All glassware in this study was soaked in 10% HCl, rinsed with deonized water and combusted at 550 °C for 2 h. All seawater samples were frozen (at −20 °C) until analysis. Seawater samples were separately analyzed for total DOC $\Delta^{14}C$ and [DOC] values using UV-oxidation techniques (Beaupré et al., 2007).

Seawater samples collected from Station M are from a long-term abyssal study site (4100 m), located ~220 km west of Point Conception, CA in the NE Pacific (Smith and Druffel, 1998). The California current flows southward at Station M and has well-developed spring blooms. NBP is a coastal site, impacted by occasional urban river discharge from the Santa Ana River (5 km north of NBP) during discharge events in southern California. There were no river discharge events recorded by the gauge on the Santa Ana River in the City of Santa Ana on August 8, 2013, nor a month prior that may have contributed river water to the sample (available on the USGS site, Supplementary Fig. 1).

2.2. Suwannee river natural organic matter standards

We used two freshwater, organic matter reference samples (IHSS 1R101N termed SR NOM I, and IHSS 2R101N termed SR NOM II) purchased from the International Humics Substances Society (https://ihss.humicsubstances.org/) that were collected in May 1999 and May 2012, respectively. The Suwannee River drains the Okefenokee Swamp in southeastern Georgia, located at 30°48′14′N, 82°25′03′W, and has high DOC concentrations (82.7 mg C/l) with low concentrations of inorganic solutes (Serkiz and Perdue, 1990; Green et al., 2015). To create these standards, large volumes of water (~36,000 l) from the Suwannee River were concentrated by reverse osmosis, desalted by cation exchange, freeze-dried and homogenized.

When SR NOM I was sampled, two dams (built in 1950–1960) in the Suwannee River sill retained a high water level in the swamp and the site was relatively pristine and automobile vehicle access was prohibited (Green et al., 2015). The average flow rate of the river was 1.96 m^3/s. In 2012, one of the two dams had been removed and it was no longer pristine (Green et al., 2015). The water level during 2012 was lower and the flow rate was much lower (0.46 m^3/s). Both SR NOM I and SR NOM II were dissolved in Milli-Q water at DOC concentrations of 75–85 μM for SPE-BC analysis. These natural organic matter standards were also processed without SPE extraction, using only the BPCA method, and are referred as "total BC."

2.3. Solid phase extraction of DOC (SPE-DOC)

We used a styrene divinyl benzene copolymer sorbent (Sigma Aldrich Diaion 13605, HP-20, pore size 200 Å), first used by De Jesus and Aluwihare, (2008), for extraction of DOC from seawater. To minimize the resin carbon blank, extensive cleaning (~1 week) was performed using a glass soxhlet extractor with a pyrex glass insert to hold the resin during washings of methanol, acetone, ethyl acetate and dicholormethane at 65 °C, 56 °C, 77 °C and 40 °C, respectively. Each soxlet solvent washing lasted 24 h and was performed sequentially in order of decreasing solvent polarity. According to the HP-20 manufacturers guidelines, sample water was acidified to pH 2 with hydrochloric acid (Fluka Traceselect 84,415–500 ml) to increase extraction efficiency of organic components that contained exchangeable protons (Louchouarn et al., 2010).

Fig. 1 summarizes the SPE and BC methods. Briefly, large-volume frozen water samples (10–15 l) were defrosted, homogenized by shaking, acidified and loaded onto the SPE column. Samples were siphoned through 15 ml of resin in a glass Kontes column using 6 mm diameter pyrex tubing with acid cleaned silicone tubing, at a slow loading rate of 16 bed volumes per hour (240 ml/h for surface samples). This flow rate was monitored and maintained over the course of the sample loading. The sample was loaded onto the resin three times to maximize interaction of DOC with the resin bed and increase DOC recovery.

In preparation for DOC elution, two bed volumes (30 ml) of Milli-Q water were passed through the column at 30 ml/h to remove salts, and discarded. Each SPE-DOC fraction was eluted at a flow rate of 30 ml/h using two bed volumes (30 ml). Solvents with different polarities were used to elute SPE-DOC into individual, glass vials in the following order: methanol, acetone, ethyl acetate and dicholoromethane. These SPE-DOC fractions were dried under a stream of ultra-high purity (UHP) nitrogen gas. The SPE-DOC fractions were dissolved in a known volume of solvent, sub-sampled (5–10% of the volume), dried, then lyophilized for 24 h. The SPE-DOC sub-samples were combusted separately to determine the percent yield of DOC (SPE-DOC/total DOC × 100) and for SPE-DOC $\Delta^{14}C$ analyses.

2.4. Total BC and BC in solid phase extracted DOC (SPE-BC)

The SPE-DOC fractions were used to isolate BC using the Benzene Polycarboxylic Acid method, which oxidizes BC to produce marker compounds (BPCAs) for radiocarbon analysis (Ziolkowski et al., 2011; Schneider et al., 2010). The relative abundances of BPCAs produced during the oxidation step also provide qualitative BC structural information, because the more substituted BPCAs are derived from a more condensed aromatic BC network (Glaser et al., 1998; Ziolkowski et al., 2011; Coppola et al., 2013). The BPCA method characterizes only aromatic carbon as BC (Masiello and Louchouarn, 2013; Norwood et al., 2013; Myers-Pigg et al., 2015).

Briefly, eluted SPE-DOC extracts in glass vials were dried and lyophilized for 24 h. Total BC in SR NOM I and II was measured without SPE-processing. Concentrated nitric acid was added to SPE-BC and total BC sample types and placed in a pressure digestion chamber at 170 °C for 8 h to produce BPCAs (Coppola et al., 2013; Ziolkowski et al., 2011). The carbon in the carboxylic acid groups of the BPCA compounds is derived from adjacent aromatic groups of BC (B3CA, substituted with three carboxylic acids through B6CAs, those substituted with six carboxylic acids). After digestion, the solution was filtered, lyophilized and redissolved in methanol. Samples were derivatized using (trimethylsilyl) diazomethane in 2.0 M diethyl ether to convert carboxylic acid groups to methyl esters and an internal standard was added (500 μml of diphenic acid). BPCAs were collected on the preparative capillary gas chromatograph (PCGC), along with other BC standards (Hammes et al., 2007; Wiedemeier et al., 2015) using previously published techniques (Ziolkowski and Druffel, 2009; Coppola et al., 2013).