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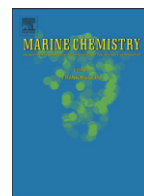
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# Solid phase extraction method for the study of black carbon cycling in dissolved organic carbon using radiocarbon



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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 ( $\Delta^{14}\text{C}$ ) 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  $\pm$  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  $^{14}\text{C}$  analysis. We report SPE-BC  $\Delta^{14}\text{C}$  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  $\Delta^{14}\text{C}$  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  $4.2 \pm 1.0\%$  of SPE-DOC in the open ocean surface sample, or  $1.4 \pm 0.1 \mu\text{M C}$ . This work provides the methodological basis by which global BC concentrations, compositions (e.g. relative abundances of BPCA marker compounds) and  $\Delta^{14}\text{C}$  values can be assessed.

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## 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  $\text{CO}_2$  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  $\mu\text{m}$  filter). While most DOC is believed to be produced by phytoplankton in the surface ocean, marine DOC is surprisingly thousands

of  $^{14}\text{C}$  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  $\Delta^{14}\text{C}$  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  $\Delta^{14}\text{C}$  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  $^{14}\text{C}$  years, providing evidence for BC stability on  $>10^4$  year time scales. BC  $\Delta^{14}\text{C}$  measurements in UDOC have limitations for evaluating the total DOC pool, because UDOC is only  $\sim 25\%$  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  $^{14}\text{C}$  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  $\Delta^{14}\text{C}$  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

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pool based on the sample type (Louchouart et al., 2010; Dittmar et al., 2008). Two studies have reported concentrations of BC in SPE-DOC of 0.6–0.8  $\mu\text{M}$  in the Southern Ocean (Dittmar and Paeng, 2009) and  $1.0 \pm 0.2 \mu\text{M}$  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  $^{14}\text{C}$  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  $\Delta^{14}\text{C}$  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  $\Delta^{14}\text{C}$  analysis. Comparisons of SPE-DOC to total UV-oxidized DOC are used to evaluate whether SPE-DOC  $\Delta^{14}\text{C}$  values are representative of total DOC  $\Delta^{14}\text{C}$ .

## 2. Materials and methods

### 2.1. Sample collection

Coastal seawater DOC samples were collected from Newport Beach Pier (NBP), in Newport Beach, California USA ( $33^{\circ}60.70'\text{N}$ ,  $117^{\circ}92.89'\text{W}$ ) 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 ( $34^{\circ}50'\text{N}$ ,  $123^{\circ}00'\text{W}$ ) on the R/V New Horizon in November 2004 using Niskin bottles. NBP samples were filtered through pre-baked  $1.0 \mu\text{m}$  Whatman GFF filters and Station M samples were filtered using Whatman Polycap AS filter capsules ( $0.2 \mu\text{m}$ ). All glassware in this study was soaked in 10% HCl, rinsed with deionized water and combusted at  $550^{\circ}\text{C}$  for 2 h. All seawater samples were frozen (at  $-20^{\circ}\text{C}$ ) until analysis. Seawater samples were separately analyzed for total DOC  $\Delta^{14}\text{C}$  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  $\sim 220$  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  $30^{\circ}48'14'\text{N}$ ,  $82^{\circ}25'03'\text{W}$ , 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 ( $\sim 36,000$  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 still 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  $1.96 \text{ m}^3/\text{s}$ . 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 ( $0.46 \text{ m}^3/\text{s}$ ). Both SR NOM I and SR NOM II were dissolved in Milli-Q water at DOC concentrations of 75–85  $\mu\text{M}$  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  $200 \text{ \AA}$ ), first used by De Jesus and Aluwihare, (2008), for extraction of DOC from seawater. To minimize the resin carbon blank, extensive cleaning ( $\sim 1$  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 dichloromethane at  $65^{\circ}\text{C}$ ,  $56^{\circ}\text{C}$ ,  $77^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ , 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 (Louchouart et al., 2010).

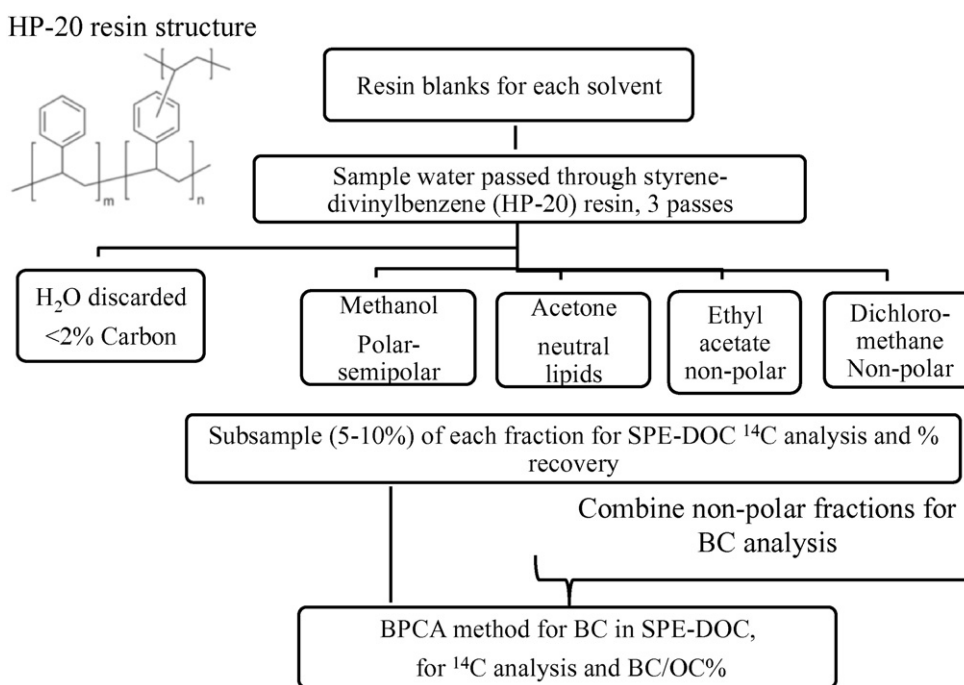
Fig. 1 summarizes the SPE and BC methods. Briefly, large-volume frozen water samples (10–15 l) were defrosted, homogenized by shaking, acidified and loaded onto the SPE column. Samples were siphoned through 15 ml of resin in a glass Kontes column using 6 mm diameter pyrex tubing with acid cleaned silicone 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 dichloromethane. 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  $\times 100$ ) and for SPE-DOC  $\Delta^{14}\text{C}$  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 Louchouart, 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  $170^{\circ}\text{C}$  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  $\mu\text{ml}$  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).



**Fig. 1.** Flow chart of methods used to isolate and analyze SPE-DOC and SPE-BC. Resin blanks are listed in Supplementary Table 1. Chemical structure of HP-20 resin from Aldrich Chemical catalog.

BC concentrations were determined from PCGC chromatographs using peak areas of each BPCA relative to the internal standard. Calibration curves (in mg C per unit mass) from commercially available BPCAs were applied for an estimate of BPCA mass. The BPCA method requires a conversion factor to convert the BPCAs formed from the nitric acid digestion into an estimate of the original BC mass. The conversion factor  $24.2 \pm 1.6\%$  was used to convert BPCAs to BC concentrations (Ziolkowski and Druffel, 2010). This conversion factor was determined from oxidizing compounds with known chemical formulas (polycyclic aromatic hydrocarbons) to calibrate the BPCA method for carbon yield. Previously used conversion factors were based on yields from activated charcoal (Glaser et al., 1998; Brodowski et al., 2005).

In preparation for  $^{14}\text{C}$  analysis, B3CA through B6CA marker compounds (including nitrated B3CA and B4CAs) were collected in U-traps ( $-20\text{ }^{\circ}\text{C}$ ) in the PCGC fraction collector. The B2CA marker compounds were not collected, because they may be derived from lignins, a non-combusted material. The BPCAs in the U-trap were transferred using dichloromethane to quartz tubes, and dried under UHP nitrogen.

### 2.5. Radiocarbon analyses

For  $^{14}\text{C}$  analysis, samples were sealed in quartz tubes under vacuum with cupric oxide and silver wire and combusted to  $\text{CO}_2$  at  $850\text{ }^{\circ}\text{C}$  for 2 h. The  $\text{CO}_2$  gas produced was cryogenically purified, and quantified manometrically, and used to calculate % DOC recovery. In some cases when samples were too small for individual  $\Delta^{14}\text{C}$  measurement (e.g., ethyl acetate and dichloromethane fractions), they were combined. The resultant  $\text{CO}_2$  was converted to graphite using the hydrogen reduction method on iron catalyst for  $^{14}\text{C}$  analysis at the Keck Carbon Cycle Accelerator Mass Spectrometry (AMS) Laboratory at U.C. Irvine (Santos et al., 2007). Radiocarbon measurements were reported as  $\Delta^{14}\text{C}$  for geochemical samples without known age correction (Stuiver and Polach, 1977).

### 2.6. Carbon blanks: resin blank and process blank assessments

Three types of blanks were evaluated. First, resin blanks were processed to assess the carbon blank from each solvent that was passed

through the resin before loading a sample. Resin blanks ranged from 2 to  $6\text{ }\mu\text{g C}$  each. Second, process blanks contained Milli-Q water (10 l each) and were subjected to the same processing steps as the samples. Process blanks were used to correct SPE-DOC samples for the  $\Delta^{14}\text{C}$  value and mass of carbon blank added during processing, using a mass balance approach in Eq. 1:

$$\Delta^{14}\text{C}_{\text{SPE-DOC}} = \frac{\Delta^{14}\text{C}_{\text{measured}}C_{\text{measured}} - \Delta^{14}\text{C}_{\text{Milli-Q}}C_{\text{Milli-Q}}}{C_{\text{measured}} - C_{\text{Milli-Q}}} \quad (1)$$

where  $\Delta^{14}\text{C}_{\text{SPE-DOC}}$  is the  $\Delta^{14}\text{C}$  value corrected for SPE processing,  $\Delta^{14}\text{C}_{\text{measured}}$  and  $C_{\text{measured}}$  are the measured  $\Delta^{14}\text{C}$  value and mass of the sample, respectively, uncorrected for SPE processing, and  $\Delta^{14}\text{C}_{\text{Milli-Q}}$  and  $C_{\text{Milli-Q}}$  are the average  $\Delta^{14}\text{C}$  value and mass of the Milli-Q water SPE-DOC, respectively (Table 1).

Third, for the assessment of blank carbon added during the BPCA method, process blanks were generated using the Milli-Q water described above. The SPE-BC samples are corrected using an indirect approach as previously reported by Coppola et al., (2013) and Ziolkowski and Druffel (2009). Several BC standards from the carbon ring trial described in Hammes et al., (2007) were run alongside SPE-BC samples to correct for blank carbon. We found that approximately  $6\text{--}10\text{ }\mu\text{g}$  dead blank C and  $0.5\text{ }\mu\text{g}$  C of modern carbon was added during BC processing of water samples.

## 3. Results

### 3.1. Carbon blank assessments

The mass of resin blanks from each of the four solvents ranged from 2 to  $8\text{ }\mu\text{g C}$ , and their  $\Delta^{14}\text{C}$  values ranged from  $-499 \pm 14\%$  to  $-873 \pm 2\%$  (Supplementary Table 1). The  $\Delta^{14}\text{C}$  values of Milli-Q process blanks ranged from  $-660\%$  to  $-1000\%$ , and had masses that ranged from 2 to  $10\text{ }\mu\text{g C}$  (Table 1). Using an isotopic mass balance, we determined that Milli-Q water SPE-DOC  $\Delta^{14}\text{C}$  values ranged from  $-721 \pm 77\%$  to  $-927 \pm 54\%$  (Supplementary Table 1). The Milli-Q water total DOC  $\Delta^{14}\text{C}$  values obtained using UV-oxidation techniques ranged from

**Table 1**  
Carbon blank mass and  $\Delta^{14}\text{C}$  values of process blanks obtained from processing 10 l of Milli-Q water for each assessment. Weighted averages are in bold.

SPE-DOC fraction	Sample group	UCID lab code #	Blank size ( $\mu\text{g C}$ )	$\Delta^{14}\text{C}$ (‰) Blank corrected	$\pm$		
Methanol	MQ I	17010	4	-891	23		
	MQ III	17173	2	-877	76		
	MQ IV	17185	10	nd			
	MQ IV	17187	8	nd			
	MQ IV	17175	6	-837	66		
	MQ V	18649	7	-708	25		
	MQ VI	18842	10	-747	34		
	Average $\pm$ SD:				<b>6 <math>\pm</math> 3</b>	<b>-785</b>	<b>80</b>
	Acetone	MQ I	17026	2	-911	30	
		MQ I	17028	2	-1000	4	
MQ I		17029	2	-1000	18		
MQ II		17137	2	-815	64		
MQ III		17176	4	-858	53		
MQ IV		17190	6	nd			
MQ IV		17178	6	-815	65		
MQ V		18650	6	-836	67		
MQ VI		18843	10	-766	13		
Average $\pm$ SD:				<b>4 <math>\pm</math> 3</b>	<b>-836</b>	<b>87</b>	
Ethyl Acetate	MQ II	17138	2	-1000	6		
	MQ III	17179	6	-912	56		
	MQ IV	17191	6	nd			
	MQ IV	17192	6	nd			
	MQ IV	17184	6	-918	62		
	MQ V	18651	2	nd			
	MQ VI	18844	4	-743	34		
	Average $\pm$ SD:				<b>4 <math>\pm</math> 2</b>	<b>-866</b>	<b>107</b>
	Dichloromethane	MQ II	17030	2	-965	3	
		MQ II	17032	2	-1000	4	
MQ II		17033	2	-1000	6		
MQ III		17179	2	-858	52		
MQ IV		17194	6	-801	63		
MQ IV		17183	2	-859	61		
MQ IV		17184	6	-862	53		
MQ V		18652	2	-1000	5		
MQ VI		18845	3	-660	50		
Average $\pm$ SD:				<b>3 <math>\pm</math> 2</b>	<b>-800</b>	<b>114</b>	

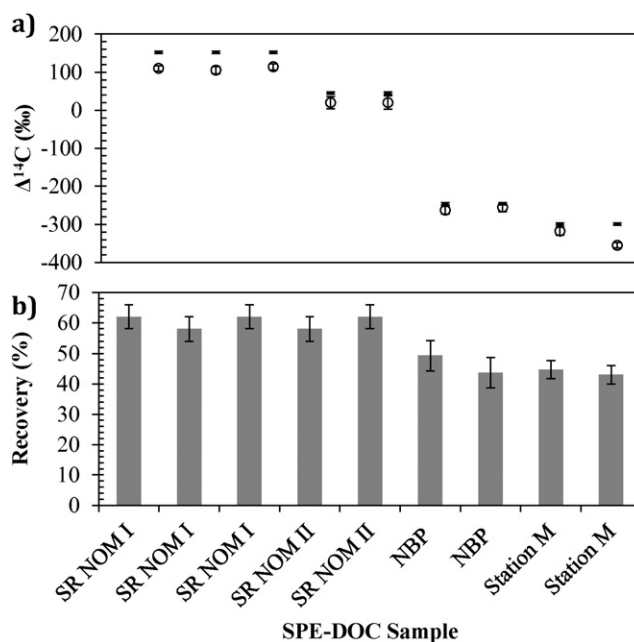
-612  $\pm$  57 to -927  $\pm$  54‰, which is equal to the range in SPE-DOC Milli-Q  $\Delta^{14}\text{C}$  values.

### 3.2. SPE-DOC recoveries and $\Delta^{14}\text{C}$ values

Percent SPE-DOC recoveries in all elutants for SR NOM I, SR NOM II, NBP and Station M samples were 62  $\pm$  5%, 61  $\pm$  4%, 43  $\pm$  6% and 44  $\pm$  3%, respectively (Fig. 2). Percent SPE-DOC recoveries for ocean samples are comparable to those reported by Dittmar et al. (2008) (42  $\pm$  8%) for surface marine DOC using a similar method (pre-made PPL cartridges with a smaller pore size of 150 Å and methanol elution).

For all samples, most of the DOC (>89%) was eluted in the methanol fraction (Table 2, Fig. 3). SR NOM I and SR NOM II standards had a very small amount of DOC (~1%) that eluted in the acetone fraction, and no DOC eluted in the ethyl acetate and dichloromethane fractions. For NBP, although the majority (92  $\pm$  4%) of coastal SPE-DOC was present in the methanol fraction, the less-polar (acetone, ethyl acetate and dichloromethane) fractions constitute 8% of the SPE-DOC. In the Station M sample, the methanol fraction was 89  $\pm$  2%, dichloromethane was 9  $\pm$  2% and there was insignificant DOC in the acetone and ethyl acetate fractions (1  $\pm$  1%).

All SPE-DOC  $\Delta^{14}\text{C}$  values were corrected using results from the process blanks (Eq. (1)). The methanol SPE-DOC  $\Delta^{14}\text{C}$  values for SRNOM I are identical within 1 sigma (+110  $\pm$  7‰, +105  $\pm$  10‰, +114  $\pm$  8‰) (Fig. 2). The acetone SPE-DOC fractions in SR NOM I are -286  $\pm$  81‰ and -124  $\pm$  68‰, significantly lower than those of the methanol fractions. The  $\Delta^{14}\text{C}$  value of total combusted SR NOM I is +152  $\pm$  3‰ (Table 2), which is significantly higher than those of the methanol



**Fig. 2.** (a.) SPE-DOC  $\Delta^{14}\text{C}$  values of methanol fractions for freshwater SR NOM samples, NBP and Station M seawater (open circles) with comparisons to total DOC  $\Delta^{14}\text{C}$  values (black dash). (b.) Corresponding percent SPE-DOC recoveries per individual sample are shown as gray columns.

fractions, indicating that the SPE-DOC fraction is selectively isolating older DOC from the bulk material.

Duplicate methanol SPE-DOC  $\Delta^{14}\text{C}$  values in SR NOM II are identical (+20  $\pm$  16‰, +20  $\pm$  18‰) (Table 2). The acetone fraction  $\Delta^{14}\text{C}$  values (-329  $\pm$  57‰ and -480  $\pm$  75‰) are significantly lower than those of the methanol fractions. The total combusted SR NOM II  $\Delta^{14}\text{C}$  value (+45  $\pm$  3‰) is within 2 sigma of the SPE-DOC  $\Delta^{14}\text{C}$  values measured in the methanol fractions (Table 2).

Duplicate methanol SPE-DOC  $\Delta^{14}\text{C}$  values in the NBP samples are identical (-263  $\pm$  10‰, -255  $\pm$  12‰) (Fig. 2). The acetone SPE-DOC  $\Delta^{14}\text{C}$  values are -717  $\pm$  24‰ and -764  $\pm$  10‰, which are much lower than those of the methanol fractions. The  $\Delta^{14}\text{C}$  values of the combined ethyl acetate/dichloromethane fractions (-543  $\pm$  41‰ to -691  $\pm$  95‰ Table 2) are intermediate to the other fractions. The NBP total DOC  $\Delta^{14}\text{C}$  values measured by UV-oxidation are -246  $\pm$  3‰, which is also equal to the methanol fraction  $\Delta^{14}\text{C}$  values.

For Station M seawater, the methanol SPE-DOC  $\Delta^{14}\text{C}$  values are -318  $\pm$  11‰ and -335  $\pm$  7‰ (Fig. 2). The other fractions have lower  $\Delta^{14}\text{C}$  values (acetone -678  $\pm$  25‰, ethyl acetate/dichloromethane -958  $\pm$  5‰) (Table 2). The total Station M DOC  $\Delta^{14}\text{C}$  value is -299  $\pm$  3‰, which was significantly higher than one of the methanol SPE-DOC  $\Delta^{14}\text{C}$  values.

### 3.3. BC concentrations, and relative BPCA distributions

The average BC/OC% values in SR NOM I, SR NOM II, NBP and Station M seawater samples are 8.2  $\pm$  1.0%, 11.9  $\pm$  2.0%, 20.5  $\pm$  2.0% and 4.2  $\pm$  1.0%, respectively (Table 3). The BC concentrations at in the NBP and Station M samples are 5.6  $\pm$  0.4  $\mu\text{M}$  and 1.4  $\pm$  0.1  $\mu\text{M}$ , respectively, in the SPE-DOC (Supplementary Table 2).

The relative BPCA abundances (i.e. B3CA, B4CA, B5CA, B6CA) in the methanol fractions of SR NOM I and II have low B3CAs and B4CAs abundances relative to those for B5CAs and B6CAs. In contrast, the NBP samples have similar abundances of B3CAs, B4CAs and B5CAs and a low abundance of B6CAs (7  $\pm$  3%). We obtained BPCA abundances for the less polar SPE-BC fractions for the NBP samples only (Fig. 4b), and the

**Table 2**

Total [DOC] and SPE-DOC  $\Delta^{14}\text{C}$  values for Suwannee River standards, NBP and Station M water samples. SPE-DOC  $\Delta^{14}\text{C}$  values are corrected using mass balance techniques using Milli-Q SPE-DOC blanks (see text for details).

Sample type	Total DOC			SPE-DOC fraction (% recovery) <sup>a</sup>	SPE-DOC				
	UCID lab code #	$\Delta^{14}\text{C}$ (‰)	±		UCID lab code #	Size ( $\mu\text{g C}$ )	$\Delta^{14}\text{C}$ (‰)	±(‰)	Recovery (%)
SR NOM I (1999)	17901–17910; (n = 10)	+152	3	Methanol (99 ± 1%)	18619	690	+110	7	62 ± 4
					17848	590	+105	10	58 ± 4
					17582	789	+114	8	62 ± 4
					17583	10	−286	81	
					17849	10	−124	68	
SR NOM II (2012)	18796–18799; (n = 4)	+45	3	Methanol (99 ± 1%) Acetone (1 ± 1%)	18846	380	+20	16	58 ± 4
					18851	390	+20	18	62 ± 4
					18847	38	−329	57	
					18852	39	−480	75	
					18806	762	−263	10	49 ± 4
NBP	17616	−246	3	Methanol (92 ± 4%) Acetone (4 ± 2%) Ethyl acetate/ Dichloromethane (2 ± 1%)	18002	690	−255	12	44 ± 5
	18270				20	−717	24		
	18276				18007	57	−764	10	
	18253				18003	6	−543	41	
					18008	6	−691	95	
					18804	6			
Station M	8253 <sup>b</sup>	−299	3	Methanol (89 ± 2%) Acetone (1 ± 1%) Ethyl acetate/ Dichloromethane (0 ± 1%/10 ± 2%)	18267	401	−318	11	43 ± 3
	8270				514	−335	7	45 ± 3	
	8271				18268	8	nd	25	
	8276				18244	8	−678		
					18245	32	−958	5	

<sup>a</sup> Recovery in each SPE-DOC fraction calculated as the percentage of the total mass in all fractions.

<sup>b</sup> Station M UV-oxidation total DOC value is reported by [Beaupre and Druffel \(2009\)](#).

only significant difference between methanol with other less-polar fractions is the absence of B6CA marker compounds. The BPCA abundances in the Station M samples (Fig. 4a) reveal a greater proportion of B3CAs than at NBP.

### 3.4. SPE-BC $\Delta^{14}\text{C}$ values

All SPE-BC  $\Delta^{14}\text{C}$  values were corrected using an indirect approach (Table 3). The methanol SPE-BC  $\Delta^{14}\text{C}$  value of SR NOM I was +148 ± 17‰. The total BC  $\Delta^{14}\text{C}$  value for SR NOM I (without SPE) was significantly lower than that for the methanol SPE-BC (−49 ± 33‰). In contrast, duplicates of the methanol SPE-BC of SR NOM II (−462 ± 40‰ and −346 ± 70‰ within 2 sigma) were lower than that for the total BC (−159 ± 55‰).

The methanol SPE-BC  $\Delta^{14}\text{C}$  values in NBP seawater are −712 ± 36‰ and −678 ± 19‰ (within 2 sigma). The SPE-BC  $\Delta^{14}\text{C}$  values of the acetone fractions are higher (−587 ± 47‰ and −615 ± 20‰). The NBP SPE-BC  $\Delta^{14}\text{C}$  value of the ethyl acetate/dichloromethane mixture was equal to the acetone fractions of NBP SPE-BC fractions (−593 ± 15‰) (Fig. 4b).

Duplicates of the methanol SPE-BC  $\Delta^{14}\text{C}$  values in the Station M samples are −592 ± 201‰ and −649 ± 121‰ (within 2 sigma), equal to the NBP methanol values (Fig. 4a). No results were obtained for the Station M acetone, dichloromethane or ethyl acetate fractions, due to their small masses.

## 4. Discussion

In the first section of the discussion, we assess the SPE-DOC method by addressing the reproducibility of concentration and isotopic measurements in replicate standards, blanks and samples. In section 4.2, we discuss the variability of  $\Delta^{14}\text{C}$  values obtained for SPE-DOC and total DOC analyses on the same samples. In section 4.3, we compare  $\Delta^{14}\text{C}$  values obtained for SPE-BC and total BC for SR NOM I and SR NOM II samples. We also compare our results to those available for a deep UDOC BC sample in the NE Pacific and a surface sample in the North Central Pacific (NCP) ([Ziolkowski and Druffel, 2010](#)). In the final section, we discuss SPE-DOC and SPE-BC composition and cycling in these aqueous environments.

### 4.1. Methods assessment: recoveries, SPE-DOC carbon blanks and reproducibility

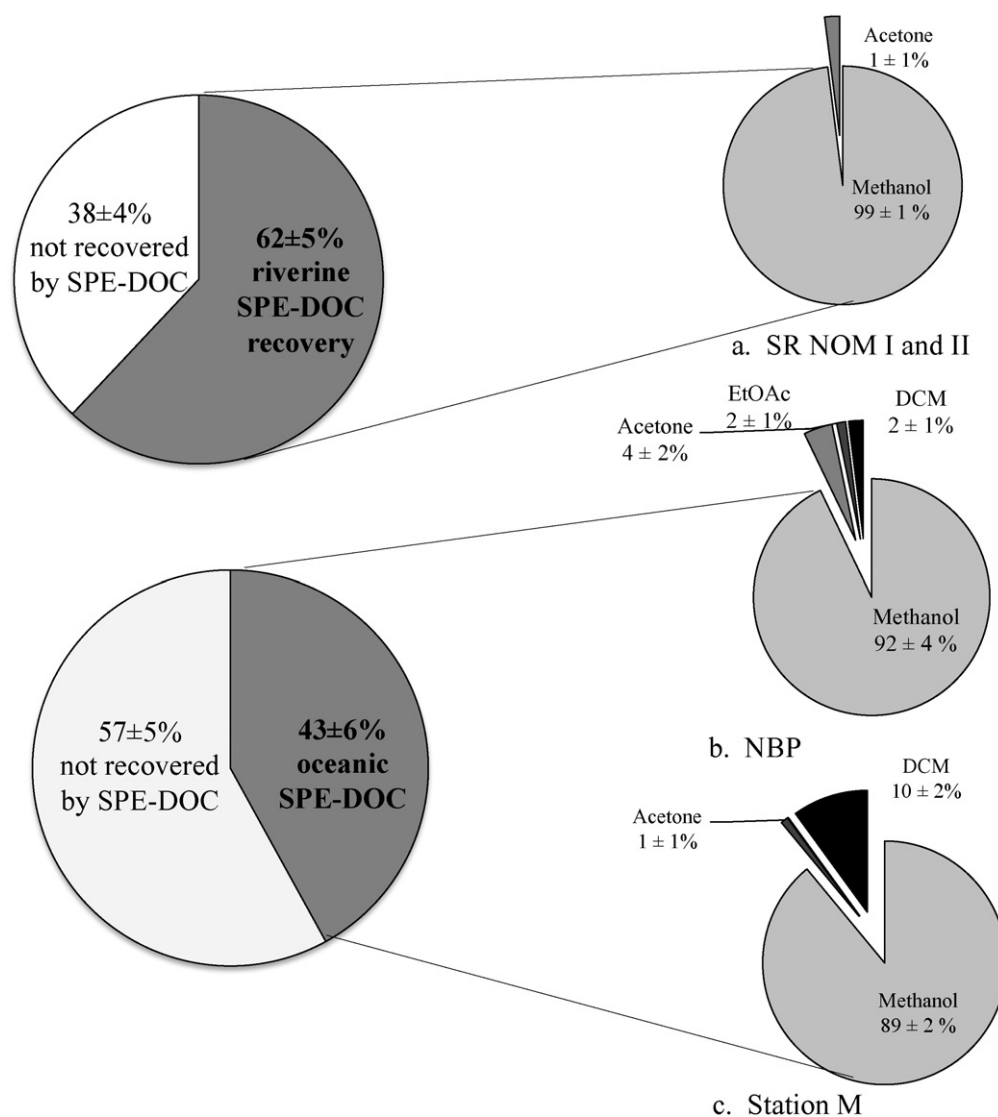
Replicate measurements of SPE-DOC and SPE-BC recoveries and  $\Delta^{14}\text{C}$  values agree within 2 sigma. This demonstrates that the method produces reproducible  $\Delta^{14}\text{C}$  results (Table 2, Table 3, Fig. 2). Recoveries are higher for freshwater samples (62 ± 5%), likely due to the absence of salt in the sample. Recoveries were also consistent and reproducible for each sample type (Fig. 2).

We report that masses of resin blanks acquired prior to sample loading on the resin, and Milli-Q process blanks are equal within error (Table 1, Supplementary Table 1), indicating that there is no additional carbon blank introduced to the large volume water samples. The SPE-DOC  $\Delta^{14}\text{C}$  values of Milli-Q process blanks are equal within error to the  $\Delta^{14}\text{C}$  values obtained for multiple 1-L UV oxidized Milli-Q blanks run from 2012 to 2014 in our laboratory (Supplementary Table 1). The SPE-Milli-Q process blank correction changed  $\Delta^{14}\text{C}$  values by less than 10‰.

The SPE-BC process blanks are similar in size and  $\Delta^{14}\text{C}$  value to of the resin and Milli-Q process blanks (Table 3). The SPE-BC process blanks are also comparable to those reported by [Coppola et al., \(2013\)](#). Together, these results suggest that no additional carbon blank is introduced by the SPE method and this method has low, consistent carbon blanks. Other studies quantify blanks by a direct approach, which is the measurement of extraneous carbon by processing in the absence of a sample ([Dittmar et al., 2008](#); [Flerus et al., 2012](#)). Our blank assessment uses large sample volumes, standards and matrices to evaluate the  $\Delta^{14}\text{C}$  value of blank carbon added during processing.

### 4.2. Comparison of $\Delta^{14}\text{C}$ values of SPE-DOC and total DOC

We present another comparison of  $\Delta^{14}\text{C}$  values between SPE-DOC and total DOC (UV oxidized) from splits of the same sample water (Table 2) ([Druffel et al., 1992](#)). Generally, we find that all methanol SPE-DOC  $\Delta^{14}\text{C}$  values are equal to or lower (−25 ± 10‰) than their corresponding total DOC  $\Delta^{14}\text{C}$  values (Fig. 2). Similarly, the  $\Delta^{14}\text{C}$  values of SPE-DOC from SR NOM I and II standards are significantly lower (−35 ± 10‰) than total DOC  $\Delta^{14}\text{C}$  values (Fig. 2). The polarity-driven SPE method and its lower extraction efficiency for dissolved organic



**Fig. 3.** SPE-DOC recoveries for two sample types, riverine and marine DOC. Fraction compositions from methanol fraction (more polar, gray), acetone, ethyl acetate (dark gray) to dichloromethane (less polar, black) are shown in a.) SR NOM I and II b.) NBP, and c.) Station M sites. There was no significant difference between SR NOM I and II with regard to SPE-DOC composition.

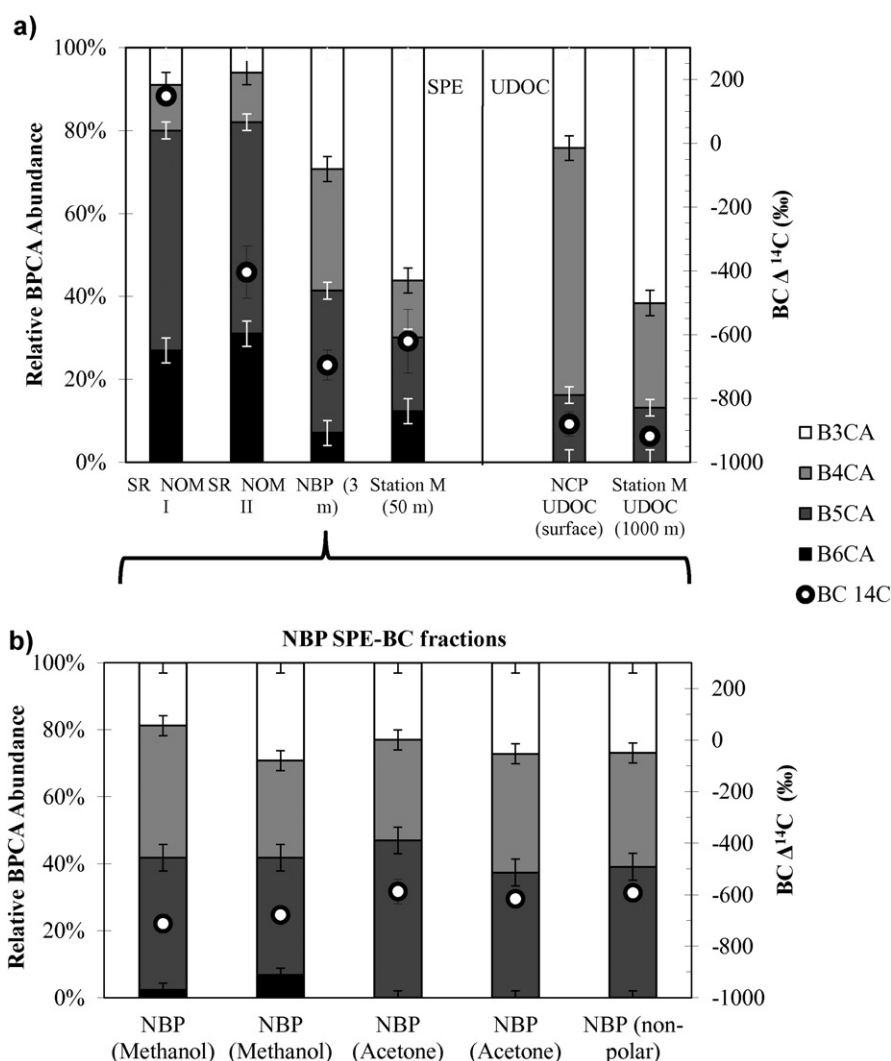
**Table 3**

SPE-BC  $\Delta^{14}\text{C}$ , relative BPCA abundance and total BC/OC percentages for Suwannee River standards, and NBP and Station M seawater samples.

Sample type	SPE-BC Fraction	UCID lab code#	Size ( $\mu\text{g C}$ )	SPE-BC $\Delta^{14}\text{C}$ (‰)	$\pm$	BPCA relative abundance <sup>a</sup> B3CA:B4CA:B5CA:B6CA	Total BC/OC (%)	
SR NOM I (1R101N)	Methanol	17586	112	+148	17	SPE-BC 9:11:53:27 total 16:22:38:21 <sup>b</sup>	8 ± 2	
SR NOM II (2R101N)	Methanol	18623	31	-462	40	SPE-BC 6:10:53:30	12 ± 2	
		18850	20	-346	70	SPE-BC 6:12:51:31 total 11:33:37:19 <sup>b</sup>		
NBP	Methanol	17940	43	-678	19	18:39:38:4	21 ± 2	
		17719	25	-712	36	29:29:34:7		
		17720	16	-587	47	23:30:47:0		
		17941	42	-615	20	27:35:37:0		
Station M	Methanol	Ethyl acetate/Dichloromethane	17942	62	-593	15	26:33:39:0	4 ± 1
		nd					27:35:36:0	
		18247	12	-592	201	56:14:18:12		
Process blanks		18271	15	-649	121	58:16:18:8		
		17590	8	-867	2			
		17448	6	-864	3			
		17490	6	-767	4			
		17261	10	-917	2			

<sup>a</sup> Errors for the BPCA relative abundance determined by peak areas in FID trace is  $\pm 3\%$  for B3CA,  $\pm 4\%$  for B4CA,  $\pm 3\%$  for B5CA and  $\pm 2\%$  for B6CA.

<sup>b</sup> Total BPCA relative abundances were determined from processing SR NOM I and SR NOM II through the BPCA method.



**Fig. 4.** (a.) The relative BPCA abundances and  $\Delta^{14}\text{C}$  values (white circles) of the methanol SPE-BC fractions for SR NOM I, SR NOM II, NBP, Station M SPE-BC. The right side shows UDOC relative BPCA abundances from Ziolkowski and Druffel, (2010) at Station M (1000 m) and the North Central Pacific (20 m, NEHLA pipe, Hawaii). (b.) The relative BPCA abundance and  $\Delta^{14}\text{C}$  values of all SPE-BC (white circles) fractions in the NBP samples.

nitrogen compared to organic carbon may be responsible for the difference between total DOC and SPE-DOC  $\Delta^{14}\text{C}$  values (Flerus et al., 2012). Another possible explanation for this  $\Delta^{14}\text{C}$  offset could be selective concentration of younger humic materials that were precipitated out of solution at pH 2 during the collection of the standards (a step that we use in our SPE method). Our results suggest that SPE-DOC selectively isolates older DOC from the riverine standards, and to a lesser or no extent for seawater samples.

Using a mass balance between the SPE-DOC that is recovered ( $43 \pm 6\%$ ) and total DOC, we find the non-adsorbed DOC ( $57 \pm 5\%$ ) is higher in  $\Delta^{14}\text{C}$  than their SPE-DOC counterpart by 67‰, 38‰, 9‰ and 17‰ for SR NOM I, SR NOM II, NBP and Station M, respectively (Supplementary Fig. 2). For freshwater systems, the non-adsorbed DOC  $\Delta^{14}\text{C}$  value is significantly different from the SPE-DOC  $\Delta^{14}\text{C}$  value. For marine samples, the non-adsorbed DOC  $\Delta^{14}\text{C}$  value is within error to the total DOC and SPE-DOC  $\Delta^{14}\text{C}$  values (Supplementary Fig. 2). While our sample set is limited, these results suggest that SPE-DOC  $\Delta^{14}\text{C}$  results are equal to or lower than the  $\Delta^{14}\text{C}$  of the total DOC pool.

#### 4.3. Comparison of SPE-BC, total BC and UDOC BC $\Delta^{14}\text{C}$ values and BPCA distributions

In contrast to SPE-DOC and bulk DOC, comparisons between SPE-BC and total BC of SR NOM I and SR NOM II standards show that BPCA

distributions and  $\Delta^{14}\text{C}$  values are dissimilar to one another (Table 3). This may indicate different sources, or differential cycling of BC within DOC. For SR NOM I and II, SPE-BC had a more aromatically condensed structure (greater abundance of B6CAs) than that for total BC (Table 3). Therefore, SR NOM I and SR NOM II BC that was not absorbed by SPE must have a greater proportion of less aromatic BPCA marker compounds (B3CAs) to result in an overall lower B5CA and B6CA abundance in total BC.

The BPCA relative abundances revealed that SPE-BC isolates are more aromatically condensed than BC from the total BC pool. Additionally, the SPE-BC  $\Delta^{14}\text{C}$  value of SR NOM I is higher than that of total BC, while that for SR NOM II is lower than that of the total BC. This may be due to variations in the environmental conditions present during sample collection of the two standards, or by differential cycling between SPE-BC and total BC. Ultrafiltration concentrates DOC based on size, whereas SPE chemically sorbs DOC based on polarity. We show that a more aromatically condensed BC structure (higher relative abundance of B6CAs) and higher  $\Delta^{14}\text{C}$  values were found for the SPE-BC (Fig. 4a) than for the UDOC (Ziolkowski and Druffel, 2010). This contrasted to expectation that the higher molecular weight (UDOC) fraction of BC might also be younger than the SPE-BC if BC would follow the size reactivity relationships observed in DOC (see review by Benner and Amon, 2015). BC concentration has been found to correlate with DOC concentration (Myers-Pigg



et al., 2015; Jaffe et al., 2013) in river waters. This suggests that with a larger DOC sample pool (43% SPE-DOC compared to 25% for UDOC), total BC may not be as aged as previously thought, or that there is discrete cycling of BC within these DOC fractions. Nonetheless, a larger sample set and comparisons of BC isolated by UDOM and SPE are needed to explain the relationship of the BC DOC fractions.

#### 4.4. SPE-DOC and BC cycling

Here, we investigate the different polarities of the SPE-DOC eluent fractions in the context of understanding DOC composition and cycling within these pools. By comparing the recovery of SPE-DOC in each of the polar and less-polar fractions, we found that the riverine SR NOM I and SR NOM II standards were exclusively polar with no significant differences in SPE-DOC composition between the two collection periods (Fig. 3, Table 2). Methanol SPE-DOC fractions from both standards are composed of younger (perhaps humic, and/or carbohydrate-like) materials (Nwosu and Cook, 2014; Kuhn et al., 2015).

In contrast, NBP and Station M seawater samples have higher proportions of SPE-DOC eluting in the less polar fractions (Fig. 3). Approximately 10% of oceanic SPE-DOC at Station M eluted with less-polar solvents. This agrees with previous studies that showed individual DOC fractions can have distinct compositions and low  $\Delta^{14}\text{C}$  values in the ocean, such as total extractable lipids or acid insoluble fractions in DOC and particles (Loh et al., 2004; Hwang and Druffel, 2003).

SR NOM I and SR NOM II have different total DOC and SPE-BC  $\Delta^{14}\text{C}$  values. SR NOM II may contain different amounts of anthropogenic BC. We observe similar BC concentrations, yet different BC  $\Delta^{14}\text{C}$  values in these river standards. SR NOM I BC has a higher  $\Delta^{14}\text{C}$  value, perhaps indicative of the extensive fires in the swamp during the mid-1950s (Green et al., 2015). Both DOC and BC  $\Delta^{14}\text{C}$  values were higher in 1999 (SR NOM I) than in 2012 (SR NOM II) (Fig. 2), suggesting an older DOC and BC source contribution in SR NOM II. The lower BC  $\Delta^{14}\text{C}$  value of SR NOM II may suggest anthropogenic BC inputs, as the Suwannee River sampling site had no longer been considered pristine (Green et al., 2015) (Fig. 4a). Hydrophobic acid isolates from reverse osmosis of SR NOM II collected in 2012 have a higher average molecular weight, and  $^{13}\text{C}$  NMR studies revealed more aromatic functional groups than for SR NOM I (Kreller et al., 2015; Nwosu and Cook, 2014). This suggests that this site may have been influenced by aerosol anthropogenic input (Stubbins et al., 2012b; Spencer et al., 2014).

Our oceanic BC samples appear chemically distinct from the riverine standards we studied. Using the relative BPCA abundance as an indicator of BC aromaticity, we observed a smaller contribution of B3CAs in SPE-BC of SR NOM I and SR NOM II versus those in marine SPE-BC (Fig. 4a). Our oceanic sample results also provide us with a glimpse of DOC-BC cycling at coastal and open ocean sites. Coastal NBP is the only sample with significant amounts of SPE-BC in all four solvent fractions (SPE-BC =  $5.6 \pm 0.4 \mu\text{M C}$ ). Given the high BC content, we believe this site was influenced by local aged sources. Similarly, total suspended solids for a nearby river (~75 miles north, Santa Clara River, CA) had 44.3% BC/OC%, suggesting a large BC riverine flux from the Ventura Basin, with a low  $\Delta^{14}\text{C}$  value of  $-644 \pm 58\text{‰}$  (Masiello and Druffel, 2001). This may explain the high BC/OC% we observe in NBP samples ( $20.5 \pm 2.0\%$ ). Seasonal hydrology plays a role in the quality of exported BC (Wagner et al., 2015). Based on a riverine study in the Colorado Rocky Mountains by Wagner et al. (2015), we expect a riverine source of smaller BC structures (B3CAs) during low flow ( $\ll 500 \text{ ft}^3/\text{s}$ ) periods. However, variations of BC structure during high and low flow river periods and its impact on the oceanic BC have yet to be investigated in urban environments.

Although the SPE-BC  $\Delta^{14}\text{C}$  values at NBP and Station M are equal within error, their relative BPCA abundances are different, which may reveal reprocessing of the oceanic BC pool. We assume BC at Station M is representative of open ocean BC (with small contributions from riverine anthropogenic sources) (Coppola et al., 2014; Masiello and Druffel,

1998). UV oxidation plays a role in degrading highly aromatic BC in the land-to-ocean transit and may remove these structures upon entering the open ocean (Stubbins et al., 2012a; Masiello and Louchouart, 2013; Myers-Pigg et al., 2015). Coastal BC may be influenced by anthropogenic riverine BC more directly, as urban water discharge is a primary source of Southern California coastal water pollution (Dwight et al., 2002). The structure of BC at Station M has a greater relative abundance of B3CAs than that at NBP (Fig. 4a) and a lower BC concentration. This may indicate degradation processes that remove aromatic BC with transport to the open ocean (e.g. photo-oxidation; Stubbins et al., 2012a).

Despite the limited number of BC  $^{14}\text{C}$  studies, it is interesting to note the disparity between  $\Delta^{14}\text{C}$  values as isolated by SPE and UDOC. At Station M, SPE-BC is about 12,000  $^{14}\text{C}$  yrs. younger than BC isolated from UDOC ( $20,100 \pm 3000 \text{ }^{14}\text{C}$  yrs.; Ziolkowski and Druffel, 2010). This may suggest differential cycling of BC in chemical versus size fractionated DOC pools (Wagner and Jaffe, 2015). The discrepancy in BC  $\Delta^{14}\text{C}$  values highlights the need for additional BC measurements in DOC to constrain BC sources, cycling and the  $^{14}\text{C}$  ages in the global ocean.

## 5. Summary and implications

We report a modified, low-blank SPE method that isolates nearly half of the DOC pool ( $43 \pm 6\%$ ) from marine water samples. We present  $\Delta^{14}\text{C}$  blank assessments of the SPE-DOC method from a limited set of solid river standards and surface ocean water samples. Our results suggest that SPE-DOC selectively isolates slightly older DOC from the riverine standards, and to a lesser or no extent for seawater samples. We observe similar SPE-BC  $\Delta^{14}\text{C}$  values in our coastal and open ocean sites, but different BPCA relative abundances.

Further measurements are needed to determine BC concentration,  $\Delta^{14}\text{C}$  and structure (using relative BPCA distributions) to better understand the sources, sinks, and cycling of BC in aquatic environments. One limitation of these analyses was the sample sizes of less-polar SPE-DOC fractions, which prevented analysis of their relative BPCA abundances and  $\Delta^{14}\text{C}$  values at our open ocean site. The use of larger water samples would allow for less-polar BC to be evaluated and placed into the context of total and SPE-DOC  $\Delta^{14}\text{C}$  values. Chemical characterizations of SPE-DOC fractions at the molecular level (e.g. nuclear magnetic resonance and Fourier transform ion cyclotron resonance mass spectrometry, FT-ICRMS) reveal compositional relationships between SPE-DOC and SPE-BC.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2015.10.010>.

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