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Radiocarbon Studies of Black Carbon in the Marine Environment

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Radiocarbon Studies of Black Carbon in the Marine Environment

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Earth System Science

by

Alysha Inez Coppola

Dissertation Committee:
Professor Ellen R.M. Druffel, Chair
Professor Eric S. Saltzman
Assistant Professor Claudia I. Czimczik

2015

DEDICATION

To

my mother, brother and step-father,

Lorelei Tinkham, Matthew Coppola and Malcolm Tinkham

for their unending love, encouragement, and inspiration

TABLE OF CONTENTS

Page

CHAPTER 4: Solid Phase Extraction Method for Quantification and Compound-Specific Radiocarbon Analysis of Black Carbon in Marine Dissolved Organic Carbon 53

LIST OF FIGURES

Page

LIST OF TABLES

Page

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PhD Candidate, Earth System Science, University of California Irvine, 2009-present

Laboratory Coordinator, Department of Chemistry, Pima Community College, 2008-2009

Undergraduate Researcher, Paleoceanography, Julia Cole Research Lab, 2006-2008

Undergraduate Researcher, Inorganic Chemistry, Richard Glass Lab, 2008

Summer Research Guest, Woods Hole Oceanographic Institution, Summer 2007

Research Technician, NSF-Acceleratory Mass Spectrometry Lab, Tucson, AZ, 2004-2006

FIELD EXPERIENCE

A22 Clivar Cruise –*R/V Atlantis* Cape Cod, MA to Barbados, April 2011

Collected marine dissolved organic carbon samples, inorganic carbon and total dissolved organic carbon samples for 3 weeks

A10 Clivar Cruise- *R/V Brown* Cape Town, South Africa to Rio de Janerio, Brazil August 2010

Collected salinity, marine dissolved organic carbon samples, inorganic carbon and total dissolved organic carbon samples for 5 weeks

Amazon-PIRE Amazon Climate Interactions, Manaus, Brazil 2008

Worked with a diverse group of scientists (hydrologists, soil scientists, chemists) on a novel ground based approach to measuring the recoveries of variously aged logged forests using remote sensing (LiDAR) in the Tapajos Rainforest Reserve

TEACHING EXPERIENCE

Lecturer, *University of California, Irvine*

- Oceanography, ESS 3, Summer 2014, Class size: 40

Created, delivered and designed material to engage students with different scientific backgrounds. Provided an introduction of the scientific, technological, environmental, economic aspects underlying oceanography and climate change. Generated exams, quizzes, homework and evaluated work. Provided feedback in one on one meetings for improvement.

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ORAL PRESENTATIONS

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2. University of Florida, Gainesville, (2015) Invited speaker, Coppola, A.I., "Black carbon cycling in the marine environment."
3. AGU Fall Meeting, San Francisco, (2014), Coppola, A.I., Walker, B.W. and E.R.M. Druffel "Black carbon in marine dissolved organic carbon: Abundance and radiocarbon values in the global ocean." Abstract ID: 19010
4. UC Irvine, AGS Symposium, Irvine, CA (2014), Coppola, A.I., Walker, B.W., Griffin, S., E.R.M. Druffel "Compound specific radiocarbon analysis of black carbon in marine dissolved organic carbon."
5. International Water Association Natural Organic Matter, Costa Mesa, CA. (2011), Coppola, A.I. and E.R.M. Druffel, "Black carbon concentrations in sedimentary organic carbon."
6. Amazon-Pire Meeting, Para, Brazil, (2008), Coppola, A.I., V. Leitold, S. Stark, J. Schietti, and S. Saleska, "Selective logging, vegetation, canopy structure and energy partitioning in the Tapajos National Forest."
7. University of Arizona Geology Symposium, Tucson, AZ, (2007), Coppola, A.I., J. Cole, H. Barnett, and T.R. Ault, "A new elemental and isotopic record of tropical sea surface temperature and salinity inferred from a 14 ka Tahitian coral." Abstract #60.

POSTER RESENTATIONS

8. AGU Ocean Sciences Meeting, Honolulu, Hawaii (2014), Coppola, A.I., Walker, B.W., E.R.M. Druffel, "Compound Specific Radiocarbon Analysis of Black Carbon Isolated in Marine Dissolved Organic Carbon using Solid Phase Extraction." Abstract#A0066
9. 21st International Radiocarbon Conference, Paris, France (2012), Coppola, A.I., L.A. Ziolkowski, D. Zheng, X. Xu and E.R.M. Druffel, "Extraneous carbon corrections for radiocarbon measurements in Black Carbon sediments using the Benzene Polycarboxylic Acid method."
10. AGU Ocean Sciences Meeting, Salt Lake City, Utah (2012), Coppola, A.I., L.A. Ziolkowski, and E.R.M. Druffel, "Isolation of Black Carbon in Marine Bulk Dissolved Organic Carbon using a Revised Solid Phase Extraction Method." Abstract # 9646
11. UC Irvine Water Research Center, Irvine, CA, (2010), Coppola, A.I., L.A. Ziolkowski, and E.R.M. Druffel, "Black Carbon in Sedimentary Organic Carbon in the NE Pacific using the Benzene Polycarboxylic Acid Method."
12. AGU Fall Meeting, San Francisco (2010), Coppola, A.I., L.A. Ziolkowski, and E.R.M. Druffel, "Black Carbon in Sedimentary Organic Carbon in the NE Pacific using the Benzene Polycarboxylic Acid Method." Abstract # OS33A-1469.
13. AGU Fall Meeting, San Francisco (2007), Coppola, A.I., J. Cole, H. Barnett, A.W. Tudhope and T.R. Ault, "Tropical Sea Surface Temperature during Deglaciation Inferred from a New Tahitian Sr/Ca Record." Abstract ID PP11A-0218.

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2. Druffel, E.R.M., Griffin, S.M., Walker, B.D., and A.I. Coppola (in prep for **Geophysical Research Letters**), Radiocarbon in dissolved organic carbon in the Atlantic Ocean.

3. Coppola, A.I, Walker, B.W, and E.R.M. Druffel (in revision, **Marine Chemistry**), Solid phase extraction method for quantification and compound-specific radiocarbon analysis of black carbon in marine dissolved organic carbon

4. Coppola, A.I., Ziolkowski, L.A., Druffel, E.R.M., and C. Masiello (2014), Aged black carbon in marine sediments and sinking particles, **Geophysical Research Letters***,* 41 (7): 2427–2433. DOI: 10.1002/2013GL059068

5. Coppola, A.I., Ziolkowski and E.R.M. Druffel (2013), Compound Specific Radiocarbon Analysis of Black Carbon in environmental matrices: assessments of sources and radiocarbon signatures of extraneous carbon. **Radiocarbon** 55 (3–4): 1631–1640. doi:10.2458/azu_js_rc.55.16303

6. Druffel, E.R.M., Griffin, S., Walker, B.D., Coppola, A.I., and D.S. Glynn (2013), Total uncertainty of radiocarbon measurements of marine dissolved organic carbon and methodological recommendations. **Radiocarbon** 55 (2): 1135–1141

ABSTRACT OF THE DISSERTATION

Radiocarbon Studies of Black Carbon in the Marine Environment

By

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Doctor of Philosophy in Earth System Science

University of California, Irvine, 2015

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The incomplete combustion of biomass and fossil fuels produces black carbon (BC). BC is recalcitrant and serves as a long term holding pool for carbon, with a mean residence time of one to two orders of magnitude greater than unburnt carbon on land. Yet the known sources of BC are far larger than the known sinks, which led to studies of BC in the ocean's dissolved organic carbon (DOC) reservoir.

The goal of this dissertation was to measure the abundance and residence times of BC in sediment, sinking particles and DOC in order to understand the cycling of BC in the ocean. I found that BC in northeast Pacific sediments was older by 6,200 ± 2,200 ^{14}C years than the concurrently deposited sedimentary organic carbon, suggesting that BC ages within DOC for millennia before deposition to sediments. Sinking particulate organic carbon may provide the main transport mechanism of aged BC into sediments.

A solid phase extraction (SPE) technique was modified to extract DOC from seawater, and provided the methodological basis by which BC composition, concentration and Δ^{14}C

values were determined. This SPE method isolated 43 ± 6% of the DOC from seawater. I found that the composition of SPE-BC was less aromatic in the ocean samples than those in a set of river standards. The average concentration of SPE-BC in the surface ocean samples was 1.6 ± 0.1 μM and 1.2 ± 0.1 μM in a deep ocean sample. The average ^{14}C age of surface SPE-BC is 4,500 ± 3,000 ^{14}C years, and is much older in the deep water sample from the Sargasso Sea (23,000 ± 3,000 ^{14}C years). I calculate that the SPE-BC pool is approximately 14 ± 2 Gt C in the open ocean. This value is a minimum estimate, because it does not include the BC content in 57% of the DOC that was not isolated using SPE methods in this work. BC can explain a small part of the 4,000 – 6,500 ^{14}C years age of DOC, but is not the major cause. The range of SPE-BC structures and $\Delta^{14}C$ values found in this work suggest that oceanic SPE-BC is not homogeneous, but that it contains several distinct pools of BC with widely ranging residence times.

Chapter 1

Introduction

1.1 Black Carbon in the Earth system

Black carbon (BC) is the polyaromatic byproduct from the incomplete combustion of biomass and fossil fuels. Biomass burning is the major source of BC to the environment, producing 0.112-0.377 Gt BC per year (Santín et al., 2015) (Figure 1.1). Incomplete combustion of fossil fuel produces 0.005-0.024 Gt BC per year (Bond et al., 2013; Andreae et al., 1996) (Figure 1.1). A fraction of the carbon released from biomass burning (3-28%) and fossil fuel combustion (~0.3%) is retained as BC instead of being emitted to the atmosphere as greenhouse gases (Santín et al., 2015; Kuhlbusch and Crutzen, 1995).

BC is transported from land to the global ocean by rivers and atmospheric aerosols. Larger-sized BC particles become partially oxidized in soils and then are transported by rivers to the ocean (0.027±0.0018 Gt BC yr^{-1}) (Jaffé et al., 2013) (Figure 1.1). Smaller (submicron) BC aerosols have a relatively short lifetime in the atmosphere and are deposited to the open ocean at a rate of 0.002-0.010 Gt BC yr^{-1} (Jurado et al., 2008; Cape et al., 2012) (Figure 1.1).

The fraction of BC in soil organic matter (2-45%) is lower than expected, given the large production rate and relatively stable aromatic structure (Masiello, 2004). Burial in ocean sediments is considered to be the ultimate fate of BC, but BC concentrations in sediments are also low (Bird et al., 2015). Another sink is photo-oxidation of BC (Stubbins et al., 2012). Overall, BC production (0.13–0.40 Gt BC yr^{-1}) is much greater than the estimated storage and decomposition (0.03–0.04 Gt BC yr^{-1}) rates.

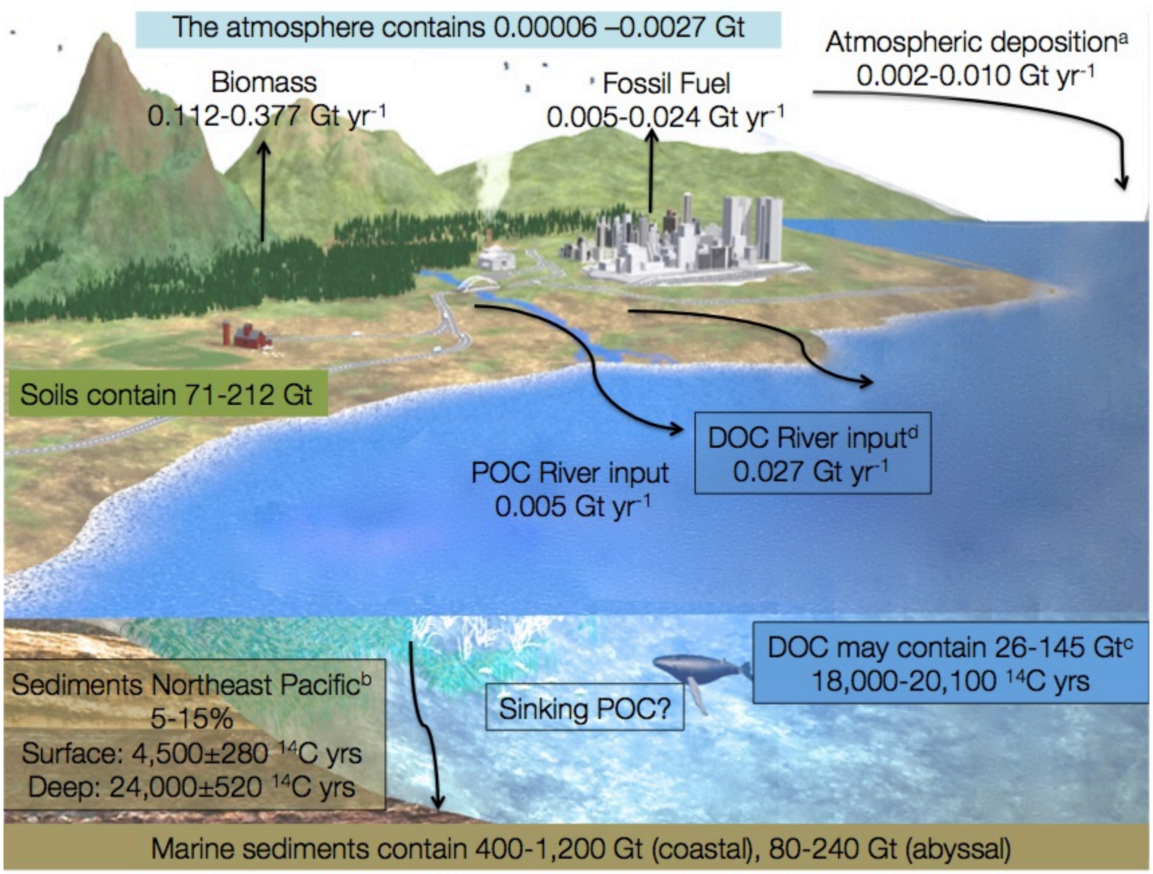

Figure 1.1. The global BC cycle, showing major sources, pathways and reservoirs. Black outlined boxes represent the major carbon pools that are the focus of this dissertation. Estimates of BC stocks in the atmosphere, soils and sediments are from Santín et al., 2015 and Bird et al., (2015).

[a] Jurado et al., (2008)
[b] Maisello and Druffel (1998)
[c] Ziolkowski and Druffel (2010)
[d] Jaffé et al., (2013)

1.2 Storage of BC in the oceans

Marine DOC is the largest exchangeable pool of organic carbon in the ocean (662 Pg C; Hansell et al., 2009), and is operationally defined as organic carbon that passes a 0.2-1.0 μm filter. Marine DOC originates mostly from primary production by phytoplankton in the surface ocean, and should have young radiocarbon (^{14}C) ages, similar to those of dissolved inorganic carbon (DIC). DIC has ^{14}C ages that reflect the transport time of deep water along the deep ocean conveyor. DIC is 700 and 2,400 ^{14}C yrs in the deep North Atlantic and North Pacific, respectively (Stuiver et al., 1983; Broecker et al., 1996). Paradoxically, the observed marine DOC ^{14}C ages are 4,000 and 6,000 ^{14}C yrs in the North Atlantic and North Pacific, respectively (Druffel et al., 1992).

The $\Delta^{14}C$ value of surface DOC is explained by a two component mixing model (Williams and Druffel, 1987). Mixing of a modern component (from primary production) and an uncharacterized, aged component (deep DOC) explains the concentrations and $\Delta^{14}C$ values in the surface ocean at the Southern Ocean, North Pacific and Sargasso Sea (Druffel et al., 1992; Williams and Druffel, 1987). The aged component was hypothesized to include ancient BC (Masiello and Druffel, 1998; Ziolkowski and Druffel, 2010).

1.3 Goals of the dissertation

In this dissertation, measurements of BC concentration, structure and $\Delta^{14}C$ values were made in DOC, and sedimentary and particulate organic carbon (SOC, POC) to understand how BC cycles in the marine environment. The primary goal of this dissertation was to determine the residence times of BC in oceanic DOC. Aged BC has been identified in ultra-filtered DOC (UDOC, high molecular weight DOC) from the northeast Pacific (Ziolkowski and Druffel, 2010), though UDOC is only 25% of the DOC pool. Measurements of BC $\Delta^{14}C$ in a larger fraction of DOC were performed to address the following questions:

1. What are the concentrations of BC in the marine environment?
2. What are the residence times (^{14}C ages) of BC in the marine environment?
3. Is the presence of long-lived BC in DOC responsible for the old age of DOC?
4. Does oceanic BC provide an intermediate reservoir for the BC cycle?

Chapter 2 was published in *Radiocarbon* (Coppola et al., 2013) and validated the benzene polycarboxylic acid (BPCA) method for measurements of BC in SOC and POC samples. I addressed challenges of BC $\Delta^{14}C$ measurements in samples that contained non-BC organic matter, fine siliceous dust and heavy metals. I evaluated the variability, mass and $\Delta^{14}C$ values of the extraneous carbon added to standards and samples during processing.

Chapter 3 was published in *Geophysical Research Letters* (Coppola et al., 2014) and addressed the sources of aged BC to the sediments at a deep site in the northeast Pacific. Masiello and Druffel (1998) reported that BC in these ocean sediments had a mean residence time of thousands of years compared to the non-BC SOC. However, the dichromate-sulfuric acid oxidation method used in their study did not oxidize all of the non-BC organic matter (Hammes et al., 2007). This work reported the first multi-pool, BC inventory using sediments and sinking POC.

Chapter 4 (Coppola et al., in revision, *Marine Chemistry*) reports an improved solid phase extraction (SPE) method to concentrate DOC from seawater. The goal was to obtain representative BC measurements from the DOC pool with a greater recovery, and without a size-age bias than was obtained using UDOC. SPE-BC was extracted from SPE-DOC from three sample types (riverine, coastal, and open ocean). This work provided the methodological groundwork to measure the residence times of SPE-BC in SPE-DOC.

In Chapter 5, measurements of the concentration, composition and residence time of BC in seawater from the Atlantic, Pacific and Arctic oceans were presented. I determined the fraction of SPE-BC in SPE-DOC, and measured the residence time of SPE-BC in seawater.

The final chapter (Chapter 6) summarized the results of the dissertation and presents ideas for future research avenues.

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Santín, C., S. H. Doerr, E. S. Kane, C.A. Masiello, M. Ohlson, J.M. de la Rosa, C. M. Preston, and T. Dittmar, (2015), Towards a Global Assessment of Pyrogenic Carbon from Vegetation Fires. *Global Change Biology*, doi:10.1111/gcb.12985.

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Chapter 2

Extraneous Carbon Assessments in Radiocarbon Measurements of Black Carbon in Environmental Matrices

Coppola, A.I., Ziolkowski and E.R.M. Druffel, (2013), Compound Specific Radiocarbon Analysis of Black Carbon in environmental matrices: assessments of sources and radiocarbon signatures of extraneous carbon. *Radiocarbon* 55 (3–4): 1631–1640. doi:10.2458/azu_js_rc.55.16303

Abstract

Extraneous carbon (C_{ex}) added during chemical processing and isolation of black carbon (BC) in environmental matrices was quantified to assess its impact on Compound Specific Radiocarbon Analysis (CSRA). Extraneous carbon is added during the multiple steps of BC extraction, such as incomplete removal of solvents, and carbon bleed from the gas chromatographic and cation columns. We use two methods to evaluate the size and $\Delta^{14}C$ values of C_{ex} in BC in ocean sediments that require additional pre-treatment using a cation column with the Benzene Polycarboxylic Acid Method. First, the direct method evaluates the size and $\Delta^{14}C$ value of C_{ex} directly from the process blank, generated by processing initially empty vials through the entire method identically to the treatment of a sample. Second, the indirect method quantifies C_{ex} as the difference between processed and unprocessed (bulk) $\Delta^{14}C$ values in a variety of modern and ^{14}C-free or 'dead' BC standards. Considering a suite of hypothetical marine sedimentary samples of various sizes and $\Delta^{14}C$ values and BC Ring Trial standards, we compare both methods of corrections and find agreement between samples that are >50 μg C. Because C_{ex} can profoundly influence the measured $\Delta\ ^{14}C$ value of compound specific samples, we strongly advocate the use of multiple types of process standards that match the sample size to assess C_{ex} and investigate corrections throughout extensive sample processing.

2.1 INTRODUCTION

Black Carbon (BC) is produced from the incomplete combustion of fossil fuels and biomass, ubiquitous in the atmosphere, sediments, soils, and water, and influences a wide range of biogeochemical processes (Schmidt and Noack, 2000; Watson et al., 2005). With the new technological developments and smaller AMS sample size requirements (Santos et al., 2007), the ability to isolate individual compounds, using Compound Specific Radiocarbon Analysis (CSRA) allows for better understanding of the time scales of individual compounds from a C pool (Eglinton et al., 1996; Ingalls and Pearson, 2005). The turnover times of BC within these pools is determined by partially oxidizing aromatic BC in environmental matrices using the using the Benzene Polycarboxylic Acid (BPCA) Method to form marker compounds, Benzene Polycarboxylic Acids (BPCAs). These environmental matrices contain non-BC organic matter, fine siliceous dust and heavy metals in a heterogeneous mixture, which can complicate the processing of a BC sample. In turn, for BC to be separated from the matrix, extensive treatment is needed to remove metals that interfere with BC extraction using the BPCA Method (Brodowski et al., 2005, Ziolkowski and Druffel, 2009).

However, extensive processing adds extraneous (C_{ex}) carbon, thereby influencing the size and $\Delta^{14}C$ value of the BC sample (Ziolkowski and Druffel, 2009; Santos et al., 2007). The C_{ex} originates from two major sources: (1) the chemical processing associated with extracting the BC from the sample (in this case, the BPCA method and pre-treatment) and (2) the purification of BPCA marker compounds on a preparative capillary gas chromatograph (PCGC). After correction for graphitization and combustion (Santos et al., 2007), the mass of C_{ex} and the $\Delta^{14}C$ value of CSRA sample ($C_{measured}$) originates from the contributions of two sources (eq.1):

$$C_{measured} = C_{BPCA} + C_{chemistry} + C_{PCGC} = C_{BPCA} + C_{ex} \qquad (1)$$

where C_{BPCA} is the mass of the BC isolated from the sample and C_{ex} is the mass of the extraneous C added due to processing ($C_{chemistry}$) and PCGC collection (C_{PCGC}). In previous studies, ^{14}C analysis of standards of known chemical and isotopic composition have revealed deviations from consensus $\Delta^{14}C$ values, highlighting the need for correction of C_{ex} (Hwang and Druffel, 2005; Ziolkowski and Druffel, 2009; Santos et al., 2007).

For the purpose of correcting BC $\Delta\,^{14}C$ measurements, the size and isotopic composition of C_{ex} can be assessed using two different approaches. First, to implement direct method $\Delta^{14}C$ assessments, we evaluate process blanks, which are initially empty vials that are processed through the entire method, identically to the treatment of a sample or standard. These process blanks serve as direct estimates of the size and isotopic signature of C_{ex}, which are evaluated periodically over time. The mass of C_{ex} added during sample preparation ($C_{chemistry}$) and purification (C_{PCGC}) can be evaluated by process blanks. To evaluate C_{PCGC}, we use a direct blank, generated by solvent injection onto the PCGC. The difference between the direct blank (C_{PCGC}) and process blank ($C_{chemistry+PCGC}$) is the $C_{chemistry}$. It is particularly important for new users to distinguish how much C_{ex} originates from both the chemical preparation of the sample ($C_{chemistry}$) and PCGC (C_{PCGC}) when to determine the quality and total uncertainty of the BC $\Delta\,^{14}C$ results.

The second method, the indirect method, assesses the C_{ex} assuming a two-end member approach. We assume C_{ex} has a dead ($\Delta\,^{14}C$= -1000‰) component and a modern

(Δ ^{14}C= 0‰) component. Then, using process BC standards of known isotopic values (modern and dead), the size of C_{ex} is estimated by the deviation of the process standard from the consensus Δ^{14}C value. After corrections for graphitization and combustion in AMS measurements are made, a carbon mass balance is applied using the mass and isotopic signature of C_{ex} determined by indirect and direct methods to correct samples and standards (eq.1) (Ziolkowski and Druffel, 2009).

The aim of this study is to determine C_{ex} added in the extraction of BPCA marker compounds in marine sediment throughout pre-treatment, nitric acid oxidation, derivitization and PCGC collection. Using direct and indirect assessments of C_{ex}, we evaluate the magnitude and ^{14}C signature of C_{ex}, which allows us to calculate the true BC Δ^{14}C value (C_{BPCA}) of the sample. The sum of the different sources of C_{ex} can lead to significant contamination of samples, particularly for samples <50 μgC. This results in a size-related bias of the Δ^{14}C values reported by AMS laboratories, which usually include corrections only for combustion and graphitization of samples. We compare both direct and indirect C_{ex} assessments by applying corrections of C_{ex} to a suite of hypothetical Sedimentary Organic Carbon (SOC) samples. Thus, based on these assessments, we demonstrate corrections for C_{ex} added during BC extraction in marine sediments with the routine use of processed standards and blanks.

2.2 METHODS

2.2.1 Black Carbon Standards

Black carbon rich standard reference materials were selected from the multi-laboratory, method and standard comparison called the BC Ring Trial (Hammes et al., 2007). Two types of dead and modern process standards were used to facilitate comparative analyses of BC: 1) laboratory produced BC-rich and 2) BC-containing environmental matrices containing fine siliceous clays and heavy metals. Grass char (*Oryza sativa*) and wood char (*Castanea sativa*) BC standards were used as modern standards to estimate for ^{14}C-depleted C_{ex} added during processing (Elmquist et al., 2006; Hammes et al., 2006). An isotopically depleted ^{14}C laboratory produced standard, hexane soot (Goldberg, 1985; Akhter et al., 1985; Hammes et al., 2007) was also used to estimate modern C_{ex}. Environmental BC standards that contained a silicate and metal matrix, including urban dust aerosol NIST Standard Reference Material (SRM 1649a) (Currie et al., 2002; Masiello et al., 2002; National Institute of Standards and Technology, 2004), NIST Standard Reference Material marine sediment (SRM 1941b) and U.S. Geological Survey Green River Shale (Abbey, 1983, Gladney; Roelandts, 1988; Govindaraju, 1994) were used to estimate modern C_{ex}. To observe the matrix effect in marine sediments samples (Coppola et al., in prep), wood char was added to SRM 1941b that had previously been baked in a muffle furnace for 2 hrs at 550^0C to remove organic carbon. Duplicates of standards were processed to assess total uncertainty of $\Delta^{14}C$ measurements.

2.2.2 Elimination of polyvalent metals, BPCA oxidation and purification

Standards that contained polyvalent metals were treated with trifluoroacetic acid (TFA) to remove metals that interfere with BPCA analysis (Hammes et al., 2007; Brodowski et al., 2005, Ziolkowski and Druffel, 2009). First, metals in the environmental matrices standards were removed by high temperature (104°C) and high-pressure digestion in TFA for 4 hrs (Brodowski et al., 2005). The solution was passed through a 0.8 μm quartz filter into a vacuum filtration flask, and the filter was rinsed with Milli-Q water. Sample retained on the quartz filter was dried at 30-40°C for at least 3 hrs before high temperature, high pressure digestion in 65% nitric acid, at 170°C for 8 hrs for the BPCA method (Browdoski et al., 2005; Ziolkowski, 2009; Schramel et al., 1980). The BPCA method partially oxidizes aromatic BC converting it to BPCA marker compounds (Ziolkowski, 2009; Glaser et al., 1998; Brodowski et al., 2005, Hammes et al., 2008). The solution was filtered and the filtrate was passed through a cation exchange column (Browdowski et al., 2005) and eluted into erylermeyer flasks. Briefly, following the method of Ziolkowski et al. (2011), dehydrated BPCAs were dissolved in methanol that contained biphenyl-2,2'-dicarboxylic acid (internal standard) and titrated with (trimethylsilyl)diazomethane (Sigma Aldrich) in 2.0 M ethyl ether to derivatize the carboxylic acids to methyl esters. Methanol was evaporated by a stream of nitrogen gas and dichloromethane was used to transfer the samples into freshly baked vial inserts (0.3 ml) for PCGC analysis and separation.

Methylated BPCAs were quantified for BPCA distributions and isolated for ^{14}C analysis using a Hewlett Packard 6890 Preparative Column Gas Chromography (PCGC) with an HP 7683B auto-injector, Gerstel cooled injection system (CIS-4) with a split/splitless inlet. The CIS injector was operated in “solvent vent” mode, with a vent flow adjusted to 60 ml/min and 20 psi. The solvent venting time was 0.3 min, and the split vent time was 1 min. The injection volume was 4 µL for all collections. The temperature of the inlet was 40°C, then increased to 300°C at a rate of 10°C/s, then kept isothermal for 3 minutes. A megabore fused-silica capillary column (50 m length) coated with 1 µm of DB-XLB was used for all samples in this study. Ultra-high purity hydrogen gas was used as the carrier gas at a flow rate of 8.7 ml/min. The temperature program on the PCGC for separating BPCAs started at 100°C, 10°C/min to 250°C (isothermal for 15 minutes), 5°C/min to 280°C (isothermal for 5 min), then 25°C/min to 320°C (isothermal for 3 minutes). Approximately one percent of the flow was diverted to the FID, while the other 99% was sent to the fraction collector. The fraction collector was computer controlled to collect samples at specific retention times. The fraction collector switch temperature and transfer line was kept at 320°C, and the traps were chilled at -10°C. To standardize C_{ex} to samples that have different numbers of injections, time windows of collection, and injection volumes, we normalized the C_{ex} mass determined by a manometer measurement of pressure in a known volume to units of µg C per min collection per 50-1 µL injections, after Ziolkowski and Druffel (2009). In all direct evaluations of C_{PCGC}, the 4-min collection window set for each blank injection reflected the same time window in which BPCAs were collected in a sample run.

Briefly, following the method of Ziolkowski et al. (2011), BPCA marker compounds were identified using commercially available BPCAs (Sigma Aldrich; 1,2,3 benzene tricarboxylic acid, pyromelletic acid, benzene pentacarboxylic acid, mellitic acid) and mass fragmentation patterns when run on a Finnigan Trace MS and GC/MS ESI at UC Irvine. The preparative fraction collector on the PCGC captured BPCA marker compounds with three to six substituted carboxylic acid groups from the partial oxidation of aromatic BC, including the nitrated BPCAs (about half of the BPCAs were nitrated). The collection windows were set to capture the eluting peaks of interest, for a total time period of 4 minutes. The BPCA marker compounds with only two-substituted carboxylic acid groups were not collected because they can be derived from recalcitrant lignin or other non-BC material that may survive oxidation (Brodowski et al., 2005). Between sample collections (30 injections), the GC column was baked out twice at 320°C for 10 minutes, the injection needle was cleaned with dichloromethane and a freshly baked (550°C for 2 hrs) injection liner was installed. Also, to remove any contamination or memory from the previous sample, the first 10 injections were discarded for ^{14}C measurements as per Ziolkowski et al. (2011). After combustion, graphitization and C_{ex} assessments, standards were corrected for the ^{14}C-free derivative C added during the derivatization (Ziolkowski and Druffel, 2009).

2.2.3 Radiocarbon measurements

In preparation for ^{14}C analysis, BPCA marker compound isolates from the PCGC were transferred using dichloromethane to clean quartz tubes, dried and combusted to CO_2 at 850°C with cupric oxide and silver. The volume of the CO_2 gas produced from combustion was cryogenically purified, then quantified manometrically and reduced to graphite for ^{14}C analysis (Santos et al., 2007). Measurements were made at UC Irvine in the Keck Carbon Cycle Acceleration Mass Spectrometry Facility and normalized to the AMS $\delta^{13}C$. Radiocarbon results were reported as $\Delta^{14}C$ without known-age correction (Stuiver and

Polach, 1977).

2.2.4 Preparation of standards for bulk measurements

In order to facilitate the indirect assessment of C_{ex}, the $\Delta^{14}C$ values of the unprocessed standards were measured. Inorganic carbon was removed by acidification with 3% phosphoric acid (Hwang et al., 2005). Standards were prepared in small and large sizes to match the sizes of the BC samples.

2.3 RESULTS AND DISCUSSION

2.3.1 Direct blank evaluation of mass and $\Delta^{14}C$ value of C_{ex}

We directly evaluated the C_{ex} mass and $\Delta^{14}C$ value using two types of blanks: 1) process blanks and 2) direct blanks on the PCGC. The process blank contained no sample but was subjected to the same preparatory steps as samples so it includes both C_{PCGC} and $C_{chemistry}$ (eq.1). The direct blank from the PCGC only is determined by injecting solvent onto the PCGC (C_{PCGC}).

We found the process blank ($C_{chemistry+PCGC}$) was 1.4 ± 0.7 μg C min^{-1} per 50-1 μL injections in 2012 and 0.3± 0.2 μg C min^{-1} per 50-1 μL injections in 2011 and the $\Delta^{14}C$ values were -957 ± 46‰ and -963 ± 54‰ respectively. The difference in the magnitude of C_{ex}

between these two time periods highlights the imperative need for routine blank assessments.

In order to deduce the relative sizes of $C_{chemistry}$ and C_{PCGC}, we evaluated C_{PCGC} alone from the injections of clean solvent directly onto the PCGC. We made 230 injections to obtain enough C for an AMS analysis. We report a direct blank C_{PCGC} of 0.1 ± 0.1 μg C min^{-1} per 50-1 μL injections with a $\Delta^{14}C$ value -982 ± 15‰ (Table 2.1). Using a mass balance approach from the difference between the total $C_{chemistry+PCGC}$ determined from the process blank and C_{PCGC} using the direct blank, we calculate that the $C_{chemistry}$ in 2012 was 1.3 ± 0.8 μg C min^{-1} per 50-1μL injections. In 2012, we find that ~10% of C_{ex} is C_{PCGC} (0.1± 0.1 μg C min^{-1} per 50-1μL injections and ~90% is $C_{chemistry}$ (1.3 ± 0.7 μg C min^{-1} per 50-1μL injections). Additional $C_{chemistry}$ may originate from the treatment of samples in the cation exchange column following the BPCA method. Interpretations of the $C_{chemistry}$ suggests that these extra steps add twice the amount of $C_{chemistry}$ as that found by Ziolkowski and Druffel (2009) who did not use the cation column and pre-treatment steps.

Table 2.1 Standards subjected to various treatments to evaluate the Cex in the determination of BC in marine sediment. The uncertainty of the mass of Cex was estimated as 50% of the sample mass (but no lower than 0.1 µg of C/min per 50 1-µL injections). The uncertainty of the Cex mass using the indirect method correction was estimated at 50% of the mass value.

							Extraneous carbon, C_{ex}	
Type of standard	Evaluates for	Process standard	*n*	Cation column and pretreatment	BPCA	PCGC	Average µg C/min per fifty 1-µL injections[a]	$\Delta^{14}C$ (‰)
Indirect blank								
Dead	Modern C_{ex}	SRM 1649a	4	Yes	Yes	Yes	0.1 ± 0.1 (2012)	0
		Hexane soot	2	Yes	Yes	Yes	0.2 ± 0.1 (2011)	
		Green River Shale	2	Yes	Yes	Yes		
Modern	Dead C_{ex}	Grass char	3	No	Yes	Yes	1.5 ± 0.8 (2012)	–1000
		Wood char	4	No	Yes	Yes	1.8 ± 0.9 (2011)	
		Wood char in muffled SRM1941b	2	Yes	Yes	Yes		
Total indirect							1.6 ± 0.9 2.0 ± 1.0	–933 ± 25 (2012) –842 ± 26 (2011)
Direct blank								
Process blank (collected in 2012)	Dead and Modern	—	1	Yes	Yes	Yes	1.4 ± 0.7	–957 ± 46
Process blank (collected in 2011)	Dead and Modern	—	1	Yes	Yes	Yes	0.3 ± 0.2	–963 ± 54
Assessment of C_{PCGC}								
Solvent injection into PCGC (2012)	Dead and Modern	—	1	No	No	Yes	0.1 ± 0.1	–982 ± 15

[a] The masses of C_{ex} were normalized to µg C min^{-1} per fifty 1-µL injections.

2.3.2 Indirect blank evaluation of mass and $\Delta^{14}C$ value of C_{ex}

The second method of evaluating C_{ex}, the indirect method, involves processing standards of known consensus $\Delta^{14}C$ value and measuring the deviation from the unprocessed consensus $\Delta^{14}C$ value. Differences between the $\Delta^{14}C$ values of processed and unprocessed standards are used to measure the mass and $\Delta^{14}C$ value of the C_{ex} to thereby correct sample $\Delta^{14}C$ values of samples (Ziolkowski and Druffel, 2009; Santos et al., 2010; Hwang and Druffel, 2005). Incorporation of C_{ex} in standards is assumed to be the same as that in samples that are processed identically. In this study, modern and dead standards were processed throughout the entire pre-treatment, chemical extraction, cation exchange column, and PCGC isolation. When using the indirect method, C_{ex} is assessed as two-end members, one modern ($\Delta\ ^{14}C= 0‰$) and one dead ($\Delta\ ^{14}C= -1000‰$), the mass-weighted sum which equals C_{ex}.

Modern process standards are used to assess the dead component of C_{ex}, while dead standards are used to assess the modern component of C_{ex}. After standards are corrected for graphitization and combustion, dead C_{ex} is evaluated using a simple mass balance approach (eq.1) (Ziolkowski and Druffel 2009); Santos et al. 2010). The measured AMS $D^{14}C$ values of BPCAs produced from wood and grass char were lower than the consensus values because of the presence of low-^{14}C C_{ex}. The mass of dead C in grass char and wood char standards were 1.8 ± 0.9 μg C min^{-1} per 50-1μL injections and 1.5 ± 0.8 μg C min^{-1} per 50-1μL injections, in 2011 and 2012, respectively. Low-^{14}C standards are used to assess the modern component of C_{ex} (e.g. hexane soot) and samples that contain a silicate matrix (e.g.

SRM 1649a aerosol dust and Green River Shale). The masses of modern C_{ex} in these standards were 0.2 ± 0.1 μg C min^{-1} per 50-1μL injections and 0.1 ± 0.1 μg C min^{-1} per 50-1μL injections, in 2011 and 2012 respectively.

From these modern and dead components of C_{ex}, the calculated $\Delta^{14}C$ values of C_{ex} are -842 ± 26‰ and -933 ± 25‰ in 2011 and 2012, respectively (Table 1). Variables such as different users and GC column degradation change with time, making it imperative that standards are routinely processed to document the inevitable variability of C_{ex}. To maintain consistency with these C_{ex} variations, standards processed with the same suite of BC samples should be used to correct the $\Delta^{14}C$ data. In other words, C_{ex} evaluations using the indirect method should be performed with every suite of BC measurements to adequately correct BC sample $\Delta^{14}C$ values.

2.3.3 Correction of standards using C_{ex} assessments

We report corrected $\Delta^{14}C$ values for standards using the mass and $\Delta^{14}C$ value of C_{ex} determined by both methods. More than half of the standard $\Delta^{14}C$ values corrected using the direct method were outside 2σ from the consensus values (Table 2.2). In contrast, all but two of the standards corrected using the indirect method agreed within 2σ of the consensus values (Table 2.2). There were greater deviations in corrected $\Delta^{14}C$ values of modern standards, because the majority of C_{ex} is ^{14}C-depleted, thereby affecting the modern $\Delta^{14}C$ values more substantially. The low-^{14}C standards (SRM 1649a aerosol dust, hexane soot and Green River Shale) had corrected $\Delta^{14}C$ values that were closer to their consensus values (Table 2.2).

Table 2.2 Mass and Δ^{14}C of the unprocessed and isolated BPCAs in the processed standard before and after corrections for C_{ex}.

		BPCA compound class		
Standard type (lab code UCID-)	Consensus BC Δ^{14}C values (‰)	µg C	Direct method corrected Δ^{14}C (‰)	Indirect method corrected Δ^{14}C (‰)
Grass char	53 ± 5[a]	52	–69 ± 19	+27 ± 25
(13206)	(n = 4)	85	+53 ± 11	+89 ± 49
(13103)				
Wood char	165 ± 5[a]	108	+149 ± 14	+186 ± 33
(13180)	(n = 4)	178	+106 ± 27	+139 ± 34
(13179)		108	+138 ± 31	+143 ± 28
(16519)		60	+147 ± 21	+144 ± 53
(16520)				
Wood char in a matrix	165 ± 5[a]	40	+299 ± 25	+129 ± 28
SRM 1941b	(n = 2)	50	+175 ± 23	+130 ± 43
(16509)				
(16510)				
Aerosol SRM 1649a	–885 ± 50[b]	21	–653 ± 28	–884 ± 50
(13183)		37	–899 ± 10	–963 ± 29
(13101)		25	–742 ± 24	–859 ± 40
(13102)		77	–906 ± 8	–924 ± 47
(13184)				
Hexane soot	–982 ± 8	102	–986 ± 3	–992 ± 4
(16511)	(n = 3)	35	–998 ± 2	–992 ± 4
(16512)				
Green River Shale	<–976	42	–823 ± 32	–894 ± 38
(13207)	(n = 3)	73	–796 ± 15	–834 ± 18
(13182)				

[a] Determined by the combustion of unprocessed samples.

[b] Aerosol 1649a is a mixture of BC and other aerosols containing organic carbon. The unprocessed BC Δ^{14}C values are from Ziolkowski and Druffel (2009) and Currie et al. (2002) (–620 ± 50‰; n = 5).

The direct correction applies one mass and one Δ^{14}C value from the process blank, whereas the indirect correction is determined using the average value of dead and modern C_{ex} for a large range of standard types. The indirect method includes the variability of sample processing with multiple standards that mirrors the variability of C_{ex}. The ability of indirect evaluations to correct standards illustrates why we recommend using the indirect method for correcting BC Δ^{14}C measurements.

2.3.4 Evaluation of the sediment matrix on corrected $\Delta^{14}C$ values

We needed to verify the presence or absence of a matrix effect associated with the metals contained in our sediment samples. The effect on C_{ex} of a sediment matrix was evaluated by comparing corrected $\Delta^{14}C$ values of wood char run with and without a sediment (SRM 1941b) matrix. We processed two wood char standards that had added SRM 1941b marine sediment. Results showed that both standards had the same mass of C_{ex} (1.5 ± 0.8 μg C min^{-1} per 50-1 μL injections)(not shown), indicating that C_{ex} is unaffected by the presence of a sediment matrix. When the indirect corrections were applied to wood char standards containing a sediment matrix, the corrected $\Delta^{14}C$ values were 129 ± 28‰ and 130 ± 43‰ (Table 2.2), within 2σ of the consensus value (165 ± 5‰). The corrected $\Delta^{14}C$ values of the wood char standards without a matrix (n=4) were also equal to the consensus value (average $\Delta^{14}C$ =153 ± 10 ‰).

2.3.5 Hypothetical Marine Sediment BC $\Delta^{14}C$

To test how the addition of C_{ex} impacts the $\Delta^{14}C$ values of BC in sediment samples of various sizes, we applied these corrections to a suite of hypothetical samples of different sizes (25 to 150 μg C) and $\Delta^{14}C$ values ($\Delta^{14}C$ =-250 to -750). We assumed that the C_{ex} associated with these hypothetical samples was the same as those obtained in 2012 (Table 2.1). Corrected $\Delta^{14}C$ values associated with both indirect and direct method corrections are within 2σ of the consensus values (Figure 2.1). The differences between indirect and direct corrections diverge for samples that are <25 μg C, where the "true" $\Delta^{14}C$ values (C_{BPCA}) of samples are close to modern (>-250‰) (Figure 2.1). Deviations in the corrected $\Delta^{14}C$ values for samples <25 μg C illustrate the difficulty of assessments of both the mass and $\Delta^{14}C$ variability of C_{ex} within samples suites. Gaining insights with the use of multiple standards and duplicate samples is necessary to constrain C_{ex}.

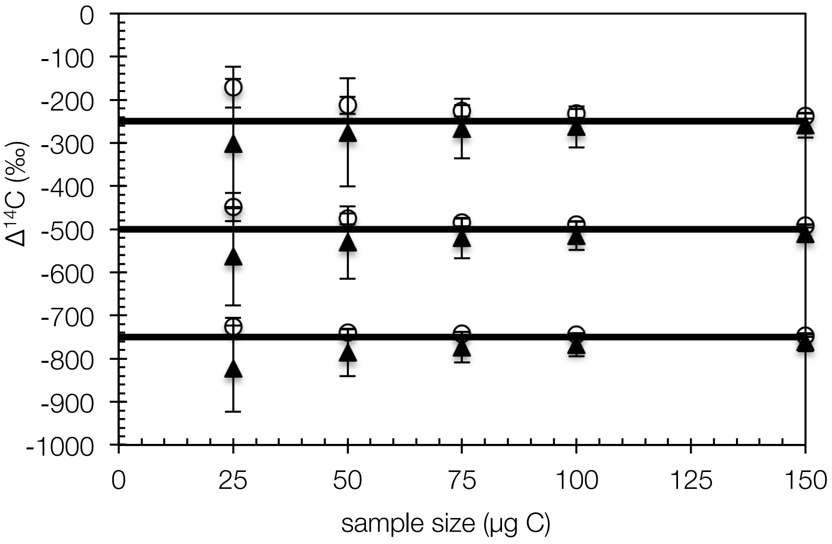

Figure 2.1. Masses of hypothetical BC in sediment samples plotted versus corrected $\Delta^{14}C$ values to illustrate the difference between direct (open circles) and indirect (black triangles) corrections. Solid black lines represent the consensus $\Delta^{14}C$ values for each hypothetical sample.

2.4 CONCLUSION

The main challenge for reporting meaningful BC $\Delta^{14}C$ values in sedimentary matrices involves multiple evaluations of C_{ex} added during extensive chemical processing and PCGC separation. The mass of C_{ex} is significant and variable, therefore requiring a correction beyond that made for graphitization and combustion. Correction for C_{ex} is critical, especially for samples <25 μg C.

We were unable to reliably correct standards to their consensus $\Delta^{14}C$ values using the direct method. We recommend use of the indirect method to capture the variability of sample processing by the use of multiple standards. Standard sizes should match the sample sizes and approximate $\Delta^{14}C$ values. Although processing dead and modern BC standards is time consuming, it is crucial because C_{ex} is variable over time. To gain the most information about the mass and isotopic signatures of C_{ex}, the indirect method is recommended.

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2.1 Supplementary Materials

Calculation of uncertainties in Δ^{14}C corrected values

To determine the propagated total uncertainty of $\Delta^{14}C_{sample}$ (eq 2), we applied the following equation:

$$\sigma\Delta^{14}C_{BPCA}{}^{2} = \left(\frac{\partial\Delta^{14}C_{BPCA}{}^{2}}{\partial\Delta^{14}C_{reported}}\right)^{2}\sigma\Delta^{14}C_{reported}{}^{2} + \left(\frac{\partial\Delta^{14}C_{BPCA}{}^{2}}{\partial\Delta^{14}C_{ex}}\right)^{2}\sigma\Delta^{14}C_{ex}{}^{2} +$$

$$\left(\frac{\partial\Delta^{14}C_{BPCA}{}^{2}}{\partial C_{reported}}\right)^{2}\sigma C_{reported}{}^{2} + \left(\frac{\partial\Delta^{14}C_{BPCA}{}^{2}}{\partial C_{ex}}\right)^{2}\sigma C_{ex}{}^{2}$$

where, $\sigma\Delta^{14}C_{CSRA}$ is the propagated error of the corrected Δ^{14}C values, $\sigma\Delta^{14}C_{reported}$ is the AMS uncertainty of $\Delta^{14}C_{reported}$ machine uncertainty), $\sigma\Delta^{14}C_{ex}$is the uncertainty for$\Delta^{14}C_{ex}$, $\sigma C_{reported}$ is the uncertainty for $C_{reported}$ (uncertainty in graphitization), and $\sigma C_{ex}$is the uncertainty in C_{ex} (assigned as 50%). The total uncertainty for $\Delta^{14}C_{ex}$and $C_{ex}$was used as the direct process blank.

Chapter 3

Aged Black Carbon in Marine Sediments and Sinking Particles

Coppola, A.I., L.A. Ziolkowski, C.A. Masiello and E.R.M Druffel, (2014), Aged Black Carbon in Marine Sediments and Sinking Particles." *Geophysical Research Letters*, 1–29.

Abstract

We report measurements of oceanic black carbon (BC) to determine the sources of BC to abyssal marine sediments in the northeast Pacific Ocean. We find that the average ^{14}C age of BC is older (by 6,200 ± 2,200 ^{14}C yrs) than that of the concurrently deposited non-BC organic carbon. We investigate sources of aged BC to sediments by measuring a sample of sinking particulate organic carbon (POC) and find that POC may provide the main transport mechanism of BC to sediments. We suggest that aged BC is incorporated into POC from a combination of re-suspended sediments, and sorption of ancient DOC BC onto POC. Our BC flux estimate represents ~8-16% of the global burial flux of organic carbon to abyssal sediments and constitutes a minimum long-term removal estimate of 6-32% of biomass-derived BC using the present day emission flux.

3.1 INTRODUCTION

Black carbon (BC), formed by incomplete combustion of organic matter, cycles on annual to millennial time scales [*Masiello and Druffel,* 1998; *Middelburg et al.,* 1999]. Black carbon is defined as a continuum from slightly charred plant material to highly graphitized soot [*Goldberg,* 1985*; Schmidt and Noack*, 2000*; Masiello*, 2004]. Char BC is produced by the incomplete combustion of biomass, coals and other materials, while soot BC is formed from the condensation of combustion gases. Black carbon has been found in marine dissolved organic carbon (DOC) [*Dittmar,* 2008*; Ziolkowski and Druffel*, 2010a], particulate organic carbon (POC) [*Lohmann et al.,* 2009; *Zigah et al.,* 2012; *Flores-Cervantes et al.,* 2009] and sedimentary organic carbon (SOC) [*Goldberg,* 1985; *Masiello and Druffel,* 2003; *Ohkouchi and Eglinton,* 2006].

Black carbon enters the ocean by rivers and atmospheric deposition. Modern biomass derived-BC is mainly transported by surface erosion of soils and rivers, delivered to watersheds, and then to the ocean [*Foereid et al.,* 2011; *Major et al*., 2010; *Rumpel et al.,* 2006; *Hockaday et al.*, 2007; Jaffé *et al.,* 2013]. Because of its sub-micron size, soot BC can travel long distances before it is deposited into the ocean [*Lohmann et al.,* 2009; *Posfai et al.,* 2010; *Gustafsson and Gschwend,* 1998; *Ohkouchi and Eglinton*, 2006]. Once BC enters the ocean's DOC pool, its chemical and isotopic composition (as measured in ultrafiltered, high molecular weight DOC) show dramatic changes between coastal and open ocean regions, suggesting that there are loss processes of BC from the marine DOC pool [*Ziolkowski and Druffel,* 2010]. Two proposed loss processes are photochemical oxidation in the sea surface

[*Stubbins et al.,* 2012] and transport to sediments via sorption to POC [*Flores-Cervantes et al.,* 2009; *Zigah et al.,* 2012].

Marine sediments contain a significant amount of BC in organic carbon, with BC/OC% values ranging from 15 ± 2% to 21 ± 6% in abyssal sediments and up to 50 ± 40 % in coastal sediments [*Verardo and Ruddiman,* 1996, *Masiello and Druffel,* 1998; *Masiello and Druffel,* 2003; *Gustafsson and Gschwend,* 1998; *Middelburg et al.,* 1998; *Lohmann et al.,* 2009]. The variability of sediment BC/OC% values is partly due to differences in methods used to quantify BC, and to environmental transformations not accounted for by the analytical method used [*Hammes et al., 2007; Currie et al., 2002*]. Masiello and Druffel [1998] measured 15 ± 2% BC/OC in sediment (0-50 cm) from the Northeast Pacific. The ^{14}C ages of the BC in SOC was 2,400 ± 120 to 5,400 ± 520 ^{14}C yrs older than concurrently deposited non-BC SOC. This suggested that BC is pre-aged for thousands of years prior to deposition in the sediments.

Here, we report that BC is removed from seawater via sorption to marine POC and subsequently transported to sediments. We compare BC concentration, ^{14}C analyses, and qualitative BC structural information to provide the first analysis of multiple pools of oceanic BC. We used the benzene polycarboxylic acid (BPCA) method, which partially oxidizes BC to aromatic carboxylic acids [*Ziolkowski,* 2009; *Glaser et al.,* 1998; *Brodowski et al.,* 2005]. Greater aromaticity of a BC sample results in a greater number of acid functional groups on each remaining BPCA. All BPCAs greater than B3CAs were operationally defined as BC while B2CAs were not quantified because they may be derived from lignin and humic materials [Brodowski et al., 2005]. Recent modifications of the BPCA method have improved the analytical range of BC detection in the continuum from char to soot

[*Ziolkowski et al., 2011*]. The resulting relative BPCA abundances provide structural information [*Glaser et al.,* 1998; *Dittmar,* 2008; *Ziolkowski and Druffel*, 2010a] that aids in identifying BC sources and transformation processes. Using the BPCA method, combined with ^{14}C analyses, we find that sinking POC is likely the main delivery mechanism of BC to abyssal sediments in the NE Pacific.

3.2 METHODS

Sediments were collected from 4100 m depth at Station M (34°50'N 123°00'W), located on the Pacific abyssal plain. The California Current flows southward at Station M, and has well-developed chlorophyll spring blooms that last until the summer [*Smith et al.,* 1988]. The sinking POC sample analyzed here is sediment trap material from several time periods collected at Station M at 3450 m depth (650 m above bottom) from 1994-1996 (Table 3.2, Auxiliary Materials) using a conical, moored sediment trap [*Smith et al.,* 2001]. Sediments were stored at -20˚C and later dried at 40˚C prior to analysis. Additional details of these samples are described in Hwang et al. [2004]. We used sediment from a box core (0-14 cm depth, Event 3109), and from a gravity core (26-28 cm, Event 3142) collected in October 1996 [*Masiello and Druffel,* 1998]. The mixed layer was in the top 8 cm of the sediment [*Bauer et al.,* 1995].

Marine sediments were pre-treated to remove polyvalent cations and metals that interfere with BPCA analysis [*Brodowski et al., 2005; Coppola et al., 2013*] through high temperature and high-pressure digestion in trifluoroacetic acid. The pre-treated sediment solution was passed through pre-baked, quartz filters and washed with Milli-Q water.

Sediment retained on the quartz filters was dried, then placed in a quartz vial for high temperature, high-pressure digestion with concentrated nitric acid [Ziolkowski, 2009]. Filtrates were passed through a cation exchange column to remove heavy metals and then freeze-dried. The carboxylic acids on BPCAs were derivatized with (trimethylsilyl) diazomethane according to *Ziolkowski,* [2009]. Radiocarbon values were corrected for the ^{14}C-free C introduced from this methylation [see Coppola et al., 2013]. The BPCAs were identified by comparison with commercially available BPCAs and mass fragmentation patterns run on a Finnigan Trace MS and GC/MS ESI at UC Irvine [*Coppola et al.,* 2013]. Methylated BPCAs were quantified to measure relative BPCA abundances and isolated for ^{14}C analysis using a Hewlett Packard 6890 preparative gas chromatography with a flame ionization detector coupled to preparative fraction collector (PCGC). Based on retention times of known standards, the PCGC fraction collector was programed to collect B3CAs (BPCA substituted with 3 carboxylic acids) through B6Cas (those substituted with 6 carboxylic acids) into a single trap, including the nitrated BPCAs. The BPCA method requires a conversion factor to convert the mass of BPCA C to an estimate of total BC mass in the original sample. We used the conversion factor 25.8 ± 6.8% C determined by Ziolkowski and Druffel [2010b].

For ^{14}C analysis of bulk samples, dried sediment (~ 50 mg) and a POC (~15 mg) samples were acidified with 3% phosphoric acid in quartz tubes and subsequently dried according to Hwang et al., [2005]. Percent organic carbon (%OC) was determined by the manometric measurement of CO_2 produced from single-tube combustions. Due to the large sediment sample size (1000 mg) required for BC ^{14}C analysis, only one SOC sample was measured in duplicate, and no POC samples were measured in duplicate for ^{14}C. BPCA isolates from the PCGC fraction collector were transferred to quartz tubes, dried and combusted to CO_2 at 850°C with CuO and Ag. Graphite was produced according to standard methods [*Santos et al.,* 2007]. Radiocarbon results are reported as $\Delta^{14}C$ [*Stuiver and Polach,* 1977]. Uncertainties of the $\Delta^{14}C$ measurements are determined from the $\Delta^{14}C$ difference between duplicate values [*Coppola et al.,* 2013]. Process blank assessments were made and BC reference materials were analyzed to account for extraneous carbon introduced during chemical processing, PCGC collection and graphitization [*Santos et al.,* 2007; *Ziolkowski and Druffel,* 2010b; *Coppola et al.,* 2013]. BC reference materials, such as wood char and grass char [*Hammes et al.,* 2007], were prepared in varying sizes that bracketed the sample sizes.

3.3 RESULTS

Sediment samples contained 1.0 ± 0.3 to 1.7 ± 0.2 %OC with an average value of 1.4 ± 0.2 %OC (Table 3.1). The BC/OC% in SOC ranged from 3 ± 2 to 9 ± 3% (Table 3.1, Figure 3.1A) with an average value of 6 ± 2 BC/OC%. There was no significant trend of BC/OC% with depth (Figure 3.1A). For the POC sample, OC% was 2.9 ± 0.5% and BC/OC% was 6 ± 2%. Both POC BC and surface SOC BC have the same BC/OC% values.

The $\Delta^{14}C$ values of bulk SOC ($\Delta^{14}C_{bulk}$) ranged from -231 ± 4‰ to -904 ± 7‰ (Table 3.1). In the mixed layer (0-8 cm depth), $\Delta^{14}C_{bulk}$ values ranged from -231 ± 4 ‰ to -286 ± 5‰, and those just below the mixed layer (8.5 and 13 cm) were -312 ± 4 and -428 ± 6‰, respectively. At 27 cm, $\Delta^{14}C_{bulk}$ values of duplicate samples were both -904 ± 7‰.

The $\Delta^{14}C$ values of BC ($\Delta^{14}C_{BC}$) for the sediment samples are all lower than SOC $\Delta^{14}C_{bulk}$ values from the corresponding depths (Table 3.1). Within the mixed layer, $\Delta^{14}C_{BC}$

Table 3.1 Measurements of BC isolated from northeast Pacific sediments and POC using the BPCA method. Bold UCID numbers indicate duplicate measurements.

UCID No.	Depth (cm)	OC%	BC/OC%	g BC/kg dry weight	$\Delta^{14}C_{BC}$ (‰)	$^{14}C_{BC}$ Age (^{14}C Years BP)	$\Delta^{14}C_{bulk}$ (‰)	$\Delta^{14}C_{non\text{-}BC\ OC}$ (‰)
Sedimentary Organic Carbon								
13187	0.25 ±0.25	1.4 ± 0.4	6 ± 2	0.8 ± 0.4	−530 ± 7	6050 ± 180	−246 ± 4	−229 ± 61
13234	0.75 ±0.25	1.7 ± 0.2	3 ± 2	0.5 ± 0.1	−740 ± 36	10800 ± 1600	−245 ± 4	−238 ± 90
13241	1.25 ±0.25	1.5 ± 0.3	7 ± 2	1.1 ± 0.2	−795 ± 18	12700 ± 1030	−242 ± 5	−200 ± 60
13233	1.75 ± 0.25	1.5 ± 0.2	5 ± 2	0.7 ± 0.3	−697 ± 16	9590 ± 620	−242 ± 3	−220 ± 69
13188	2.25 ± 0.25	1.4 ± 0.4	6 ± 2	0.8 ± 0.3	−605 ± 16	7460 ± 470	−238 ± 4	−216 ± 80
13240	2.75 ± 0.25	1.6 ± 0.6	4 ± 2	0.7 ± 0.2	−664 ± 15	8800 ± 520	−263 ± 4	−245 ± 76
13239	2.75 ± 0.25	1.6 ± 0.2	3 ± 2	0.5 ± 0.2	−592 ± 30	7210 ± 870	−263 ± 6	−251 ± 81
13189	4.25 ± 0.25	1.5 ± 0.2	7 ± 2	1.1 ± 0.2	−534 ± 10	6400 ± 270	−231 ± 4	−265 ± 85
13232	6.5 ± 0.5	1.6 ± 0.2	5 ± 2	0.7 ± 0.1	−596 ± 19	7200 ± 540	−260 ± 4	−200 ± 83
13190	7.5 ± 0.5	1.4 ± 0.4	7 ±3	1.0 ± 0.2	−653 ± 10	6100 ± 240	−286 ± 5	−243 ± 94
13231	8.5 ± 0.5	1.5 ± 0.2	4 ± 2	0.5 ± 0.2	−596 ± 33	7300 ± 790	−312 ± 4	−267 ± 87
13230	13 ± 1	1.5 ± 0.2	6 ± 2	0.9 ± 0.2	−730 ± 18	10500 ± 1300	−428 ± 6	−300 ± 88
12181	27 ± 1	1.0 ± 0.3	9 ± 3	0.9 ± 0.1	−966 ± 21	24300 ± 1700	−904 ± 7	−897 ± 21
12182	27 ± 1	1.0 ± 0.4	9 ± 3	0.9 ± 0.2	−952 ± 15	23600 ± 1400	−904 ± 7	−899 ± 23
Particulate Organic Carbon								
16515	3450m[c]	2.9 ± 0.5	6 ± 2	2.0 ± 0.4	−192 ± 24	2360 ± 260	−12 ± 2	−4 ± 25
Ultrafiltered Dissolved Organic Carbon[b]								
11955	1000 m[c]				−918 ± 31	20100 ± 3000	−445 ± 3	−192 ± 24

[a] Bold UCID numbers indicate duplicate measurements.

[b] *Ziolkowski and Druffel* [2010a].

[c] Collected from the water column at Station M.

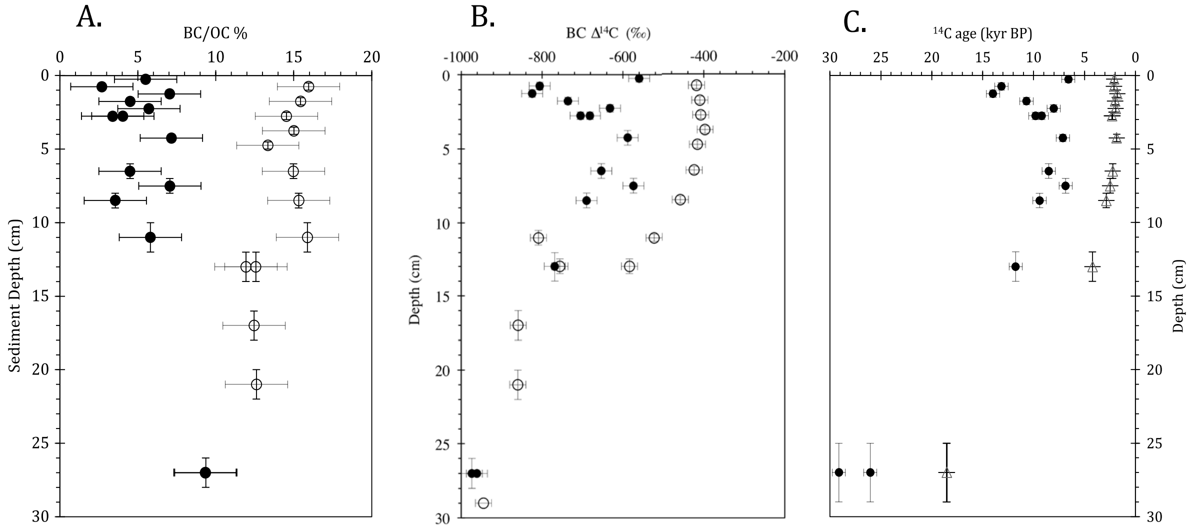

Figure 3.1 A) BC/SOC% with depth in the sediment from Station M. Closed circles represent measurements using the BPCA method (this work). Open circles represent values from Masiello and Druffel [1998] using the Cr_2O_7 oxidation method. Sediment depths 0-13cm were obtained from a box core. A gravity core was used for samples from deeper depths. B) $\Delta^{14}C_{BC}$ values of sediment samples. Closed circles represent measurements from this work. Open circles represent measurements from Masiello and Druffel [1998] for the same sediment samples. C) Black carbon ^{14}C ages (closed circles) plotted with non-BC ^{14}C ages (open triangles) in sediment using the BPCA method. Non-BC SOC $\Delta^{14}C$ values were calculated using a mass balance approach (Aux. Materials, eqn. 1), then converted to ^{14}C ages in years BP.

values ranged from -530 ± 7‰ to -795 ± 18‰. Just below the mixed layer, $\Delta^{14}C_{BC}$ values were −596 ± 33‰ and -730 ± 18‰, respectively. At 27 cm depth, the average of duplicate analyses was -959± 13‰ (Figure 3.1B). The $\Delta^{14}C_{bulk}$ value of POC was -12 ± 2‰ and the $\Delta^{14}C_{BC}$ value was -192 ± 24‰. Just as for the sediments, the $\Delta^{14}C_{BC}$ value for POC is lower than the $\Delta^{14}C_{bulk}$ value.

The relative abundances of B5CAs and B6CAs in SOC BC (compared to the sum of B3CA+B4CA+B5CA+B6CA) were similar for all depth horizons, averaging 26 ± 1% (stdev n=12) and 25 ± 4% (n=12), respectively (Table S2 Supplementary Materials). These relative abundances did not vary significantly with depth in the sediment. In contrast, the

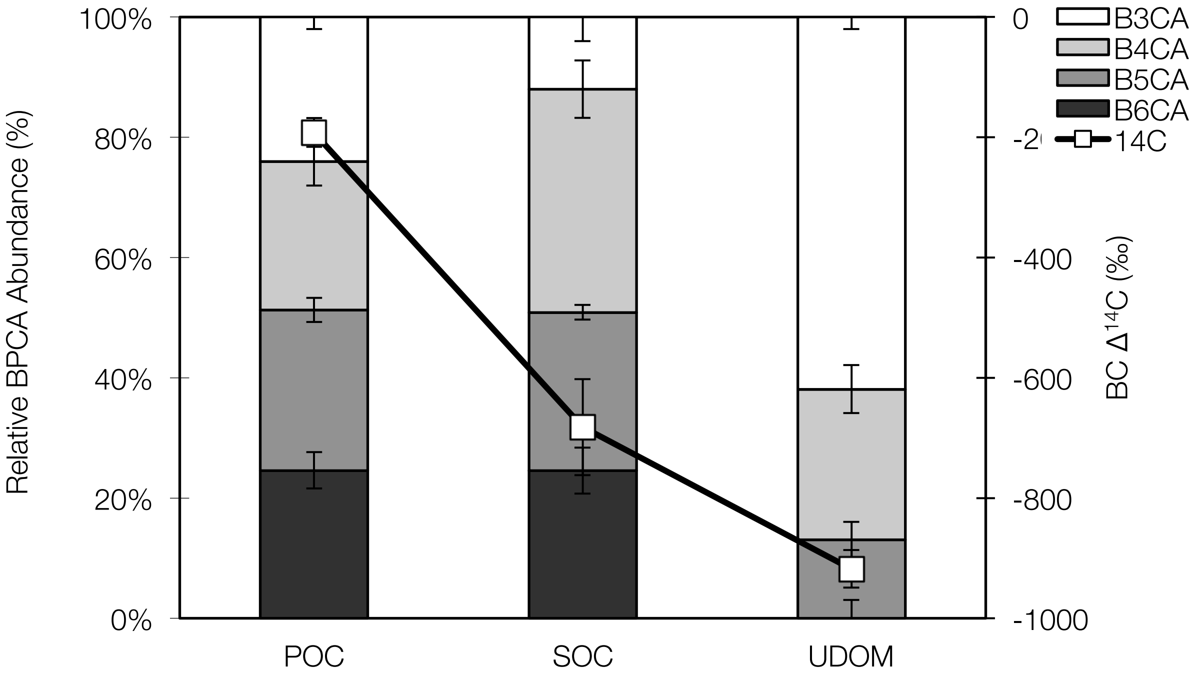

Figure 3.2. Relative BPCA abundances and $\Delta^{14}C$ values in SOC BC, POC BC(this work) compared with ultrafiltered DOC BC collected from 1000 m depth (Ziolkowski and Druffel, 2010a) at Station M. Error bars are the standard deviation of measurements. B3CA=hemimellitic, trimellitic and trimesic acids, B4CA=pyromellitic, prehnitric, and mellophanic acids; B5CA= benzene pentacarboxylic acid; B6CA=mellitic acid.

relative abundances of B4CAs and B3CAs averaged 36 ± 4% and 13 ± 4%, respectively, but the deepest sediment horizon had lower B3CA and higher B4CA relative abundances than those at at shallower depths (Figure S2 Supplementary Materials). In POC BC, the relative abundances of B3CAs, B4CAs, B5CAs, and B6CAs were similar to those in SOC BC (Figure 3.2).

3.4 DISCUSSION

Combustion conditions determine the relative structure of BC. The BPCA method is a powerful tool for constraining the source of BC, because the relative BPCA abundances serve as a fingerprint of the combustion conditions that formed the BC. Hotter combustion conditions, such as during fossil fuel burning, produce a highly condensed BC structure, while cool combustion conditions of biomass burning produce a less condensed BC structure [*Schneider et al.,* 2010]. Additionally, environmental reworking of BC, such as by photochemistry [e.g. *Stubbins et al.,* 2009], can decrease the aromaticity of BC. Therefore, coupling the relative BPCA abundances with compound specific radiocarbon analysis allows us to unravel the sources of BC to marine sediment.

While the main source of OC to POC and SOC at an abyssal ocean site, such as Station M is water column derived biological material [*Smith et al.,* 1988] with a modern ^{14}C content [*Hwang et al.*, 2004], the $\Delta^{14}C_{BC}$ values of SOC and POC are lower than their corresponding $\Delta^{14}C_{bulk}$ values. Therefore, BC in SOC and POC is not of recent biologic origin; instead, it is pre-aged before it is incorporated into the POC and SOC pools.

A source of old BC to POC and SOC may be sorption of DOC BC onto sinking POC. Ultrafiltered DOC BC from 1000 m depth at Station M is very old (20,100 ± 3000 ^{14}C yrs) [*Ziolkowski and Druffel*, 2010] and a small amount would reduce the age of BC in POC substantially. Below we discuss possible sources of pre-aged BC including sediment re-suspension, input via sorption onto sinking POC, and sorption of ancient DOC BC to sinking POC.

First, a source of aged BC to POC and SOC is likely from resuspended sediments that are laterally transported by bottom currents from the continental shelf to the abyssal plain [*Hwang et al.,* 2010]. Using aluminum content and $\Delta^{14}C$ values of sinking POC from several open ocean sites, Hwang et al., [2010] estimated that 35 ± 13% of sinking POC is derived from resuspended sediment, and is the primary reason that sinking POC has lower $\Delta^{14}C$ values than those in the surface ocean [Hwang and Druffel, 2003]. Bioturbation by macrofauna burrowing and feeding in the mixed layer decreases $\Delta^{14}C$ values of SOC at the surface by transporting deeper, older sediments upward from depth making it older than its chronological "age" [*Benninger et al.,* 1979; *Fauchald and Jumars,* 1979]. Re-suspension of the old, surface SOC provides a source of old OC and BC to sinking POC. The similarity of the relative BPCA abundances in POC BC and SOC BC (Figure 3.2) supports the recycling of resuspended sediment into the sinking POC pool.

A second, though unlikely, source of aged BC to POC and SOC is aerosol soot BC ($\Delta^{14}C$= -400 to -600‰, *Gustfasson et al.*, 2009) that has entered the surface ocean during the past 150 years primarily by atmospheric deposition. In coastal regions, aerosol BC has been shown to play a significant role in transporting BC to the sediments [*Flores-Cervantes et al.,* 2009; *Zigah et al.,* 2012; *Lohmann et al.,* 2009]. Due to the slow sedimentation rate at Station M (1.9 cm/kyr [*Cai et al.,* 1995]), this old BC would constitute a very small amount (<4%) of the BC in the surface sediment, and we do not observe lower $\Delta^{14}C_{BC}$ values in the mixed layer of the sediment relative to those at deeper depths (Figure 3.1C). Although it could be speculated that deposition has increased at this site, the age offset between BC and non-BC SOC does not appear to change down core, suggesting that the input of pre-aged BC to SOC was constant before and during the industrial revolution. Therefore, we conclude that this source of ^{14}C-free BC via aerosols is minimal in these sediments.

The third, and likely the largest source of aged BC to sinking POC and SOC is from DOC. The average ^{14}C age offset between BC and non-BC SOC of 6,200 ± 2,200 ^{14}C yrs (Figure 3.1C, Equation 1 Supplementary Materials) may represent a residence time for BC in the "holding pool" of DOC before its deposition to the sediments. There are two possible explanations for the different chemical structures of BPCAs in ultrafiltered DOC (no B6CAs) [*Ziolkowski and Druffel*, 2010] compared to those in POC and SOC (equal amounts of B3CAs, B4CAs, B5CAs and B6CAs), taking into account the different methodological treatments of these samples (POC and SOC were pretreated with trifluoroacetic acid). We hypothesize that DOC BC may be preferentially sorbed onto sinking POC by a) aggregation during photolysis, or b) hydrophobic bonding in microgel formation to explain our measurements.

Studies have shown that highly aromatic compounds similar to BC, such as carboxylated multiwalled carbon nanotubes (MWCNTs) and C_{60}, lose stability in solution after exposure to UV light, leading to aggregation and deposition in saline solutions [*Hou et al.,* 2010; *Hwang et al.,* 2013*; Chen and Jafvert,* 2011]. These authors suggested that photochemical transformations can play an important role in the aggregation and deposition of MWCNTs in aquatic systems [*Hwang et al.,* 2013; *Saleh et al.,* 2008]. This mechanism may be important for the transfer of hydrophobic, highly aromatic BC from DOC to POC, leading to an accumulation of smaller, hydrophilic BC structures (yielding B3CA-B5CAs) in oceanic DOC [*Ziolkowski and Druffel*, 2010a; *Masiello and Louchouarn,* 2013] (Figure 3.2).

Alternatively, abiotic transfer of BC from DOC to POC may occur synchronously with hydrophobic bonding during marine microgel formation [*Verdugo,* 2012; *Verdugo et al.,* 2004]. Hydrophobic interactions are low energy attractions that can cause aggregation and production of POC. It seems likely that hydrophobic BC has a higher aromaticity than hydrophylic BC, and would produce a higher B6CA abundance using the BPCA method. Previous work has shown that DOC self-assembled microgel formation facilitates ~10% of the OC transfer from DOC to POC [*Verdugo,* 2012; *Verdugo et al.,* 2004]. Whether these processes discriminate between structures of BC is an open question. We hypothesize that aged BC can be incorporated into POC by a combination of resuspended sediments laterally transported from the continental shelf, and sorption of aged DOC BC onto POC.

These results can be used to help constrain the flux of BC transported to abyssal sediments via POC, although the flux to coastal sediments is considerably higher [*Flores-Cervantes et al.,* 2009] and limit the scope of our estimate to the open ocean. If we assume that sorption of BC from DOC to POC is the main source of BC to the sediments, the POC flux to the deep ocean is 2 mg C m^{-2} d^{-1} [*Smith et al.,* 1999], and BC/OC% of POC is 6%, we estimate that the average global BC flux is 0.12 mg BC m^{-2} d^{-1} or 0.016 Gt BC yr^{-1}. Because the BC is pre-aged, this estimate represents the pre-industrial era and is at the low end of the range of measured BC flux ranges (0.01 to 360 mg m^{-2} yr^{-1}) reported from several studies in the open ocean [see review by *Mitra et al., 2013*]. Our estimate of BC flux represents ~8-16% of the global burial flux of organic carbon to sediments (0.1 to 0.2 Gt C yr^{-1})[*Hedges and Keil,* 1995]. Compared to a pre-industrial BC flux estimate from biomass burning (0.0014 Gt BC yr^{-1} *Dentener et al.,* 2006; *Bond et al.,* 2013), our estimate of POC BC flux to the abyssal ocean represents >100% removal of biomass-derived BC. This estimate implies that all of BC is removed through sediment burial during pre-industrial times. Compared to present day BC biomass emission fluxes (0.050-0.270 Gt BC yr^{-1} *Kuhlbusch and Crutzen,* 1995), our estimate of POC BC flux to the abyssal ocean represents a removal of 6-32% of biomass-derived BC.

In summary, this multi-pool data set leads us to conclude that a significant fraction of BC produced from biomass burning could be transported to ocean sediments. However, multiple POC BC and DOC BC measurements are needed to provide a more representative view of BC dynamics in the ocean. Ultrafiltered DOC, from which the only deep ocean BC value was derived [*Ziolkowski and Druffel,* 2010a], includes only ~25% of the marine DOC pool [*Benner,* 2002] and does not include the low molecular weight fraction [*Hansell et al.,* 2012; *Santschi et al.,* 1995]. Solid phase extraction of DOC [*Dittmar et al.,* 2008] has revealed the presence of B6CAs in North Atlantic Deep Water [*Stubbins et al.,* 2013], which also has a different relative BPCA abundance to that of SOC and POC. Reverse osmosis coupled to electrodialysis (RO/ED) is another method than can be used to isolate >60% of the DOC pool [*Vetter et al.,* 2007; *Koprivnjak et al.,* 2009]. RO/ED has an even greater efficiency for colored DOM absorbance, suggesting it may provide excellent yields of the aromatic compounds responsible for colored DOM absorbance [*Helms et al.,* 2013]. These data sets would further our understanding of BC cycling in both dissolved and particle phases. Additionally, updated global estimates of sources and sinks of BC are sorely needed to put into context the fate of BC upon entering the ocean.

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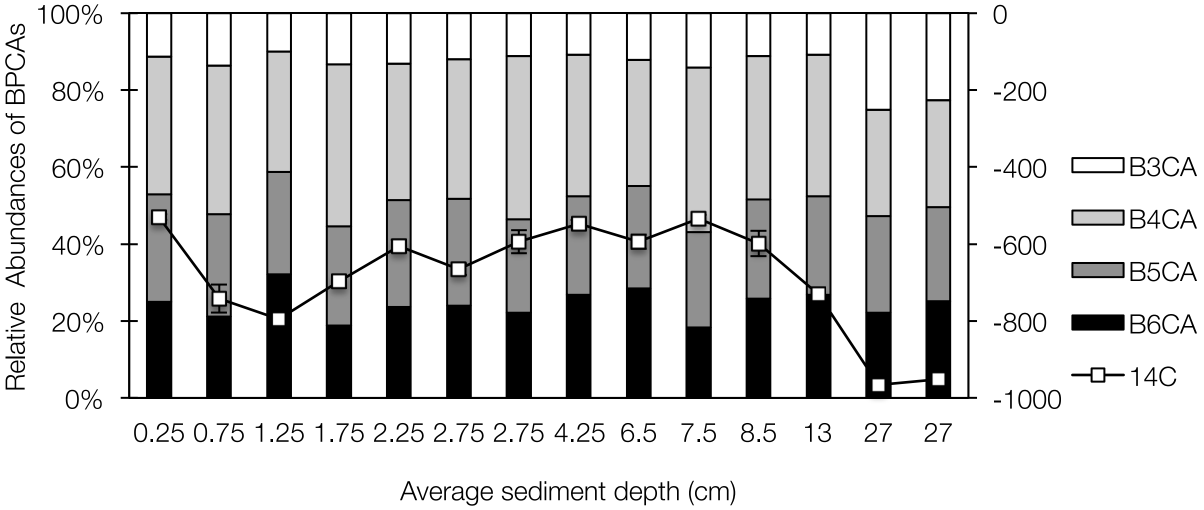
Table S.3.1. Samples combined to make up the POC sample (see text for details). Carbon isotopic ratios ($\Delta^{14}C$, $\delta^{13}C$) and C/N values are from Hwang [2004].

Lab code UCID #	Date	Pulse Cruise	Cup number	$\Delta^{14}C$	$\delta^{13}C$	C/N	Mass used in combined sample (mg)	% of combined POC sample
4304	7/94	20	4	37	-22.8	9.8	10.6	1.4
4293	11/95	27	8	37	-22.7	9.3	34.86	4.5
4294	11/95	27	9	30	-23.0	9.4	87.56	11.3
4332	2/95	29	2	3	-22.6	10.2	53.30	6.9
4286	11/95	27	1	-18	-21.8	9.5	73.93	9.5
4290	11/95	27	5	31	-23.6	9.5	46.63	6.0
4292	11/95	27	7	15	-23.2	9.8	65.29	8.4
4295	11/95	27	10	29	-23.1	10.0	17.85	2.3
4296	11/95	27	11	33	-22.8	9.3	32.20	4.2
4297	11/95	27	12	19	-22.8	9.7	63.08	8.1
4298	11/95	27	13	2	-22.6	8.4	14.97	1.9
4299	11/95	27	14	10	-22.8	8.4	146.45	18.9
4300	11/95	27	15	12	-22.8	9.3	92.64	12.0
3552	11/96	36	11	-13	-22.0	9.0	35.69	4.6

Table S.3.2. Relative BPCA abundances in sediments samples and one POC sample. B3CA=hemimellitic, trimellitic and trimesic acids, B4CA=pyromellitic, mellophanic acids; B5CA= benzene pentacarboxylic acids; B6CA=mellitic acids.

		Relative BPCA Abundance (%)			
		B3CA	B4CA	B5CA	B6CA
UCID	Depth	(± 2)	(± 4)	(± 3)	(± 3)
13187	0.25 ± 0.25	11	36	28	25
13234	0.75 ± 0.25	14	39	26	21
13241	1.25 ± 0.25	10	31	27	32
13233	1.75 ± 0.25	13	42	26	19
13188	2.25 ± 0.25	13	35	28	24
13240	2.75 ± 0.25	12	36	28	24
13239	2.75 ± 0.25	11	43	24	22
13189	4.25 ± 0.25	11	37	26	27
13232	6.5 ± 0.5	12	33	27	28
13190	7.5 ± 0.5	14	43	25	18
13231	8.5 ± 0.5	11	37	26	26
13230	11 ± 1	10	35	27	28
12182	27 ± 1	25	28	25	22
12181	27 ± 1	23	28	24	25
16518	650 mab	24	25	27	24

Figure S.3.1. Relative BPCA abundances and Δ^{14}C values in sediments at each depth. Error bars are the standard deviation of measurements in the depth bin.



Equation S.31. Calculation of the non-BC SOC fraction in sediment samples corresponding to Figure 1C in the text.

$$\Delta^{14}C_{soc}=BC/OC*\Delta^{14}C_{BC}+(1-BC/OC)*\Delta^{14}C_{non\text{-}BC\ SOC} \qquad \text{(eq S1)}$$

Where $\Delta^{14}C_{soc}$ is the $\Delta^{14}C$ value of SOC, $\Delta^{14}C_{non\text{-}BC\ SOC}$ is the $\Delta^{14}C$ value of non-BC SOC, BC/OC is the ratio of BC to OC in SOC, $\Delta^{14}C_{BC}$ is the BC $\Delta^{14}C$ value. The residence time of BC was determined as the difference between the ^{14}C ages of BC and those of non-BC SOC concurrently deposited for each sample depth using the Libby half-life of 5568 yrs.

Chapter 4

Solid Phase Extraction Method for Quantification and Compound-specific Radiocarbon Analysis of Black Carbon in Dissolved Organic Carbon

Coppola, A.I., B.D. Walker, and E.R.M. Druffel, (in review), Solid phase extraction method for quantification and compound-specific radiocarbon analysis of black carbon in dissolved organic carbon. *Marine Chemistry.*

Abstract

Compound specific radiocarbon analysis (CSRA) is a powerful tool for understanding the cycling of individual components within total carbon pools, such as black carbon (BC) within dissolved organic carbon (DOC). Radiocarbon ($\Delta^{14}C$) measurements of BC provide insight into one source of aged, recalcitrant DOC. We have developed a solid phase extraction (SPE) method that uses a wide polarity range of solvents to concentrate 43±6% of DOC from seawater and 62±5% from freshwater. We use the Benzene Polycarboxylic Acid (BPCA) method to isolate BC from polar to non-polar SPE-DOC for subsequent CSRA. We report SPE-BC $\Delta^{14}C$ values, BC concentrations, and the relative BPCA distributions from Milli-Q water process blanks, two riverine reference standards, and coastal and open ocean surface samples. 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 5±2% of SPE-DOC in the open ocean surface sample, or 1.4±0.1 μM C. This work provides the methodological basis for which global BC concentrations, compositions (eg. relative abundances of BPCA marker compounds) and $\Delta^{14}C$ values can be assessed.

4.1 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 forcing (Bond et al., 2013; Husain et al., 2007; 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). The structure of BC 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 (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; Stubbins et al., 2012; Ziolkowski and Druffel, 2010; Suman et al., 1997; Masiello and Druffel, 1998; Coppola et al., 2014).

Once BC enters the ocean, it contributes to one of Earth's major organic carbon reservoirs, dissolved organic carbon (DOC, 0.2-1.0 μm). While most DOC is produced by phytoplankton in the surface ocean, marine DOC is surprisingly thousands of years old (Williams and Druffel, 1987). The presence of recalcitrant BC within the marine DOC pool may explain this mystery, as DOC may act as a "holding pool" for BC (Ziolkowski and Druffel, 2010; Masiello and Druffel, 1998). Two studies have identified BC in solid phase extracted DOC (SPE-DOC) with concentrations ranging from 0.6 to 0.8 μM (1 to 2% of total DOC) in the Southern Ocean (Dittmar and Paeng, 2009) and 1.0 ±0.2 μM BC in surface North Atlantic Deep Water at the Bermuda Atlantic Time Series site (Stubbins et al., 2012). Ziolkowski and

Druffel (2010) made the only BC Δ^{14}C measurements in the DOC pool using ultrafiltered DOC (UDOC). They found open ocean BC had a range of ages from 15,680 to 20,100 ^{14}C yrs in UDOC, providing evidence for BC stability on millennial time scales. Corresponding BC in UDOC ranged from 0.09 μM to 0.33 μM C in the North Central Pacific (NCP) and Northeast Pacific open ocean.

BC Δ^{14}C measurements in UDOC have limitations for evaluating the entire DOC pool, because UDOC is only ~25% of DOC and primarily 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 and complexity 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 BC Δ^{14}C in a larger fraction of the DOC pool using SPE, without an inherent size bias. The SPE method concentrates DOC based on chemical composition, retaining polar and non-polar DOC compounds. This BC extraction method for Compound Specific Radiocarbon Analysis (CSRA) is an improvement over UDOC, because SPE recovers approximately half of the total DOC pool (Dittmar, 2008), without the time required for laborious UDOC isolations.

We use a styrene divinyl benzene copolymer (HP-20, 200 Å pore size) resin to concentrate DOC. Most of the DOC we isolate is hydrophilic; we use additional non-polar solvents to elute the hydrophobic DOC fraction that is adsorbed on the resin bed. We measure the mass and Δ^{14}C value of SPE-DOC from Milli-Q water, two riverine reference standards, and marine samples from a coastal and an open ocean site off California. We assess blanks, reproducibility and the robustness of this SPE-DOC method. 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 $\Delta^{14}C$.

We then isolate BC from the SPE-DOC samples (SPE-BC) using the Benzene Polycarboxylic Acid (BPCA) method, which oxidizes BC into marker compounds (BPCAs) for CSRA. 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 structural composition and $\Delta^{14}C$ values of SPE-BC provides insight into the composition of recalcitrant DOC, which escapes decomposition for thousands of years (Hansell et al., 2012; Ziolkowski and Druffel 2010; Jiao et al. 2010; Stubbins et al., 2012). Our primary motivation is to use this SPE method to investigate aged BC contributions to recalcitrant DOC by determining the distribution and ^{14}C age of BC in the ocean.

4.2 MATERIALS AND METHODS

4.2.1 Sample Collection

Coastal seawater DOC samples were collected from Newport Beach Pier (NBP) (33^{o}60.70'N, 117^{o}92.89'W) on August 8, 2013 at 1 m depth in 1-gallon jugs. Open ocean seawater DOC samples were collected from 20 m depth at Station M located on the 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 1.0 μm Whatman filters and Station M DOC 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 hrs. 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 urban river discharge from the nearby Santa Ana River (5 km north of NBP) during rain events in southern California. There was no river events recorded by the rain gauge on the Santa Ana River in the City of Santa Ana on August 8, 2013 (available on the USGS site, see Supplementary Figure 4.1).

4.2.2 Suwannee River Natural Organic Matter Standards

We used two freshwater, organic matter reference samples from the International Humics Substances Society (https://ihss.humicsubstances.org/) collected in 1999 and 2012. 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/L) with low concentrations of inorganic solutes (Serkiz and Perdue, 1990; Green et al., 2015). To create these standard, large volumes of water (~36,000 L) from the Suwannee River were concentrated by reverse osmosis, desalted by cation exchange, freeze-dried and homogenized.

We used two Suwannee River Natural Organic Matter standards collected using the same methodology at different times. Suwannee River I (IHSS 1R101N termed SR NOM I) was collected from May 1-9, 1999. Suwannee River Natural Organic Matter II (IHSS2R101N termed SR NOM II) was collected from May 3-15, 2012 (Green et al., 2012). 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 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 much lower than in 1999 (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 BC analysis.

4.2.3 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). 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^{o}C, 56^{o}C, 77^{o}C and 40^{o}C, respectively. Each soxlet solvent washing lasted 24 hours and was performed sequentially in order of decreasing polarity.

According to the HP-20 manufacturers guidelines, sample water was acidified to pH 2 with hydrochloric acid (Fluka Traceselect 84415-500 ml) to increase extraction efficiency.

Figure 4.1 summarizes the SPE and BC methods. Briefly, large-volume water samples (10 – 15 L) were defrosted, homogenized by shaking and loaded onto the 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/hr 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.

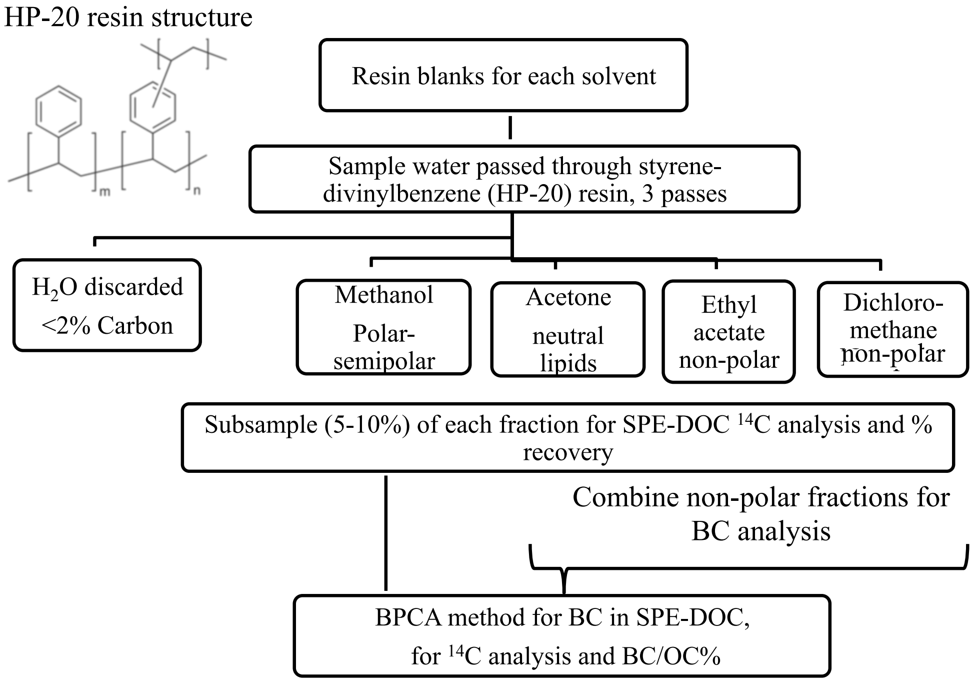


Figure 4.1 Flow chart of methods used to isolate and analyze SPE-DOC and SPE-BC. Resin blanks are listed in Supplementary Table 4.1. Chemical structure of HP-20 resin from Aldrich Chemical catalog.

In preparation for DOC elution, two bed volumes (30 ml) of Milli-Q water were passed through the column at 30 ml/hr to remove salts, and this fraction was discarded. SPE-DOC was eluted with solvents, each at a flow rate of 30 ml/hr using two bed volumes (30 ml). Solvents with different polarities were used to elute SPE-DOC into pre-combusted 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 under UHP nitrogen, then lyophilized for 24 hours. The SPE-DOC fractions were combusted separately to determine the percent yield of DOC (SPE-DOC/total DOC x 100) and for comparisons of SPE-DOC Δ^{14}Cand total DOC Δ^{14}C analyses.

4.2.4 BC in Solid Phase Extracted DOC (SPE-BC)

The SPE-DOC methanol fractions were used to isolate BC using the BPCA method (Ziolkowski et al., 2011; Schneider et al., 2011). Briefly, eluted SPE-DOC extracts were dried and lyophilized for 24 hrs. Concentrated nitric acid was added and placed in a quartz pressure digestion chamber at 170°C for 8 hours 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 re-dissolved 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 2-2', biphenol). 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). In preparation for CSRA analysis, B3CA through B6CA marker compounds (including nitrated B3CA and B4CAs) were collected in U-traps (-20°C) in the fraction collector. The B2CA marker compounds were not collected, because they may derive from lignins. The BPCAs in the U-trap were transferred using dichloromethane to clean quartz tubes, and dried under UHP nitrogen.

4.2.5 Radiocarbon Analyses

For $\Delta^{14}C$ analysis, samples were sealed in quartz tubes under vacuum with cupric oxide and silver wire and combusted to CO_2 at $850^{o}C$ for 2 hrs. The CO_2 gas produced was cryogenically purified, and quantified manometrically. The manometric determinations of SPE-DOC combusted subsamples were used to calculate % DOC recovery. In some cases when sample sizes were too small for individual $\Delta^{14}C$ measurement (e.g., ethyl acetate and dichloromethane) fractions were combined and so-labeled. For all samples, CO_2 was reduced to graphite for $\Delta^{14}C$ analysis using a sealed tube zinc reduction method (Xu et al. 2007; Khosh et al., 2010). Radiocarbon measurements were made at the UCI Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory and are reported as $\Delta^{14}C$ for geochemical samples without known age correction (Stuiver and Polach, 1977).

4.2.6 Carbon Blanks: Resin Blank and Process Blank Assessments

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 µg C. Process blanks contained Milli-Q water (10 L each) and were subjected to the same preparatory steps as the samples. Process blanks were used to correct samples for the Δ^{14}C value and mass of carbon blank added during processing, using a mass balance approach in Equation 1:

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

where $\Delta^{14}C_{SPE-DOC}$ is the radiocarbon value corrected for SPE processing, $\Delta^{14}C_{measured}$ and $C_{measured}$ are the measured Δ^{14}C value and mass of the sample uncorrected for SPE processing, $\Delta^{14}C_{Milli-Q}$ and $C_{Milli-Q}$ are the average Δ^{14}C value and mass of the Milli-Q water SPE-DOC, respectively (Table 4.1).

For the assessment of blank carbon during the BPCA method, process blanks were generated using Milli-Q water. The SPE-BC samples are corrected using an indirect approach, as previously by reported Coppola et al., (2013) and Ziolkowski and Druffel (2009). Several dead (-1000‰) and modern BC standards from Hammes et al., (2007) were run alongside SPE-BC samples to correct for blank carbon. Approximately 6 to 10 µg C dead blank C and 0.5 µg C of modern carbon was added during BC processing.

4.3 RESULTS

4.3.1 Carbon Blank assessments

The mass of resin blanks from each of the four solvents range from 2 to 8 μg C, and their $\Delta^{14}C$ values range from -499±14 to -873±2‰ (Supplementary Table 4.1). The $\Delta^{14}C$ values of Milli-Q process blanks range from -660 to -1000‰, and had masses that range from 2 to 10 μg C (Table 4.1). Using an isotopic mass balance, we determine Milli-Q water SPE-DOC $\Delta^{14}C$ values range between -721±77 to -927±54‰ (Supplementary Table 4.1). The Milli-Q water total DOC $\Delta^{14}C$ values obtained using UV-oxidation techniques range from -612±57 to -926±57‰, which is equal to the range in SPE-DOC Milli-Q $\Delta^{14}C$ values.

4.3.2 SPE-DOC recoveries and $\Delta^{14}C$ values

Percent SPE-DOC recoveries in all elutants for SR NOM I, SR NOM II, NBP and Station M samples are 62±5, 61±4, 43±6 and 44±3%, respectively (Figure 4.2, Table 4.2). Percent SPE-DOC recoveries for ocean samples are comparable to those reported by Dittmar (2008) (42±8%) for surface marine DOC using a similar method (pre-made PPL cartridges with a smaller pore size of 150 Å and methanol elution).

Table 4.1. Carbon blank mass and $\Delta^{14}C$ values of process blanks obtained from processing 10 L of Milli-Q water for each assessment. Averages are weighted averages. Total DOC $\Delta^{14}C$ values range from -926±54 to -612±57‰ (n=60, S. Griffin and B. Walker).

SPE-DOC fraction	Sample Group	UCID lab code #	Blank size (μg C)	$\Delta^{14}C$ (‰) Blank corrected	±
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 ±SD:		**6±3**	**-785**	**80**
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 ±SD:		**4±3**	**-836**	**87**
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 ±SD:		**4±2**	**-866**	**107**
Dicholoromethane	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 ±SD:		**3±2**	**-800**	**114**

For all samples, most of the DOC (>89%) was eluted in the methanol fraction (Table 4.2). Suwannee River NOM I and 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±4%) of coastal SPE-DOC was present in the methanol fraction, the non-polar fractions constitute 8% of the SPE-DOC (acetone 4±2%, ethyl acetate 2±1% and dichloromethane 2±1%). At Station M, the methanol fraction is 89±2%, dichloromethane is 9±2% and there were insignificant DOC in the acetone and ethyl acetate fractions (1±1%) for BC measurements.

The methanol SPE-DOC $\Delta^{14}C$ values for SR NOM I are identical within 1 sigma (+110±7, +105±10, +114±8‰) (Figure 4.2). The acetone SPE-DOC fractions in SR NOM I are -286±81 and -124±68‰, significantly lower than those of the methanol fractions. The $\Delta^{14}C$ value of total combusted SR NOM I is +152±3‰ (Table 4.2), which is significantly higher than that of the methanol fractions, indicating that the SPE-DOC fraction is selectively isolating older DOC from the bulk material.

Duplicate methanol SPE-DOC $\Delta^{14}C$ values in SR NOM II are identical (+20±16, +20±18‰) (Figure 4.2.b). The acetone fraction $\Delta^{14}C$ values (-329±57 and -480±75‰) are significantly lower than the methanol fractions. The total combusted SR NOM II $\Delta^{14}C$ value (+45±3‰) is within 2 sigma of the SPE-DOC $\Delta^{14}C$ values measured in the methanol fractions (Table 4.2). Duplicate methanol SPE-DOC $\Delta^{14}C$ values in NBP seawater are identical (-263±10, -255±12‰) (Figure 4.2). The acetone SPE-DOC $\Delta^{14}C$ values are -717±24 and -764±10‰, which were much lower than those of the methanol fractions. The $\Delta^{14}C$ values of the ethyl acetate/dichloromethane combined fractions are intermediate or equal to the two other fractions (-543±41 to -691±95‰, Table 4.2). The NBP total DOC

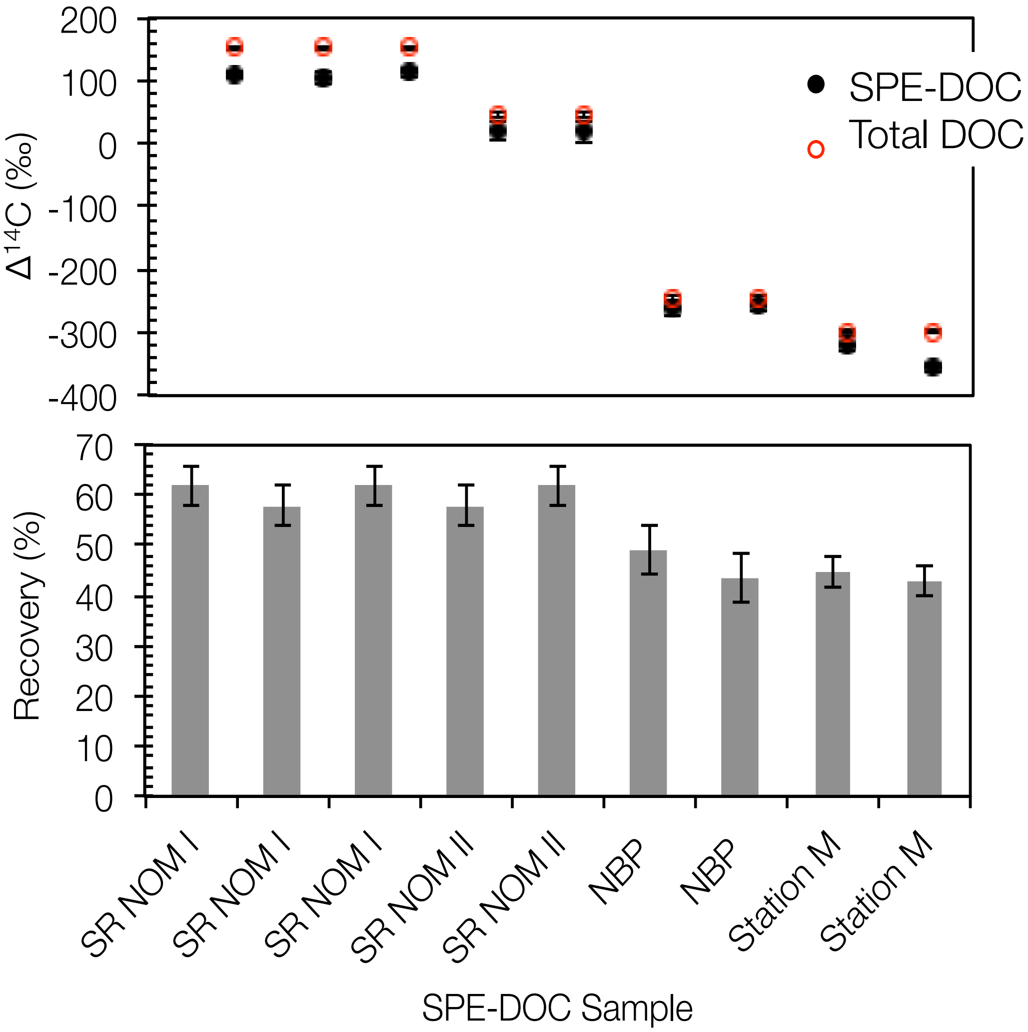


Figure 4.2.a. SPE-DOC Δ^{14}C values of methanol fractions for freshwater SR NOM samples, NBP and Station M seawater (solid black circles) with comparisons to total DOC Δ^{14}C values (open squares). b. Corresponding percent SPE-DOC recoveries per individual sample are shown as grey columns.

Table 4.2 Total [DOC] and SPE-DOC $\Delta^{14}C$ values for Suwannee River standards, NBP and Station M water samples. SPE-DOC $\Delta^{14}C$ values are corrected using mass balance techniques using Milli-Q SPE-DOC blanks (see text for details).

	Total DOC			SPE-DOC					
Sample type	UCID lab code #	$\Delta^{14}C$ (‰)	±	SPE-DOC fraction (% recovery)[1]	UCID lab code #	Size (µg C)	$\Delta^{14}C$ (‰)	± (‰)	Recovery (%)
Suwannee River standard 1R101N (1999)	17901-17910; (n=10)	+152	3	**Methanol**	18619	690	+110	7	62±4
				(99±1%)	17848	590	+105	10	58±4
					17582	789	+114	8	62±4
				Acetone	17583	10	-286	81	
				(1±1%)	17849	10	-124	68	
Suwannee River standard 2R101N (2012)	18796-18799; (n=4)	+45	3	**Methanol**	18846	380	+20	16	58±4
				(99±1%)	18851	390	+20	18	62±4
				Acetone	18847	38	- 329	57	
				(1±1%)	18852	39	-480	75	
NBP	17616	-246	3	**Methanol**	18806	762	-263	10	49±4
	18270			(92±4%)	18002	690	-255	12	44±5
	18276			**Acetone**	18007	20	-717	24	
	18253			(4±2%)	18003	57	-764	10	
				Ethyl acetate/	18008	6	-543	41	
				Dichloromethane (2±1%)	18804	6	-691	95	
Station M	8253[2]	-299	3	**Methanol**	18267	401	-318	11	43±3
	8270			(89±2%)	18243	514	-335	7	45±3
	8271			**Acetone**	18268	8	nd		
	8276			(1±1%)	18244	8	-678	25	
				Ethyl acetate/ Dichloromethane (0±1%/10±2%)	18245	32	-958	5	

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[1] Recovery in each SPE-DOC fraction calculated as the percentage of the total mass in all fractions.

[2] Station M UV-oxidation total DOC value is reported by Beaupre and Druffel (2009).

$\Delta^{14}C$ values measured by UV-oxidation are -246±3‰, which is also equal to the methanol fraction $\Delta^{14}C$ value.

For Station M seawater, the methanol SPE-DOC $\Delta^{14}C$ values are -318±11 and -335±7‰ (Figure 4.2). The other fractions have lower $\Delta^{14}C$ values (acetone -678±25‰, ethyl acetate/dichloromethane -958±5‰) (Table 4.2). The total Station M DOC $\Delta^{14}C$ value is -299±3‰, which was significantly higher than one of the methanol fraction values and equal to the other value.

4.3.3 BC concentration, and relative BPCA distributions

The average BC/OC% values in SR NOM I, SR NOM II, NBP and Station M seawater samples are 10±3, 11±2, 20±2 and 5±1%, respectively (Table 4.3, Supplementary Table 4.2). The BC concentrations at the NBP and Station M sites are 5.2±0.4 and 1.4±0.1 µM, respectively, in the SPE-DOC (Supplementary Table 4.2).

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. However, between SR NOM samples, there is a greater abundance of B6CAs in SR NOM II collected in 2012. In contrast, the NBP samples have similar abundances of B3CAs, B4CAs and B5CAs and a low abundance of B6CAs (7±3%). We obtained BPCA abundances for the less polar SPE-BC fractions for the NBP samples only (Figure 4b), and the only significant difference between methanol with other non-polar

Table 4.3 SPE-BC Δ ^{14}C, relative BPCA abundance and total BC/OC percentages for Suwannee River standards, and NBP and Station M seawater samples.

Sample type	Fraction	UCID lab code #	Size (µg C)	SPE-BC Δ^{14}C (‰)	±	BPCA relative abundance[1] B3CA:B4CA:B5CA:B6CA	Total BC/OC (%)
SR NOM I (1R101N)	Methanol	17586	112	+148	17	$_{\text{SPE-BC}}$ 9:11:53:27 $_{\text{total}}$ 16:22:38:21[2]	10±3
SR NOM II (2R101N)	Methanol	18623 18850	31 20	-462 -346	40 70	$_{\text{SPE-BC}}$ 6:10:53:30 $_{\text{SPE-BC}}$ 6:12:51:31 $_{\text{total}}$ 11:33:37:19[2]	11±2
NBP	Methanol	17940 17719	43 25	-678 -712	19 36	18:39:38:4 29:29:34:7	
	Acetone	17720 17941	16 42	-587 -615	47 20	23:30:47:0 27:35:37:0	20±2
	Ethyl acetate/ Dichloromethane	17942 nd	62	-593	15	26:33:39:0 27:35:36:0	
Station M	Methanol	18247 18271	12 15	-592 -649	201 121	56:14:18:12 58:16:18:8	5±1
Process blanks		17590 17448 17490 17261	8 6 6 10	-867 -864 -767 -917	2 3 4 2		

[1] Errors for the BPCA relative abundance determined by peak areas in FID trace is ±3% for B3CA, ±4% for B4CA, ±3% for B5CA and ±2% for B6CA

[2] total BPCA relative abundances were determined by SR NOM through the BPCA method

fractions is the absence of B6CA marker compounds. The BPCA abundances in the Station M samples (Table 4.3, Figure 4.4.a) reveal a greater proportion of B3CAs than at NBP.

4.3.4 SPE-BC $\Delta^{14}C$ values

SPE-BC $\Delta^{14}C$ values for the SR NOM standards, and those for the NBP and Station M seawater samples are listed in Table 4.3 and shown in Figure 4.4.a. The methanol SPE-BC $\Delta^{14}C$ value of SR NOM I are +148±17‰. Total BC $\Delta^{14}C$ for SR NOM I was -49±33‰, which is significantly lower than that for the methanol SPE-BC. In contrast, duplicates for methanol SPE-BC of SR NOM II are -462±40 and -346±70‰ (within 2 sigma), however total BC $\Delta^{14}C$ for SR NOM II (-159±55‰) is higher than the methanol $\Delta^{14}C$ SPE-BC value.

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

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

4.4 DISCUSSION

In the first section of the discussion, we highlight the application of the SPE-DOC method, addressing the reproducibility of concentration and isotopic measurements. We highlight results from standards, blanks and replicate samples. In section 4.4.1, we discuss the variability of $\Delta^{14}C$ values obtained on the same sample for SPE-DOC and total DOC analysis. In section 4.4.3, we compare $\Delta^{14}C$ values obtained for SPE-BC and total BC for SR NOM I and II. We also compare our results to those available for from a deep UDOC BC sample in the Northeast Pacific and a surface sample in the North Central Pacific (NCP) (Ziolkowski and Druffel, 2010). In the final section, we discuss SPE-DOC and BC composition and cycling in these aqueous environments.

4.4.1 Methods assessment: Recoveries, SPE-DOC carbon blanks and reproducibility

Replicate measurements of SPE-DOC and SPE-BC recoveries and $\Delta^{14}C$ values agree within 2 sigma. This demonstrates that use of the method produces reproducible $\Delta^{14}C$ results (Table 4.2, Table 4.3, Figure 4.2). 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 (Figure 4.2).

We report that masses of resin blanks acquired prior to sample loading, and Milli-Q process blanks are equal within error (Table 4.1, Supplementary Table 4.1), indicating that there is no additional carbon blank introduced to the large volume water samples. The SPE-DOC $\Delta^{14}C$ values of Milli-Q process blanks are equal within error to the $\Delta^{14}C$ values obtained for multiple 1-L UV oxidized Milli-Q blanks run from 2012-2014 in our laboratory (Supplementary Table 4.1). The SPE-Milli-Q process blank correction changed $\Delta^{14}C$ values by less than 10‰.

The SPE-BC process blanks are similar in size and $\Delta^{14}C$ value to that of resin and Milli-Q process blanks (Table 4.3). 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.

4.4.2 Comparison of SPE-DOC and total DOC $\Delta^{14}C$ values

We present the first $\Delta^{14}C$ comparison between SPE-DOC and UV oxidized total DOC from splits from the same sample water (Table 4.2). Generally, we find that all methanol SPE-DOC $\Delta^{14}C$ values are equal to or lower (~25±10‰) than their corresponding total DOC $\Delta^{14}C$ values, presumably because SPE chemically fractionates the DOC (Figure 4.2). Similarly, SPE-DOC of SR NOM I and II standards are significantly lower (~35±10‰) than total DOC $\Delta^{14}C$ values (Figure 4.2). The polarity-driven SPE method and its lower extraction efficiency for dissolved organic nitrogen compared to organic carbon may be responsible for the difference between total DOC and SPE-DOC $\Delta^{14}C$ values (Flerus et al., 2012). Another possible explanation for this offset could be selective concentration of older 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 extent for seawater samples.

Using a mass balance between the SPE-DOC that is recovered (43±6%) and total DOC, we find the non-adsorbed DOC (57±5%) is more modern than their SPE-DOC counterpart by 67‰, 38‰, 9‰ and 17‰ for SR NOM I, SR NOM II, NBP and Station M, respectively (Supplementary Figure 4.2). For freshwater systems, the non-adsorbed DOC $\Delta^{14}C$ value is significantly different from the SPE-DOC $\Delta^{14}C$ value. For marine samples, the non-adsorbed DOC $\Delta^{14}C$ value is within error to the total DOC and SPE-DOC $\Delta^{14}C$ values (Supplementary Figure 4.2). While our sample set is limited, these results suggest that SPE-DOC $\Delta^{14}C$ results may be within error of the total DOC pool.

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

In contrast to SPE-DOC and bulk DOC, comparisons between SPE-BC and total BC of SR NOM I and II standards show BPCA distributions and $\Delta^{14}C$ values that are dissimilar to one another. This may indicate different sources, or differential cycling of BC within DOC. For SR NOM I and II, non-adsorbed BC had a more aromatically condensed structure (greater abundance of B6CAs) than that for total BC (Table 4.3). The BPCA relative abundances reveal that SPE-BC isolates are more aromatically condensed than BC from the total BC pool. Additionally, the SPE-BC $\Delta^{14}C$ value of SR NOM I is higher than that of total BC, while 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 between 1999 and 2012, 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 Δ^{14}C values were found for the SPE-BC (Figure 4a) than for the UDOC (Ziolkowski and Druffel, 2010). Based on size-reactivity it was expected that the higher molecular weight (UDOC) fraction of BC would be younger than the age of SPE-BC, if BC followed the same size-reactivity relationships of DOC (see review by Benner and Amon, 2015). BC concentration has been found to correlate with DOC concentration (Jaffe et al., 2013) in environmental waters. This suggests that with a larger DOC sample pool (43%), total BC may not be as aged as previously thought, or that there is discreet cycling of BC within these DOC fractions. Nonetheless, a larger sample set is needed to explain the relationship of the BC DOC fractions.

4.4.4 SPE-DOC and BC cycling

Here, we investigate the different polarities of the SPE-DOC elutant 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 non-polar fractions, we found that the riverine SR NOM I and II standards were exclusively polar with no significant differences in SPE-DOC composition between the two collection periods (Figure 4.3, Table 4.2). Methanol SPE-DOC is composed of younger (perhaps humic, and/or carbohydrate-like) materials.

In contrast, NBP and Station M seawater samples have higher proportions of SPE-DOC eluting in the less polar fractions (Figure 4.3). Approximately 10% of oceanic SPE-DOC at Station M eluted with non-polar solvents. This agrees with previous studies that showed individual DOC fractions can have distinct compositions and low $\Delta^{14}C$ values in the ocean, such as lipid-like compounds or acid insoluble fractions in DOC and particles (Loh et al., 2006; Wang et al., 2006; Hwang and Druffel, 2003).

Total DOC $\Delta^{14}C$ values, BPCA relative abundances and BC $\Delta^{14}C$ values in SR NOM I and II are dissimilar. Suwannee River NOM I and II represent different amounts of anthropogenic influence. We observe similar BC concentrations and $\Delta^{14}C$ values of BC in these river standards. Suwannee River NOM I BC has high $\Delta^{14}C$ values, perhaps indicative of the extensive fires in the swamp in the mid-1950s (Green et al., 2015). Both DOC and BC $\Delta^{14}C$ values were higher in 1999 (SR NOM I) than 2012 (SR NOM II) (Figure 4.2), suggesting an older DOC and BC source contribution in SR NOM II. The more aromatically condensed structure and lower BC $\Delta^{14}C$ value of SR NOM II likely suggests anthropogenic fossil fuel input, as the Suwannee River sampling site is no longer considered pristine (Green et al., 2015) (Figure 4.4a). Hydrophobic acid isolates from reverse osmosis of SR NOM collected in 2012 have a higher average molecular weight, and ^{13}C NMR studies revealed more aromatic functional groups than for SR NOM I (Kreller et al., 2015; Nwosu and Cook, 2014). This suggests that riverine BC is influenced by anthropogenic input. It cannot be assumed that all riverine BC enters the ocean with modern $\Delta^{14}C$ values, as preliminary work has suggested (Ziolkowski and Druffel, 2010).

Oceanic BC appears chemically distinct from the riverine samples we studied. Using the relative BPCA abundance as an indicator of BC aromaticity, we observe a smaller

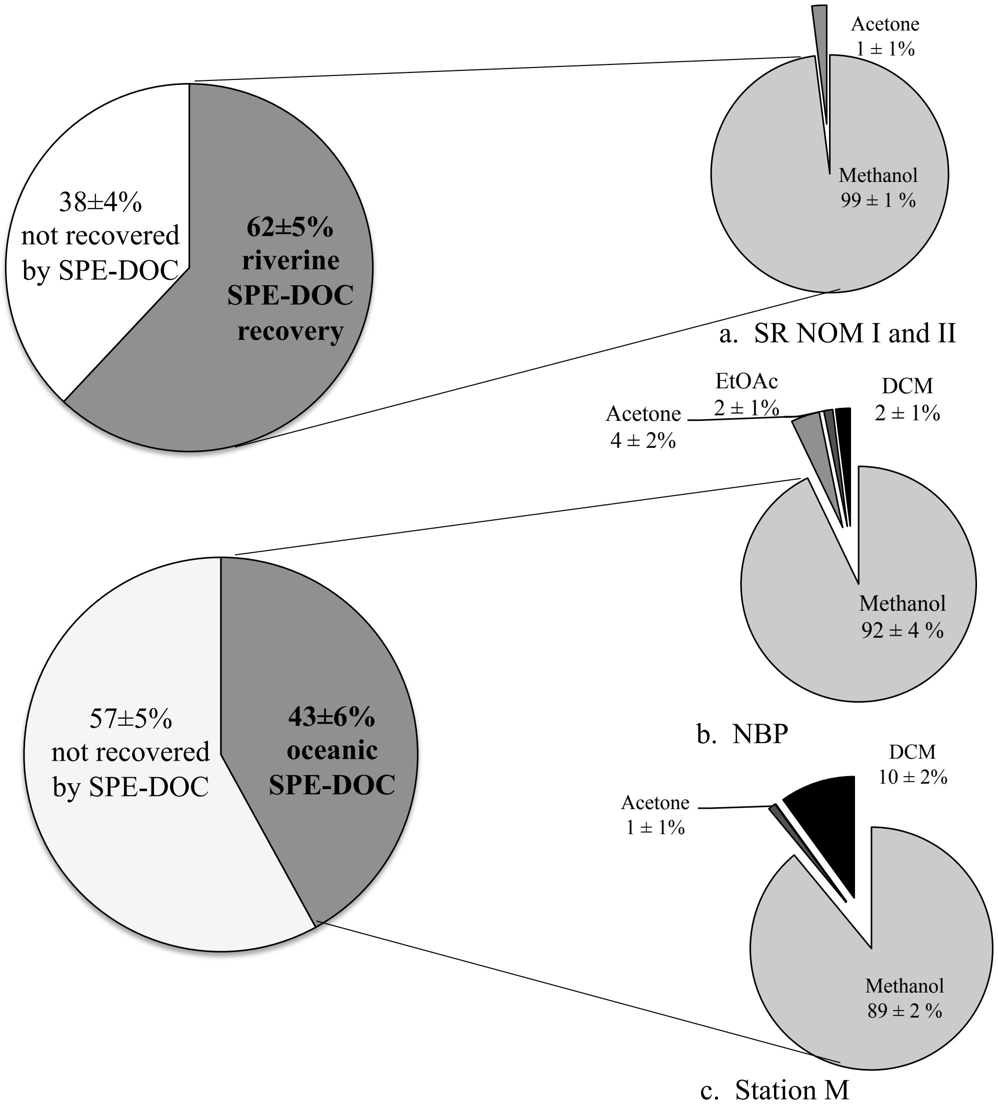

Figure 4.3 SPE-DOC recoveries for two sample types, riverine and marine DOC. Fraction compositions from methanol fraction (more polar, grey), acetone, ethyl acetate (EtOAc) (dark grey) to dichloromethane (less polar, black) are shown in a.) SR NOM I and II b.) NBP, and c.) Station M sites. There is no significant difference between SR NOM I and II with regard to SPE-DOC composition.

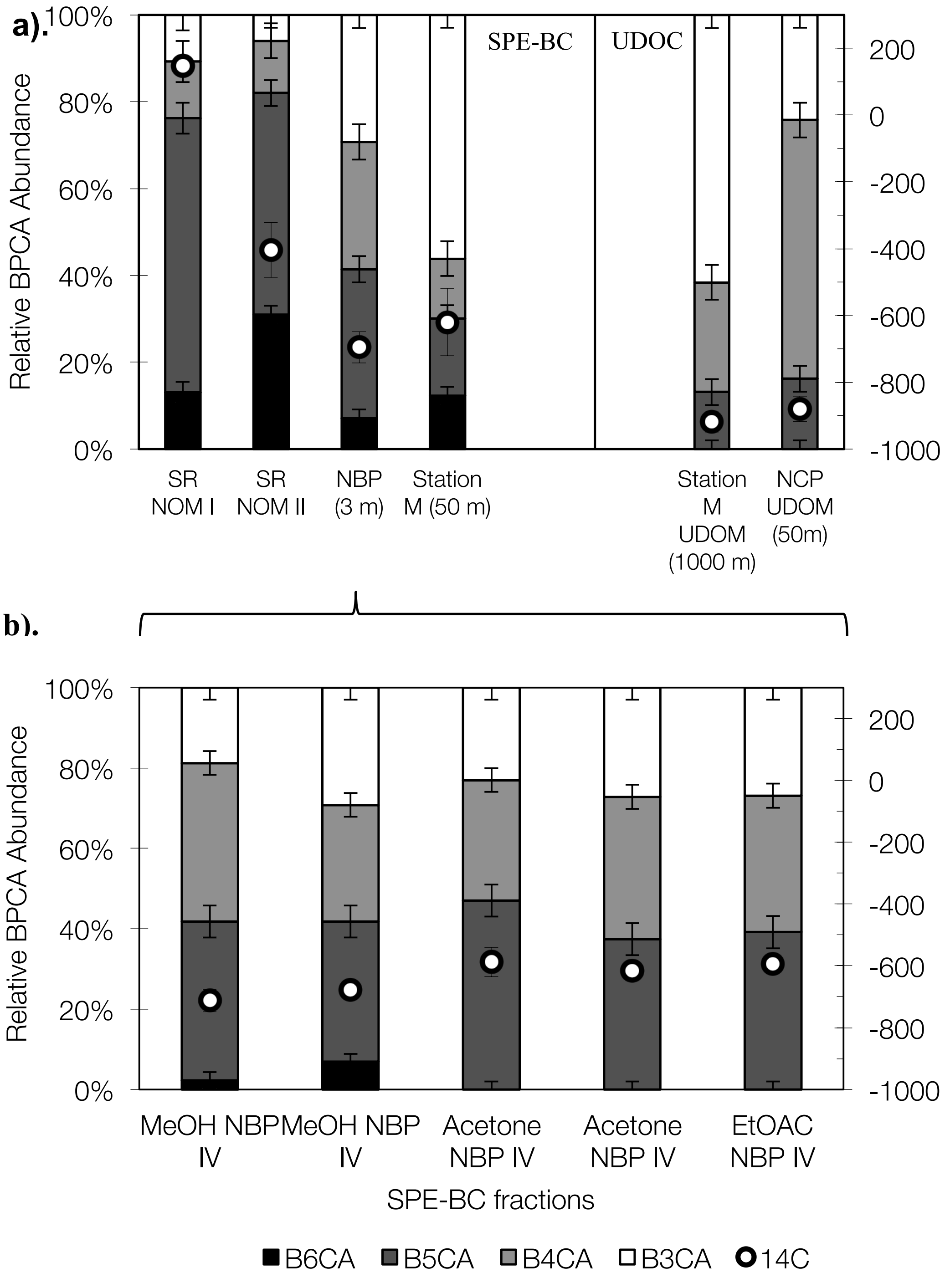

Figure 4.4.a. The relative BPCA abundance and Δ14C values (white circles) of the methanol SPE-BC fractions for SR NOM I, SR NOM II, NBP, Station M SPE-BC. The inset shows UDOC relative BPCA abundances from Ziolkowski and Druffel, (2010) at Station M (1000 m) and the North Central Pacific (50 m) (located 800 km north of Oahu, Hawaii). Surface [BC] in UDOC-BC at NCP is 0.09 μM, and is 0.33±0.05μM in the deep at Station M. b. The relative BPCA abundance and Δ14C values of all SPE-BC (white circles) fractions at NBP.

contribution of B3CAs in SR NOM I and II versus marine SPE-BC (Figure 4.4a). 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 = 4±0.4 μM C). Given the high BC content, we believe this site is influenced by fossil fuels or 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 low Δ^{14}C values of -644±58‰ (Masiello and Druffel, 2001). This may explain the high BC content we observe in NBP (20±2%) samples. This coastal site was expected to have low BC Δ^{14}C values because of possible input from the urban Santa Ana River (greater abundance of B6CAs, much like SR NOM II) (Supplementary Figure 4.1).

Although the SPE-BC Δ^{14}C values are within error at NBP and Station M, the relative BPCA abundances may reveal reprocessing of the oceanic BC pool. We assume BC at Station M is representative of open ocean BC (with no riverine anthropogenic sources), while coastal BC is influenced by anthropogenic riverine BC. The structure of BC at Station M has a greater relative abundance of B3CAs than NBP (Figure 4.4a). This may indicate degradation processes removing aromatic BPCAs with transport to the open ocean (e.g. photo-oxidation; Stubbins et al., 2012). At Station M, we suggest SPE-BC persists 7,800±1,700 ^{14}C yrs in the open ocean. SPE-BC is about 12,000 ^{14}C yrs younger than BC isolated from UDOC at Station M (20,100±3000 ^{14}C yrs; Ziolkowski and Druffel, 2010). However, more measurements are needed to constrain the sources, cycling and ^{14}C age of BC in the global ocean, in particular the apparent differential cycling between SPE-BC and UDOC.

4.5 SUMMARY AND IMPLICATIONS

We report a modified, low-blank SPE method to isolate DOC from fresh and marine water samples. We report that SPE-DOC seawater isolate constitutes nearly half of the DOC pool (43±6%). We present the first $\Delta^{14}C$ blank assessments of the SPE-DOC method from a limited set of river standards and surface ocean water samples. In comparison to total DOC $\Delta^{14}C$ values for these same samples, we found that SPE-DOC $\Delta^{14}C$ are 35 ±10‰ lower than total DOC $\Delta^{14}C$ for freshwater samples. In contrast, marine SPE-DOC $\Delta^{14}C$ values were low, but within error of total DOC $\Delta^{14}C$ values. We observe similar SPE-BC $\Delta^{14}C$ values in our coastal and open ocean sites, but different BPCA relative abundances.

Further measurements are needed to determine BC $\Delta^{14}C$ 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 size of non-polar SPE-DOC, which prevented analysis of relative BPCA abundances and $\Delta^{14}C$ values of non-polar BC at our open ocean site. The use of larger water samples will allow for non-polar BC to be evaluated and placed into the context of total and SPE-DOC ^{14}C ages. Additional research seeking chemically characterize SPE-DOC fractions at the molecular level (e.g nuclear magnetic resonance and Fourier transform ion cyclotron resonance mass spectrometry, FT-ICRMS), which will reveal compositional relationships between SPE-DOC and SPE-BC.

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Supplementary Table 4.1. Resin blanks of solvent passed through the column just previous to sample loading.

SPE-DOC resin blanks	UCID lab code #	Carbon blank size (µg C)	$\Delta^{14}C$ (‰)	±
Methanol	18239[1]	8	-640	7
	17932[1]	16	-905	2
	18351	8	-657	6
	18413[1]	11	-784	2
	18645	2	-674	6
Acetone	17933[1]	8	-602	10
	18352	7	-873	2
	18414	6	-761	4
	18646	2	-617	8
Ethyl Acetate	17667	8	-743	3
	18353	5	-812	3
	18415	6	-767	3
	18647	2	-638	7
	18416	7	-750	4
Dichloromethane	18242	6	-499	14
	17934[2]	8	-796	5
	17241[2]	4	-636	10
Mass balance MQ $\Delta^{14}C$ values (‰)				
			-721	77
			-728	49
			-868	62
			-612	57
			-927	54
$UV_{oxidation}$ Milli-Q $\Delta^{14}C$ values (n=60) range			-612±57	-926±54

[1] Indicates when a duplicate blank was combined

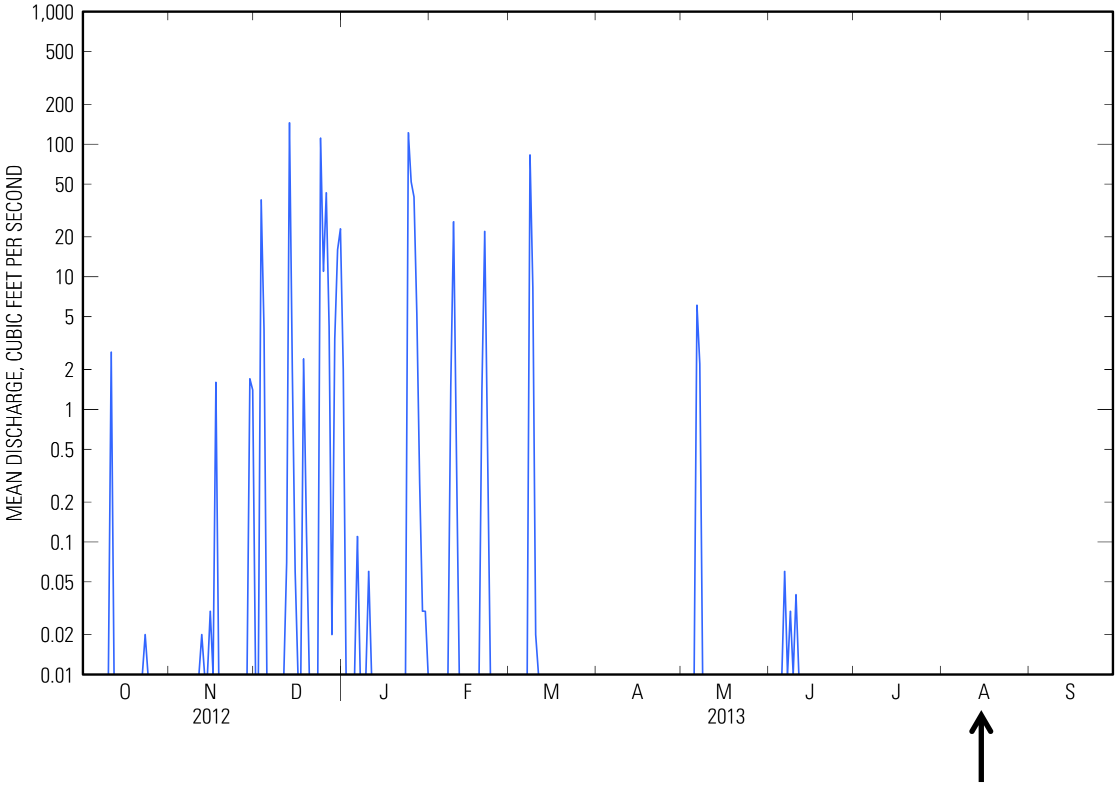
[2] Indicates when an ethyl acetate and dichloromethane blank was combined

Supplementary Table 4.2. Summary of SPE-DOC and BC concentration measurements.

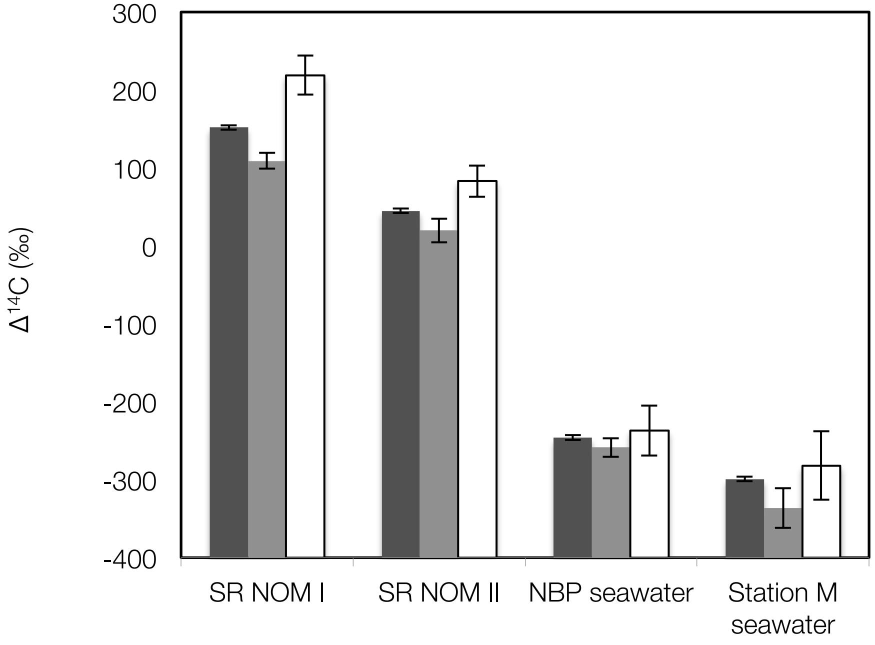
Sample description	SPE-DOC (mg)	BC[1] (mg)	BC/OC (%)	Sample volume (L)	SPE-DOC (μM)	BC (μM)
SR NOM I	13.78	1.4±0.1	10±3	14.5	n/a	n/a
SR NOM II	5.64	0.7±0.2	12±2	14.5	n/a	n/a
	5.04	0.5±0.2	10±2	10.2		
NBP	2.6±0.1	0.5±0.2	20±2	10.7	20±3	4.0±0.4
	4.4±0.1	0.9±0.2	21±2	12.2	30±3	6.5±0.6
Station M	5.1±0.2	0.2±0.1	5±1	14.5	29±2	1.5±0.1
	5.0±0.1	0.2±0.1	4±1	14.5	29±2	1.4±0.1

[1] Determined from flame ionization detector trace chromotographs peak areas using calibration curves of commercially available BPCAs (B3CA-B6CAs).

Supplementary Figure 4.1. Mean discharge in ft^3/s in 2012-2013 from USGS rain gauge hydrological unit 11078000 on the Santa Ana River (33°45 ′04′′N,117°54′27′′ W) in the City of Santa Ana. Sample was collected on August 8, 2013, as indicated by the black arrow. http://wdr.water.usgs.gov/wy2013/pdfs/11078000.2013.pdf?1430786911488



Supplementary Figure 4.2. Δ^{14}C values of total DOC (measured by UV oxidation) (in black), SPE-DOC methanol fractions (in white), and the non-adsorbed DOC (greyscale) determined by mass balance for freshwater SR NOM samples, NBP and Station M seawater samples.



Chapter 5

Black Carbon in the Ocean

Abstract

Black Carbon (BC) is produced from the incomplete combustion of biomass and fossil fuels. The concentration and ^{14}C age of solid phase extracted BC (SPE-BC) in marine dissolved organic carbon (DOC) were investigated to determine the importance of BC in the marine carbon cycle. Solid phase extraction isolated nearly half of DOC (SPE-DOC) for SPE-BC analysis. Here I show that SPE-BC is about 5±2% of the SPE-DOC pool in seawater. The average SPE-BC concentration in the surface ocean is 1.6±0.1 μM and in the deep ocean is 1.2±0.1 μM. The average ^{14}C age of surface SPE-BC is 4,500±1,200 ^{14}C yrs, and is much older in a deep water sample from the Sargasso Sea (23,000±3,000 ^{14}C yrs). SPE-BC Δ^{14}C values were equal to, or older than DOC Δ^{14}C values. The range of SPE-BC structures and Δ^{14}C values suggest that SPE-BC is not homogeneous in the ocean. Results of a simple box model reveal that there are at least two pools of SPE-BC in marine DOC, a younger pool that cycles on centennial timescales and an ancient pool that cycles on >10^5 year timescales.

5.1 INTRODUCTION

Understanding the BC cycle is crucial because it is a slower cycling component of the carbon cycle. As a result of incomplete combustion, the polyaromatic structure of BC has a higher chemical recalcitrance, causing its mean residence time in the environment to be much longer than that for plant biomass carbon (Schmidt et al., 2011). BC persists in soils for decades to millennia (Singh et al., 2014), and is hypothesized to remain in the ocean for millennia as well (Ziolkowski and Druffel, 2010; Masiello and Druffel, 1998).

From the discussion in Chapter 1, there are missing BC sinks in the global BC cycle. Intermediate reservoirs have not yet been identified. The large input by rivers and ^{14}C age offset between BC and non-BC in sediments suggests that BC may be stored in the oceans, namely within the DOC pool (Masiello and Druffel, 1998; Coppola et al., 2014; Jaffé et al., 2013). Although most DOC is produced by photosynthesis of phytoplankton in the surface ocean, the ^{14}C age of deep DOC ranges from 4,000 ^{14}C yrs to 6,000 ^{14}C yrs in the North Atlantic and North Pacific, respectively (Williams and Druffel, 1987; Druffel et al., 1992). The first ^{14}C measurements of oceanic BC was in ultra-filtered DOC (UDOC, 25% of total DOC) samples that showed an average ^{14}C age of marine BC was 20,100±3,000^{14}C yrs (Ziolkowski and Druffel 2010). It was hypothesized that ancient BC may explain the old age of DOC.

The goal of this study is to determine the concentration, structure and Δ^{14}C values of SPE-BC in the open ocean. Here, SPE-BC was measured in a larger portion of the DOC than previous BC measurements had used (e.g. UDOC). I used an SPE method that recovered 43±6% of DOC (SPE-DOC) in this study. SPE-BC was quantified as polycyclic aromatic carbon, determined from Benzene Polycarboxylic Acid (BPCA) marker compounds produced during high-temperature and pressure acidification. The relative BPCA abundances provide qualitative BC structural information. Samples were collected from the Pacific, Arctic and Atlantic oceans for this study.

5.2 METHODS

5.2.1 Sampling locations and collection

Samples were collected from a site in the northeast Pacific, 3 sites in the western Arctic, 2 sites in the North Atlantic, and a site in the southeast Atlantic (Figure 5.1) (Supplementary Table 5.1). Two duplicate northeast Pacific surface (50 m) samples were collected in October 2004 on the Pulse 45 cruise aboard the R/V New Horizon. Western Arctic samples from the Beaufort Sea (~3650–3825 m deep) were collected from adjacent stations (Stn. 40 and 41, 19.4 km apart) taken in October 2012 aboard the R/V Healy (cruise #1203). A coastal Arctic sample (125-175 m deep) was also collected during the cruise. A northeast Atlantic surface (50 m) sample was collected in October 2012 on the A16 cruise aboard the R/V Brown. Two deep (1135-2290 m) and one surface (50 m) sample were collected in the North Atlantic from the Sargasso Sea in April 2012 on the A22 cruise aboard the R/V Atlantis. The deep Sargasso Sea samples were collected from adjacent stations (Stn. 26 and 27, 83.0 km apart) and were processed separately for BC concentration and combined for the BC $\Delta^{14}C$ measurement. A south Atlantic surface (50 m) sample was collected in October 2011 on the A10 cruise aboard the R/V Brown.

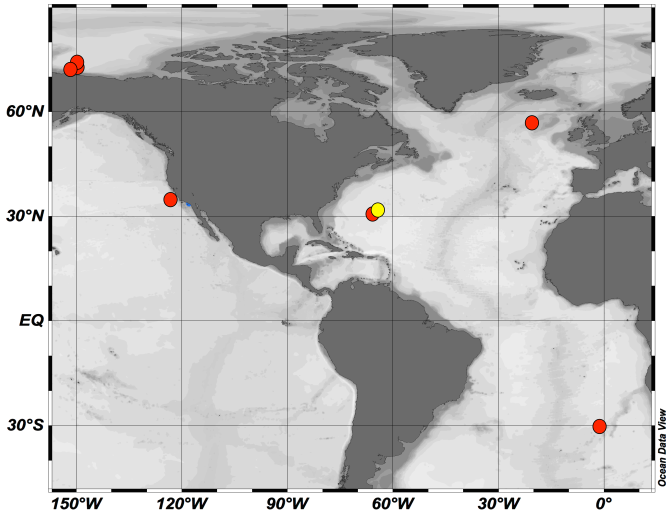


Figure 5.1. Map of sample locations (descriptions in Supplementary Table 5.1). Surface samples (50-175 m) are orange. One deep sample (collected from depths that ranged from 1135-2290 m) is yellow.

All samples were collected in Niskin bottles that had been cleaned at the beginning of each cruise with a dilute detergent solution and 10% hydrochloric acid. Surface samples were filtered using Whatman GF/F filters (0.7 μm) that had been combusted at 500°C for 2 hours. All metal and glassware in this study was cleaned, acidified in 10% HCl, rinsed with deionized water, and combusted for 2 hrs at 500°C before use to remove inorganic and organic carbon. DOC samples were collected in 1 liter amber glass bottles and BC samples were collected in 1 gallon, clear glass bottles. All seawater samples were frozen (at -20°C, at an angle to avoid breakage) until analysis in the laboratory.

5.2.2 Total DOC and SPE-DOC

Seawater samples were measured separately for total DOC using UV-oxidation (Beaupré et al., 2007) and SPE-DOC using methods described in Chapter 4. Briefly, SPE-DOC was extracted from large-volume water samples (10-15 L for surface, 25 L for deep) that had been acidified to pH 2, and siphoned through the resin column at a slow loading rate (2 bed volumes per hour, 30 ml hr^{-1}). In preparation for DOC elution, two bed volumes (30 ml) of Milli-Q water were passed through the column to remove salts and discarded. SPE-DOC was eluted with methanol into pre-combusted glass vials and dried under a stream of ultra-high purity (UHP) nitrogen gas.

5.2.3 BC in SPE-DOC

SPE-DOC methanol extracts were used to isolate BC using the BPCA (benzene polycarboxylic acid) method described in Chapter 4. Briefly, SPE-DOC extracts were dried and lyophilized for 24 hrs. Concentrated nitric acid was added to the sample in a quartz pressure digestion chamber at 170°C for 8 hours to produce BPCAs (Chapter 2). After digestion, the solution was filtered, lyophilized and re-dissolved 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 (diphenic acid). BPCAs were collected on the preparative capillary gas chromatograph (PCGC) (Chapter 2). Calibration curves were made using commercially available BPCAs to quantify the amounts of BPCAs measured from peak areas obtained from the flame ionization detector chromatographs. A BC recovery factor of 23.2±0.4% was used for the conversation of BPCAs to BC (Ziolkowski and Druffel, 2009). For $\Delta^{14}C$ analysis, B3CA through B6CA marker compounds (including nitrated B3CAs) were collected in U-traps (-20°C) in the fraction collector of the PCGC. The B2CA marker compounds were not collected, because they are derived from aromatic compounds of non-combusted origin (e.g. lignin). The BPCAs in the U-trap were transferred using dichloromethane to quartz tubes, and dried under UHP nitrogen gas for isotopic analyses.

5.2.4 Radiocarbon analyses

Samples were sealed in quartz tubes under vacuum with cupric oxide and silver wire. Sample tubes were combusted to CO_2 at 850^oC for 2 hrs. The CO_2 was cryogenically purified, quantified manometrically, and reduced to graphite using a hydrogen reduction method for small samples (<20 µg C) (Santos et al., 2010). Radiocarbon measurements were made at the University of California Irvine Keck Carbon Cycle Accelerator Mass Spectrometry (AMS) Laboratory and are reported as $\Delta^{14}C$ for geochemical samples without known age (Stuiver and Polach, 1977). Errors were determined using an indirect approach as described in Chapter 2 (Coppola et al., 2013). Stable carbon isotopes ($\delta^{13}C$) were measured on equilibrated splits of CO_2 from a subset of the samples using a Gas Bench II and Thermo Electron Delta Plus mass spectrometry with an uncertainty of ±0.2‰.

5.3 RESULTS

5.3.1 SPE-DOC and total DOC $\Delta^{14}C$ values

The SPE-DOC $\Delta^{14}C$ measurements (Table 5.1, Figure 5.2.a) from surface samples ranged from -290±3 in the coastal Arctic to -338±4‰ and Sargasso Sea. This relatively narrow range is comparable to that of the total DOC $\Delta^{14}C$ values (see below). The Beaufort Sea SPE-DOC $\Delta^{14}C$ values were identical at adjacent stations (-294±4 and -299±4‰). The northeast Atlantic, Sargasso Sea and south Atlantic SPE-DOC $\Delta^{14}C$ values were also identical (-330±4, -338±4, and -335±7‰, respectively). Two deep Sargasso Sea samples at Stn. 26 and Stn. 27 had significantly different values (-382±4 and -408±4‰, respectively).

Surface total DOC $\Delta^{14}C$ measurements (Table 5.1, Figure 5.2.a) ranged from -255±3 in the Sargasso Sea to -311±2‰ in the Beaufort Sea, respectively. The total DOC $\Delta^{14}C$ values are significantly higher than their requisite SPE-DOC $\Delta^{14}C$ values in four samples, significantly lower in one sample (Beaufort Sea, Stn. 41) and the same in one sample (Sargasso Sea, Stn. 26).

Table 5.1 Summary of DOC, SPE-DOC and SPE-BC measurements for each site.

			Total DOC					SPE-DOC						SPE-BC					SPE-DOC - SPE-BC	BPCA relative abundances			
Site Description	Cruise Description	Lab code UCID#	[DOC] (μM)	Δ14C (‰)	±	δ13C	±	[SPE-DOC] (μM)	±	Δ14C (‰)	±	δ13C (‰)	±	[BC] in SPE-DOC (μM)	±	BC/OC (%)	Δ14C (‰)	±	ΔΔ14C (‰)	B3CA (%)	B4CA (%)	B5CA (%)	B6CA (%)
Northeast Pacific	Pulse 45 Stn. M (50 m)	18271	71.8	-299	2			32.6	0.2	-327	12	n.m		1.4	0.1	4.2	-615	78	289	56	14	18	12
Coastal Arctic	Healy Stn.29 (125-175 m)	18955	60.6	n.m		-23	0.2	25.9	0.6	-290	3	-23.8	0.2	1.6	0.1	6.2	-824	5	534	30	36	19	16
Beaufort Sea Arctic Stn. 40	Healy Stn. 40 (125-175 m)	18936	54.9	n.m		-22.6	0.2	26.9	2.3	-299	4	-23.9	0.2	1.7	0.7	6.3	-262	115	-37	24	59	17	0
Beaufort Sea Arctic Stn.41	Healy Stn. 41 (125-175 m)	18998	54.9	-311	2	-22.8	0.2	30.2	2.3	-294	4	-23.7	0.2	2.6	0.9	8.6	-307	200	13	22	56	22	0
Northeast Atlantic	A16N Stn.16 (50 m)	19045	53.8	-302	2	n.m		27.7	0.5	-330	4	-23.2	0.2	1.6	0.1	5.6	-459	70	129	32	49	14	6
Sargasso Sea	A22 Stn.27 (50 m)	19117	64.0	-255	3	-20.7	0.2	35.1	0.5	-338	4	-23.2	0.2	1.9	0.3	5.5	-116	162	-222	22	56	22	0
South Atlantic	A10 Stn.35 (50 m)	18359	60.0	-272	2	-20.4	0.2	30.1	0.5	-335	7	n.m		2.5	0.4	8.2	-474	120	139	44	13	41	0
Deep Sargasso Sea ŧ	A22 Stn.26 (1700- 2250 m)	19142	42.1	-386	2	-21.3	0.2	22.1	1.0	-382	4	-24.5	0.2	1.2	0.1	5.2	-945	6	550	24	59	17	0
	A22 Stn.27 (1135-2290 m)	19148	n.m	n.m		n.m		23.5	1.0	-408	4	-22.7	0.2										

ŧDeep Sargasso Sea samples were isolated and analyzed for SPE-DOC concentration, $\delta^{13}C$ and $\Delta^{14}C$ separately. The 2 SPE-DOC samples were combined to obtain a single SPE-BC concentration and $\Delta^{14}C$ value. The two water sample locations were 30 km apart.

n.m. indicates the sample was not measured.

5.3.2 SPE-DOC and total DOC $\delta^{13}C$ values

SPE-DOC $\delta^{13}C$ and total DOC $\delta^{13}C$ measurements are shown in Table 5.1 and Supplementary Figure 5.1. Surface SPE-DOC $\delta^{13}C$ values ranged from -23.2 to -23.9‰, with an average value of -23.6±0.6‰ (n=7). The SPE-DOC $\delta^{13}C$ values of samples from adjacent stations in the deep Sargasso Sea were statistically different (-24.5 and -22.7‰). Total DOC $\delta^{13}C$ values ranged from -20.4±0.2 to -22.8±0.2‰ and were 1-3‰ higher than their respective SPE-DOC $\delta^{13}C$ values (Supplementary Figure 5.1). Also, both the total DOC and SPE-DOC $\delta^{13}C$ values in the Atlantic surface samples were significantly higher than the Arctic surface samples.

5.3.3 BC concentration in SPE-DOC (SPE-BC)

The concentration of BC was measured in SPE-DOC samples and is referred to as SPE-BC concentration (Table 5.1, Figure 5.2.b). SPE-BC concentrations in the surface samples ranged from 1.4 to 2.6 µM. The lowest surface SPE-BC concentration was in the northeast Pacific. The highest measured surface SPE-BC concentrations were in the Beaufort Sea and south Atlantic (2.6±0.9 and 2.5±0.4 µM, respectively). For all surface ocean samples, the average SPE-BC concentration was 1.6±0.1 µM. The coastal Arctic sample was excluded in this average because it was not an open ocean sample. The deep sample in the Sargasso Sea had a SPE-BC concentration of 1.2±0.1 µM.

5.3.4 BC $\Delta^{14}C$ values

Surface SPE-BC $\Delta^{14}C$ values ranged from -116±162 (Sargasso Sea) to -824±5‰ (coastal Arctic) (Figure 5.2.a). The open ocean average surface $\Delta^{14}C$ BC value was -430±44‰ (n=6) (4,500±1,200 ^{14}C yrs). The coastal Arctic sample was excluded in this average because it was not an open ocean sample. The surface northeast Pacific SPE-BC $\Delta^{14}C$ measurements of duplicate water samples were identical (-649±121 and -592±102‰). Beaufort Sea SPE-BC $\Delta^{14}C$ values at adjacent sites were also identical (-262±115 and -307±200‰) (Figure 5.2.a). The deep Sargasso Sea sample revealed an SPE-BC $\Delta^{14}C$ measurement (-945±6‰, 23,000±3,000 ^{14}C yrs) that was the lowest value obtained in this study.

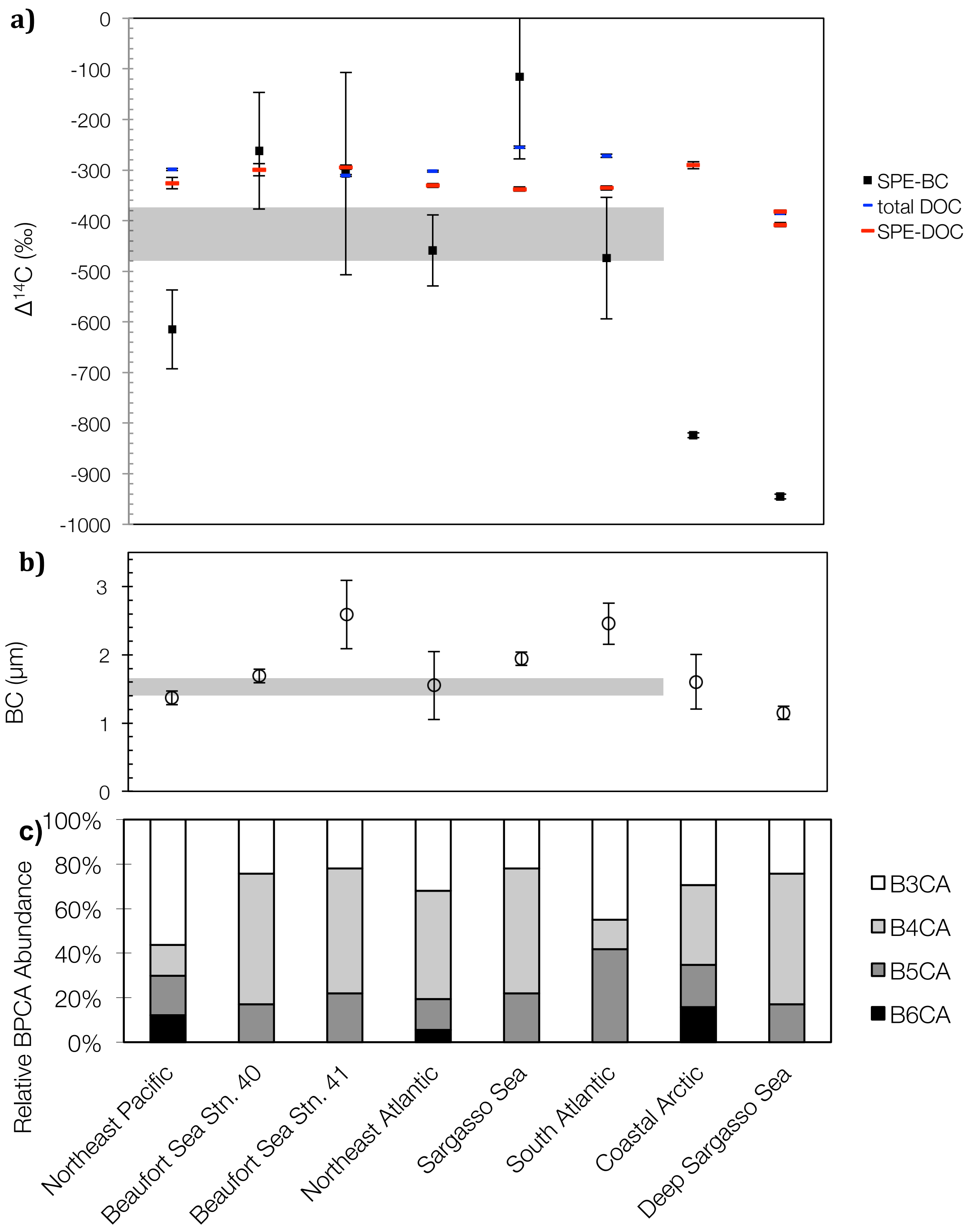


Figure 5.2.a. $\Delta^{14}C$ values of SPE-DOC (red dashes), total DOC (blue dashes) and SPE-BC (black squares) samples. All samples are from the surface, except the deep Sargasso Sea sample. The average SPE-BC $\Delta^{14}C$ value for the surface ocean (excluding the coastal Arctic) is -430±44‰ and is displayed as the grey box. b. SPE-BC concentration values. The average SPE-BC concentration for the surface samples is 1.6±0.1‰ and is displayed as the grey box. c. Relative BPCA abundances in each SPE-BC sample.

5.3.5 BC structure from relative BPCA abundances

For most SPE-BC samples, B3CAs and B4CAs were more abundant than the B5CAs and B6CAs (Figure 5.2.c). The more aromatically-condensed B5CA and B6CA marker compounds constituted 15-30% of the BPCAs. Higher relative abundances of B3CAs were observed in the northeast Pacific and south Atlantic samples. Northeast Pacific and coastal Arctic SPE-BC samples had greater relative abundances of B5CAs and B6CAs (35±4%). B6CAs were present only in the northeast Pacific, coastal Arctic and northeast Atlantic samples (6–16%). The south Atlantic sample had the highest relative abundance of B5CAs (44±3%) (Figure 5.2.c). Overall, the SPE-BC structure is less aromatically condensed than those in riverine, sedimentary and sinking particulate BC (Chapters 3 and 4) pools.

5.4 DISCUSSION

The discussion addresses the new paradigms that are revealed about BC cycling in marine DOC. The first section addresses the hypothesis that DOC contained ancient BC and that this ancient BC was responsible was responsible for the old ^{14}C age of DOC. I find that the average SPE-BC in the surface ocean is significantly older than SPE-DOC. However, at some sites, SPE-BC Δ^{14}C values are equal to or higher than their SPE-DOC Δ^{14}C counterpart. This indicates that SPE-BC is not homogeneous in the ocean. The second section uses a model to confirm that BC contains at least two pools with distinct ^{14}C ages. The third section discusses the paradigm shifts that are revealed about the cycling of BC in marine DOC (Table 5.2).

Old Paradigm (from UDOC measurements)	New Paradigm (this work, SPE-DOC)
BC in may explain the old age of DOC	BC in SPE-DOC is not abundant enough to explain the entire aged component of DOC
BC is chemically indistinct in the ocean in the surface and deep	BC is chemically distinct in the ocean
BC is 17,000-20,100 ^{14}C yrs in the surface and the deep ocean. There is not a large range in the ^{14}C ages of oceanic BC	The SPE-BC is 4,500 ^{14}C yrs (average) and 23,000 ^{14}C yrs in the surface and deep, respectively
All oceanic BC has similar, less aromatic structures	There are variations of BC structure in all ocean sites
BC in UDOC was expected to be younger than the BC that was not sampled in low molecular weight DOC pool.	BC in UDOC is older than SPE-BC.

Table 5.2 Old and new paradigms for BC cycling in the ocean using SPE and UDOC BC Δ^{14}C measurements . The old paradigm for ^{14}C age is based on BC ^{14}C measurements of UDOC (only 25% of the DOC pool, high molecular weight) (Ziolkowski and Druffel, 2010).

5.4.1 BC as the old component of DOC

The aged DOC component in the deep sea has an average concentration of ~35 μM and a Δ^{14}C value of -525‰ (Williams and Druffel, 1987). This aged component in DOC appeared to survive multiple cycles of deep ocean circulation. The composition of this aged DOC is only 10% identified and contains protein, carbohydrate and lipid compounds (Loh et al., 2004). It was hypothesized that BC could be the ancient component of DOC responsible for the old age of total DOC in the deep sea (Ziolkowski and Druffel 2010).

Based on the concentration and Δ^{14}C value of SPE-BC in the deep Sargasso Sea (1.2 µM, and -945‰), BC cannot explain the low Δ^{14}C value of SPE-DOC (20 µM, and -395‰). If SPE-BC were not present in SPE-DOC, the Δ^{14}C of SPE-DOC in the deep Sargasso Sea would be only 35‰ higher than its present value or -360‰ (-395‰ = 1.2µM/20µM*(-945‰) + 18.8µM/20µM*x). Clearly, other old components must be present in DOC to account for its great ^{14}C age.

On a per site basis, the Δ^{14}C differences between SPE-BC and SPE-DOC Δ^{14}C values ($\Delta\Delta^{14}$C = SPE-DOC Δ^{14}C minus SPE-BC Δ^{14}C) range from -222‰ to +550‰ (Table 5.1). SPE-BC in the coastal Arctic and deep Sargasso Sea are the oldest component of DOC yet identified. However, the Beaufort Sea and Sargasso Sea have SPE-BC Δ^{14}C values that are higher than their SPE-DOC counterpart ($\Delta\Delta^{14}$C = -37 and -222‰, respectively). This wide range indicates that SPE-BC is not homogeneous in the ocean, as was previously believed (Ziolkowski and Druffel, 2010) (Table 5.2).

It is important to remember that the BC in seawater that was not adsorbed onto the resin (54%) was not measured in this study (Chapter 4). However, if the BC concentration in DOC that was not captured by SPE, was the same as that in the SPE-DOC, then the BC concentration in total DOC would be about 3.4 µM in the surface ocean. Presently, the distribution of BC in total DOC is unknown. If it were assumed that the global ocean has similar SPE-BC and SPE-DOC concentrations as those found in our study, the BC pool would be estimated at 14±2 Gt C in the global SPE-DOC pool (662 Gt C DOC*0.43*0.05 = 14 Gt C).

5.4.2 Models describing oceanic BC

A simple box model for BC was constructed to assess the residence time of BC in the surface ocean. The model had a surface and a deep ocean box. Mixing between the two boxes was based on the average ocean-overturning rate. BC sources to the surface box were from atmospheric deposition and river inputs. BC losses in the model were from photo-oxidation in the surface and deposition to sediments (Supplementary Materials 5.2). The box model was solved at steady state. As expected, the amounts of BC in the surface and deep boxes were in good agreement with observations (Supplementary Materials 5.2). The isotopic content of BC calculated by the box model did not match the BC $\Delta^{14}C$ measurements. The modeled surface and deep BC $\Delta^{14}C$ values were -308‰ and -329‰, respectively (2,960 ^{14}C yrs and 3,200 ^{14}C yrs). The modeled $\Delta^{14}C$ value of BC in the deep box is far higher than the measurement (-945‰, 23,000±3,000 ^{14}C yrs) reported in this study. Clearly, it is not possible to model BC as a homogenous pool with a single $\Delta^{14}C$ value.

A Keeling plot suggests that there are multiple pools of BC in the ocean. A Keeling plot model uses a linear II regression to evaluate the SPE-BC measurements for consistency with a two-pool system. The y-intercept in the Keeling plot is the excess BC component that is added to the background aged BC pool (Supplementary Materials 5.1). The Keeling plot for BC $\Delta^{14}C$ vs. $[BC]^{-1}$ is shown in Figure 5.3.

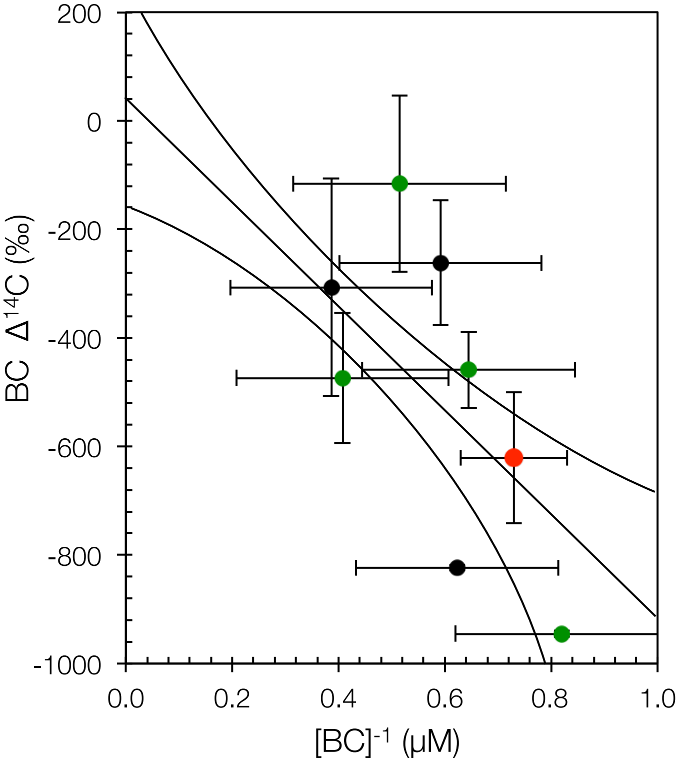


Figure 5.3. Keeling plot that shows $[BC]^{-1}$ vs. SPE-BC $\Delta^{14}C$. Samples from the Atlantic are green, Pacific are red and Arctic are black. A Model II regression was used to estimate the y-intercept of the regression line (see Supplementary Materials 5.1). The black line represents the least squares fit to all of the data shown. Curve lines are the error bars of the linear fit.

The y-intercept is +58±207‰, and reflects the $\Delta^{14}C$ value of excess BC added to an aged background BC pool (-945±5‰). This method assumes simple mixing between two homogenous pools, with only modern inputs, mixing of water masses by advection and no compositional changes over time. This correlation implies that BC may also follow the same mixing as DOC with modern and aged components. It appears that oceanic BC is heterogeneous and contains at least two pools that have distinct $\Delta^{14}C$ values. In addition, the large error of the y-intercept of the Keeling plot (Figure 5.4) suggests that BC may have multiple pools in the ocean or be the result of a limited data set.

5.4.3 New Paradigm for BC cycling in marine DOC

There are multiple pools of BC in the ocean each with distinct residence times (defined here as ^{14}C ages). This scenario is observed in soils where there are multiple BC pools with distinct chemical compositions and residence times. The residence times of BC in soils range from weeks to millennia based on BC structure (Singh et al., 2014; Bird et al., 2015; Knicker et al., 2013). If BC is coupled to riverine DOC export (Jaffé et al., 2013; Ding et al., 2014; Wagner et al., 2015), these BC pools with different structures and residence times may be preserved in the ocean. This may explain the range of BC structures that we observed.

As presented earlier (Chapter 1), the main sources of BC to the ocean are rivers and aerosols. BC from these sources has different physical properties and structures that likely affect their residence times in the ocean. The ranges of BC structures from BPCA relative abundances (Figure 5.2.c) and BC Δ^{14}C values (Figure 5.2.a) in SPE-DOC suggest that the oceanic BC pool is heterogeneous. Biosphere-derived BC may be more important in some regions (e.g. Sargasso Sea) than others (e.g. South Pacific). There are at least two BC pools, a semi-liable pool and a stable (or refractory) pool (>23,000 ^{14}C yrs). The semi-labile BC pool contains, in part, recent biosphere-derived BC that was rapidly transported to the oceans by rivers and contains bomb ^{14}C. The semi-labile BC pool likely dominates regions with high DOC fluxes from rivers (Myers-Pigg et al., 2015; Ziolkowski and Druffel, 2010).

It appears that an older, more stable BC pool exists in the deep ocean. Two recent studies show that UV-oxidation removes larger aromatic BC compounds, leaving less aromatically condensed BC that would re-associate with low molecular weight DOC size fractions (Stubbins et al., 2012; Wagner and Jaffé, 2015). BC with even longer residence times (>20,000) likely dominates the deep ocean (this work; Ziolkowski and Druffel, 2010).

5.5 CONCLUSIONS

The average ^{14}C age of SPE-BC is older than those of SPE-DOC and total DOC. Aged BC cycles in DOC for 4,500 to 23,000 ^{14}C yrs and explains, in part, but not the entire low Δ^{14}C value of total DOC. However, surface BC was significantly younger than the SPE-DOC in the Beaufort and Sargasso Sea. This suggests that SPE-BC is not a homogenous pool with one residence time, as was previous believed (Ziolkowski and Druffel, 2010). I hypothesize that oceanic BC is heterogeneous and contains multiple pools with distinct residence times.

The mass of BC in SPE-DOC is estimated at 14±2 Gt BC. This value is similar to that reported by Dittmar and Paeng (2009) (12 Gt). My estimate does not include 57% of the BC pool, because it was not sorbed onto the SPE resin. If BC is unequally distributed in the non-SPE-DOC pool, then our estimate of BC in the DOC pool will change. It is possible that the BC concentration in the non-SPE DOC is much higher than that in the SPE-DOC. Direct comparisons of BC Δ^{14}C values and BC structure between high and low molecular weight BC are needed. Additionally, riverine BC Δ^{14}C and concentration measurements will offer a greater understanding of the input and fate of BC in the DOC pool from watersheds to the deep ocean.

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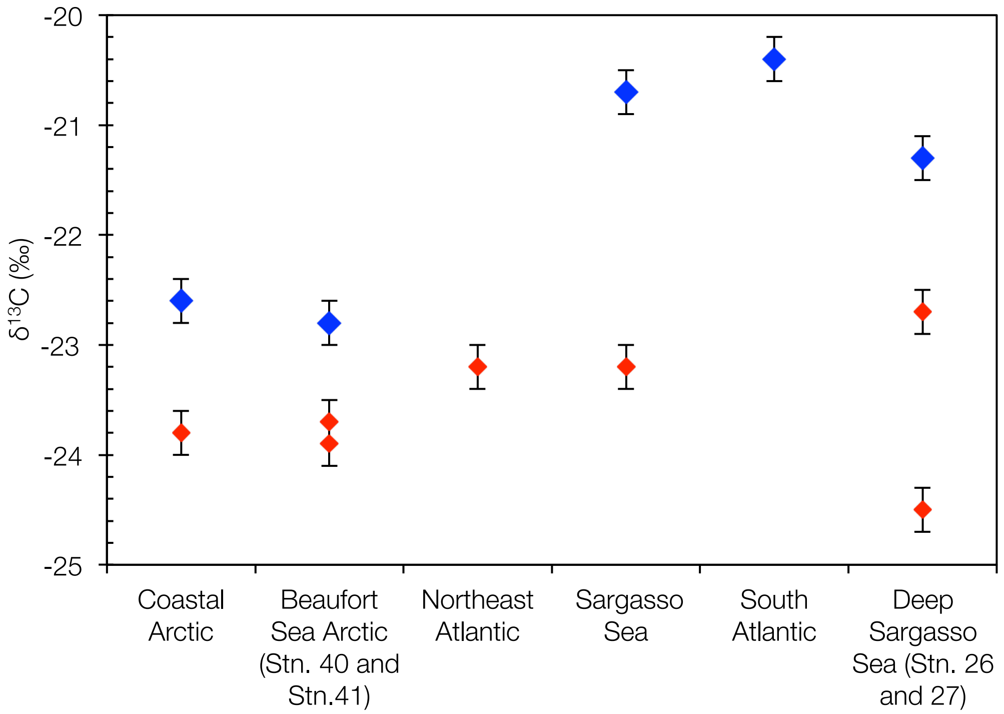
Supplementary Table 5.1. Site descriptions for sample collection.

Site Description	Cruise Description	Depth (m)	Latitude	Longitude	Date	Ship
Northeast Pacific	Pulse 45	50	34°50'N	123°00'W	27-Oct-04	R/V New Horizon
Coastal Arctic	Healy Stn.29	125-175	71°26.01'N	152°2.5'W	12-Oct-12	R/V Healy
Beaufort Sea Arctic	Healy Stn. 41	125-175	72°29.61'N	151°4.58'W	12-Oct-12	R/V Healy
Beaufort Sea Arctic	Healy Stn. 40	125-175	72°39.57'N	150°53.56'W	12-Oct-12	R/V Healy
Northeast Atlantic	A16N Stn.16	50	57°30.01'N	19°59.965'W	7-Aug-13	R/V NOAA Ronald Brown
Sargasso Sea	A22 Stn.27	50	31°54.45'N	65°2.76'W	1-Apr-12	R/V Atlantis
South Atlantic	A10 Stn.35	50	29°59.99'S	1°37.98'W	6-Oct-11	R/V NOAA Ronald Brown
Deep Sargasso Sea	A22 Stn.26	1770-2250	32°38.85'N	64°55.73'W	1-Apr-12	R/V Atlantis
Deep Sargasso Sea	A22 Stn.27	1135-2290	31°55.05'N	65°2.76'W	1-Apr-12	R/V Atlantis



Supplementary Figure 5.1 The $\delta^{13}C$ values for SPE-DOC and total DOC samples. SPE-DOC $\delta^{13}C$ values are red, and total DOC $\delta^{13}C$ values are blue.

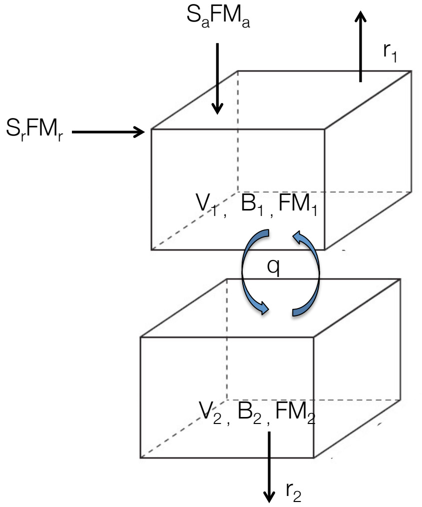
Supplementary Material 5.1. Keeling plots

SPE-BC concentration and $\Delta^{14}C$ measurements include large uncertainties, so correlations in the data were analyzed using the geometric mean approach for model-II least-squares linear regressions (Edward Pelzer, 2009 http://www.mbari.org/staff/etp3/regress.htm). The geometric mean slopes were found by dividing the slopes of Model-I regressions by their correlation coefficients. Geometric mean intercepts were calculated by solving the equation y=mx+b using the geometric mean slopes and average values of all respective x and y data (Beaupre and Aluwihare, 2010). The regression analysis in Eq. 1 was used:

$$DOC_z = (1/[DOC]_z)([DOC]_{bkgrd}\,\Delta^{14}DOC_{bkgrd} - [DOC]_{bkgrd}\,\Delta^{14}DOC_{xs}) + \Delta^{14}C_{xs} \qquad \text{(Eq. 1)}$$

where DOC concentration and $\Delta^{14}C$ at depth z ($[DOC]_{z,}\,\Delta^{14}DOC_z$) contains an older, relatively constant background component ($[DOC]_{bkgd}\,\Delta^{14}DOC_{bkgd}$) with an excess of modern DOC added at the surface ($[DOC]_{xs}\,\Delta^{14}DOC_{xs}$). The y-intercept of the plot is the excess DOC $\Delta^{14}C$ value.

Supplementary Materials 5.2. Simple BC box model



The box model's boundary conditions were based on previous studies (Figure 1.1). The lifetime of BC was chosen to agree with observations. The ocean model has a surface box (0-50m, volume$_1$=1.80x10^{16} m^3) and a deep box (50-4000 m, Volume$_2$=1.31x10^{18}m^3). The mixing exchange is described as q between the two boxes (q=100 Sv from estimations in Brocker, 1990). The surface box fluxes are from the atmosphere and rivers (S_a and S_r) and the deep ocean (Eq. 2 and 3) (using Jaffé et al., 2013 and Jurado et al., 2008 estimates). The only loss in the surface box is photo-oxidation (r_1) (Stubbins et al., 2012). The deep box has sources from mixing with the surface box (Eq. 4 and 5) and a loss by deposition to sediments (r_2) (Chapter 3). Equations 2 through 5 describe the BC concentration and Δ^{14}C values in the surface (B_1, FM_1) and deep (B_2, FM_2):

$$\frac{d}{dt}(V_1B_1) = S_a + S_r - qB_1 + qB_2 - r_1B_1 \qquad \text{(Eq. 2)}$$

$$\frac{d}{dt}(V_1B_1FM_1) = S_aFM_a + S_rFM_r - qB_1FM_1 + qB_2FM_2 - r_1B_1FM_1 - \lambda B_1FM_1 \qquad \text{(Eq. 3)}$$

$$\frac{d}{dt}(V_2B_2) = +qB_1 - qB_2 - r_2B_2 \qquad \text{(Eq. 4)}$$

$$\frac{d}{dt}(V_2B_2FM_2) = +qB_1FM_1 - qB_2FM_2 - r_2B_2FM_2 - \lambda B_2FM_2 \qquad \text{(Eq. 5)}$$

where V_1 and V_2 are the volumes for the surface and deep boxes, respectively, and losses by ^{14}C decay are described by λ. The system is assumed to be in steady state ($\frac{d}{dt} = 0$) to estimate the lifetime of BC in the ocean. The boundary conditions of the model are listed below.

Variable	Value
V_1	1.80×10^{16} m^3
V_2	1.31×10^{18} m^3
S_a	26×10^{12} g BC yr^{-1}
S_r	6×10^{12} g BC yr^{-1}
FM_a	0.10
FM_r	0.65
r_1	1/460 m yr^{-1}
r_2	1/460 m yr^{-1}
q	$100\times10^6\times3.15\times10^7$ m s^{-1} (100 Sv)
λ	Ln(2)/5730 yr^{-1}

Chapter 6

Conclusions and Future Research

6.1 SUMMARY

This dissertation addressed the role of BC in the oceanic carbon cycle. It was hypothesized that the DOC pool was an intermediate reservoir for ancient BC before deposition to sediments (Masiello and Druffel, 1998), and thus was responsible for the old age of DOC. By measuring BC in nearly half of DOC, I found that the SPE-BC pool is ~14±2 Gt C. This shows that SPE-DOC does not contain the entire missing BC sink. Updated estimates of sources and sinks, and methods that allow the analysis of 100% of the BC in DOC, are needed to understand the fate of BC in the ocean.

Chapter 2 presented a modified BPCA method for analysis of BC concentration and $\Delta^{14}C$ values in ocean sediments (Coppola et al., 2013). This study highlighted the indirect method to assess the total uncertainty of sample processing using several BC standards. Although processing dead and modern BC standards is time consuming, it is critical for $\Delta^{14}C$ measurements of sediment samples smaller than 50 μg C.

Chapter 3 presented an assessment of BC in multiple carbon pools to determine the source of BC to abyssal marine sediments in the northeast Pacific (Coppola et al., 2014).

The average ^{14}C age of BC was older (by 6,200±2,200 ^{14}C yrs) than that of the concurrently deposited non-BC SOC. Sinking POC from the deep ocean provided an important transport mechanism of BC from the water column to the sediments (Figure 6.1). Aged BC is incorporated into POC from both resuspended sediments and sorption onto POC. The BC flux estimate represents ~8–16% of the global burial flux of organic carbon to abyssal sediments and constitutes a minimum long-term removal estimate of 6–32% of biomass-derived BC using the present day emission flux.

An SPE method was modified for isolating nearly half of DOC from seawater in Chapter 4 (Coppola et al., in revision). Most SPE-BC Δ^{14}C values were lower than total DOC Δ^{14}C values. This first study demonstrated that SPE-BC cycles on longer timescales than other components of DOC in the northeast Pacific. This assessment revealed that BC is 5±2% (1.4±0.1 μM BC) of SPE-DOC in the surface northeast Pacific ocean.

In Chapter 5, I found that the average concentration of SPE-BC in surface waters from the Pacific, Arctic and Atlantic Oceans is 5±2%. SPE-BC in the surface ocean has an average ^{14}C age of 4,500±1,200 ^{14}C yrs. SPE-BC in the deep Sargasso Sea (2200 m) is 23,000±3,000 ^{14}C yrs. These ^{14}C ages are in stark contrast to the modern ^{14}C ages of phytoplankton, which is the primary source of carbon to DOC. Yet, it is still unknown what causes the ^{14}C age of DOC to be much older than expected given the inputs at the surface. Nonetheless, SPE-BC is not present in large enough quantities to explain the old SPE-DOC age (2,600±600 ^{14}C yrs) (Figure 6.1). I estimate that 14±2 Gt BC is contained in the SPE-DOC pool of the major oceans.

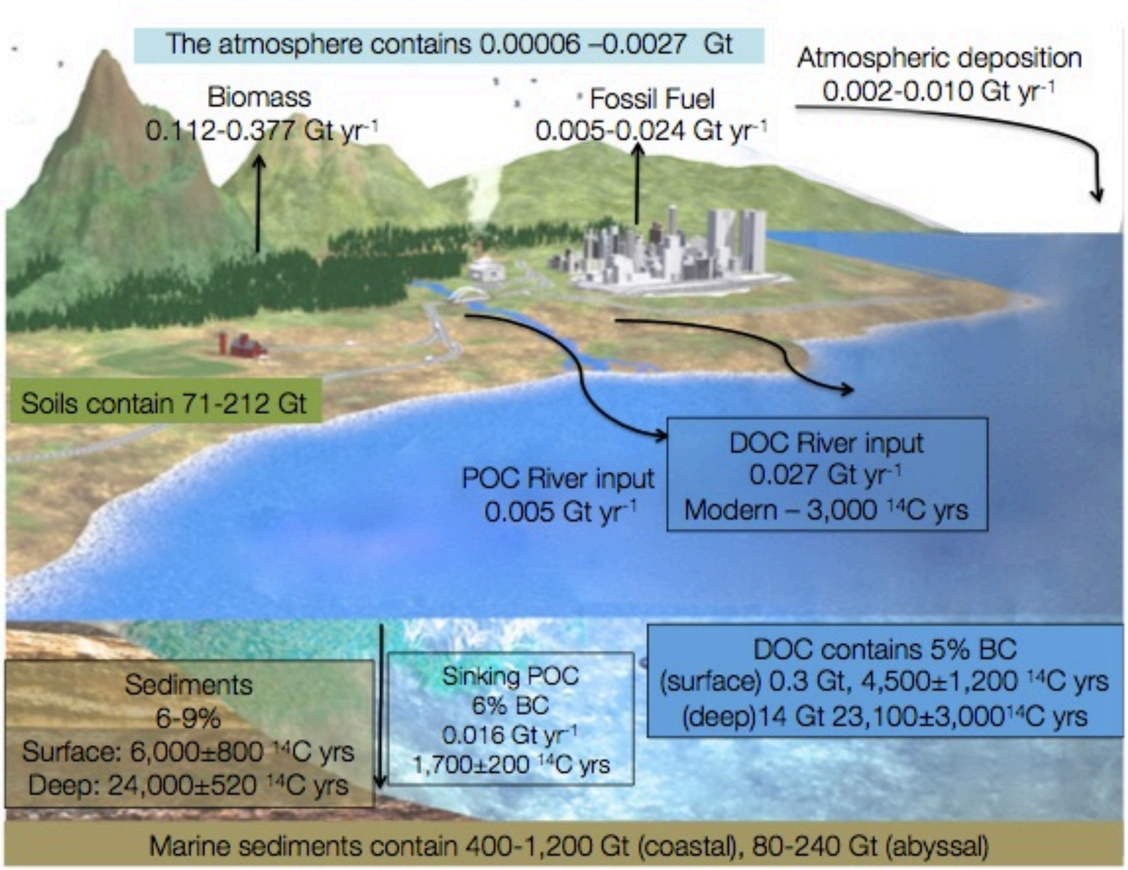


Figure 6.1 BC cycle in the Earth system. Estimates outlined in black boxes are from this dissertation. BC estimates are from the literature (Mouteva et al., (in prep), Santín et al., 2015; Penner et al., 1993; Bond et al., 2013; Jaffé et al., 2013; Masiello, 2004).

6.2 FUTURE RESEARCH

There are major gaps that remain in our understanding of the BC cycle. Several research questions that emerge from this dissertation are discussed below and are offered as guidance to researchers for future work.

1. What are the residence times of the multiple BC pools in the ocean?

This question can be addressed by incorporating BC measurements into a more detailed ocean box model. The simple box model used in Chapter 5 had a single, homogeneous BC pool, and the model severely underestimated the BC ^{14}C ages in the deep water. An improved model would include multiple pools of BC that have distinct ^{14}C ages that range from 1 to >10^4 yrs for BC pools in the surface and deep ocean. Also, these modeling studies could vary the BC amount and Δ^{14}C value from rivers and aerosols to the ocean. BC source variations may reveal local influences that may explain the range of observed BC Δ^{14}C values in the surface ocean.

2. What is the concentration and ^{14}C age of BC in the DOC not sorbed by SPE?

Differential cycling of BC within DOC should be investigated. In river systems, BC is unequally distributed across dissolved organic matter size fractions (Wagner and Jaffé, 2015). BC may also be unequally distributed within the oceanic non-SPE-DOC pool. A limitation of this study is that the estimate of BC abundance does not include 57% of the DOC pool that was not sorbed by the SPE method.

The ^{14}C ages of the multiple pools of BC can be investigated directly using a variety of techniques. For example, size exclusion chromatography, in conjunction with measurements of BC structure, concentration and $\Delta^{14}C$ in each DOC size fraction would reveal how BC is distributed in oceanic DOC. Another method, reverse osmosis coupled to electrodialysis (RO/ED), could be used to isolate 75-82% of the DOC pool (Green et al., 2014). This method can measure the abundance and $\Delta^{14}C$ of the majority of DOC for near-total BC. RO/ED was not used in this study because the method is expensive, time-intensive, and has lower a lower purity (Green et al., 2014).

3. How is non-polar BC distributed in SPE-DOC?

A limitation of this work was the insufficient sample sizes of non-polar SPE-DOC fractions. This prevented analyses of BC structure, concentration, and $\Delta^{14}C$ values of non-polar BC. At present, limited quantities of frozen seawater are shipped to the shore-based laboratory for SPE extraction. Loading a greater volume of seawater onto the SPE resin onboard ship would allow for larger SPE-DOC and BC samples to be analyzed. Larger SPE-DOC samples would also allow for non-polar BC to be collected in large enough sizes for analysis..

Loading samples at sea would also allow for more samples to be collected and provide greater spatial coverage of BC concentration, relative BPCA abundances and $\Delta^{14}C$

measurements. More measurements would improve our understanding of the complexity of BC cycling since BC is not uniform in the ocean (Chapter 5). Additionally, SPE-DOC extracts could be concentrated on quartz filters for $\Delta^{14}C$ inter-comparisons using a separate method for BC analysis (e.g. via a thermal-optical aerosol analyzer coupled to a vacuum line for $\Delta^{14}C$ analysis of each BC fraction oxidized to CO_2) (Mouteva et al., 2015).

4. What are the major losses of BC?

Burial in marine sediments is considered the primary fate of BC, yet only 8-16% of the annual production of BC is accounted for in marine sediments (Masiello, 2004; Chapter 3). This dissertation investigated the ocean as a holding pool for BC, in an effort to explain why the sources of BC outweighed the sinks of BC. However, more confidence in the BC fluxes to the ocean would reveal if truly there is a missing BC reservoir, or if estimates of sinks are incorrect. BC fluxes from river systems to the ocean are poorly understood processes for BC delivery to the ocean (Wagner et al., 2015; Myers-Pigg et al., 2015).

A major gap in our understanding of the marine BC cycle is the $\Delta^{14}C$ value and structure of BC entering the ocean. This work suggests that not all BC entering the ocean from rivers is modern and aromatically condensed, as was previously believed (see Chapter 4). Surveying the DOC $\Delta^{14}C$ values of major rivers would help to understand BC $\Delta^{14}C$ variations to the surface ocean. Studying BC in all major rivers could also help to quantify the transport of fossil fuel-derived BC to the ocean.

Research investigating losses of BC along a river-to-ocean transect would provide insight into the mechanisms that remove BC in estuarine systems. A potential loss of BC may occur in rivers by the addition of liable substrates in river plumes that may enhance decomposition of recalcitrant BC, so-called 'priming' (Bianchi, 2011). This process occurs in soils to utilize BC (Kuzyakov et al., 2009).

Another sink of BC in the ocean is UV degradation in surface waters. The current estimate of BC loss by UV oxidation (Stubbins et al., 2012; Stubbins et al., 2015) seems too large, however, because it does not agree with the apparent age of BC and concentration in the ocean (Chapter 5; Ziolkowksi and Druffel, 2010).

In closing, this is the first work presenting SPE-BC Δ^{14}C measurements of seawater in the major ocean basins. Measurements of intermediate reservoirs of BC combined with modeling studies will improve our understanding of the budget of BC going forward.

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