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## Aged black carbon identified in marine dissolved organic carbon

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[1] Produced on land by incomplete combustion of organic matter, black carbon (BC) enters the ocean by aerosol and river deposition. It has been postulated that BC resides in the marine dissolved organic carbon (DOC) pool before sedimentary deposition and may attribute to its great <sup>14</sup>C age (1500–6500 <sup>14</sup>C years). Here we report the first radiocarbon measurements of BC in high molecular weight DOC (UDOM). BC exported from rivers is highly aromatic and <500 <sup>14</sup>C years old, while open ocean samples contain less aromatic BC and have an age of 18,000 ± 3,000 <sup>14</sup>C years. The low abundance of BC in UDOM (0.5–3.5%) suggests that it is more labile than presently believed and/or the low molecular weight DOC contains a larger proportion of aged BC. **Citation:** Ziolkowski, L. A., and E. R. M. Druffel (2010), Aged black carbon identified in marine dissolved organic carbon, *Geophys. Res. Lett.*, 37, L16601, doi:10.1029/2010GL043963.

### 1. Introduction

[2] Produced in large quantities on land during biomass burning and fossil fuel combustion, the sinks of black carbon (BC) are not well understood [Masiello, 2004]. In the atmosphere, BC can lead to increased atmospheric temperatures and decreased precipitation [Ramanathan and Carmichael, 2008]. Stored in soils and lacustrine sediments where it may be slowly degraded over time [Czimczik and Masiello, 2005; Hockaday et al., 2007], BC enters the ocean through aerosol and river deposition [Masiello and Druffel, 2001; Dickens et al., 2004; Flores-Cervantes et al., 2009]. BC isolated from open ocean sediments is up to 14,000 <sup>14</sup>C years older than non-BC sedimentary organic carbon, suggesting that BC resides in an intermediate pool, such as marine dissolved organic carbon (DOC), prior to sedimentary deposition [Masiello and Druffel, 1998].

[3] Marine DOC, operationally defined as the material that passes a 0.2–1.0 μm filter, is the largest exchangeable pool of organic carbon in the ocean. Its age ranges from 1500 <sup>14</sup>C years in the surface water to 4000–6500 <sup>14</sup>C years in the deep ocean [Beaupré and Druffel, 2009] and similar DOC concentrations in the surface ocean globally (range 50–80 μM [Hansell et al., 2009]). Over 80% of the marine DOC cannot be characterized at the molecular level [Benner, 2002]. High molecular weight ultrafiltered DOC (UDOM, ≥1000 Da) has been found to contain a small portion of aged lipid-like material [Loh et al., 2004] that may include some BC. Studies directly assessing the BC and BC-like material

using various techniques (chemo-thermal oxidation at 375°C and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry), in riverine, coastal and open ocean DOC estimate that BC could be up to 5% of DOC [Kim et al., 2004; Mannino and Harvey, 2004; Dittmar and Paeng, 2009]. The great age of DOC in the ocean has yet to be explained; it remains a mystery and is the motivation of this study. The goal of this work was to use radiocarbon measurements of BC isolated from UDOM to determine the cycling and residence time of BC in the marine DOC pool.

### 2. Approach

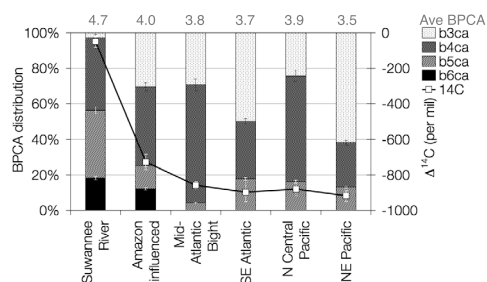
[4] BC is a heterogeneous material that is aromatic in nature. The molecular precursors of BC are believed to be polycyclic aromatic hydrocarbons (PAHs) [Lima et al., 2005]. With increased temperature and reaction time PAHs are transformed into BC with a more condensed aromatic structure and fewer alkyl carbons [Lima et al., 2005]. Char BC, formed at low combustion temperatures in an oxygen rich flame, has a less condensed aromatic structure than soot BC, which is formed during high temperature combustion. These characteristics can be determined using nuclear magnetic resonance [Czimczik et al., 2003], elemental analysis [Hammes et al., 2008] and the benzene polycarboxylic acid (BPCA) method [Glaser et al., 1998].

[5] With the BPCA method, via a high-temperature and high-pressure chemical oxidation, non-aromatic material is removed and complex aromatic structures are oxidized to benzene polycarboxylic acids (BPCAs, see Figure S1 in Text S1 of the auxiliary material).<sup>1</sup> Quantifying the number of carboxylic acid functional groups substituted on the benzene rings (3 to 6 acids) as a relative distribution and calculating the average number of acids yields general structural information about the BC. For example, the BPCAs formed from charred wood yields BPCAs with fewer acids (average number of acids = 4.5), whereas soot yields mostly fully substituted BPCAs (average number of acids = 5.5 (see Figure S2)) [Ziolkowski, 2009]. Furthermore, since no non-BC BPCAs are produced and no additional carbon is added during the oxidation process, isotopic analysis of BPCAs is a direct measure of the radiocarbon of BC.

[6] The abundance of <sup>14</sup>C in BC is indicative of its source(s). Fossil fuel produced BC contains no <sup>14</sup>C (“dead”) and thus has a <sup>14</sup>C age >50,000 years (the detection limit). In contrast, BC recently produced from biomass burning has a <sup>14</sup>C content equal to that in the contemporary biosphere C (Δ<sup>14</sup>C = 0 to 200‰). Here we present the distribution of BPCAs in conjunction with radiocarbon measurements of

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**Figure 1.** BPCA distribution and  $\Delta^{14}\text{C}$  of  $\Sigma\text{BPCAs}$  extracted from BC in UDOM samples. For each sample, the distribution of BPCAs is calculated by relating the total carbon of an individual BPCA to the total BPCA carbon. Average BPCA ( $\pm 0.2$  number of acids) are given at the top of each column. The uncertainties of BPCA distributions are less than 5%.  $^{14}\text{C}$  uncertainties, shown as scaled error bars, are the propagated blank corrected values [Ziolkowski and Druffel, 2009] and range from 20 to 55%.

$\Sigma\text{BPCAs}$  to illuminate the sources and cycling of BC in marine DOC.

[7] BC was extracted from a series of UDOM samples (see auxiliary material) and was analyzed using the BPCA method [Glaser *et al.*, 1998; Brodowski *et al.*, 2005; Ziolkowski, 2009]. These samples represent a wide range of ocean locations, sources and ages of DOC and one river sample (Table S1 and Figure S3). UDOM samples were digested in concentrated nitric acid to oxidize BC to BPCAs and were subsequently isolated and purified via preparative capillary gas chromatography (pcGC) before  $^{14}\text{C}$  analysis [Brodowski *et al.*, 2005; Ziolkowski and Druffel, 2009].

### 3. Results and Discussion

#### 3.1. BPCA Distributions and $^{14}\text{C}$ of BPCAs

[8] The large proportion of marker compounds indicative of highly condensed aromatic carbon (B5CA and B6CA) produced from BC in Suwannee River DOC illustrates that terrigenous BC is condensed in its aromatic structure (Figure 1). In contrast, BPCAs formed from open ocean UDOM-BC has a uniformly smaller and less condensed aromatic structure because of the higher proportion of B3CA and B4CAs formed (Figure 1). The BC structure of Suwannee River DOC had the most aromatic rings in a tightly packed structure (average number of acids is  $4.7 \pm 0.2$ ) and the distribution of BPCAs formed resembled that formed from charred wood BC (see Figure S2). In the Amazon-influenced sample, that contains a mixture of marine and riverine DOC,

the average BC structure (average number of acids is  $4.0 \pm 0.2$ ) was less condensed than that of the Suwannee River sample. The structure of the BC in the open ocean samples (average number of acids is 3.5 to  $3.9 \pm 0.2$  (Figure 1)) is less condensed and similar in composition, irrespective of depth or ocean location.

[9] The  $\Delta^{14}\text{C}$  values of bulk UDOM ranged from +152‰ in the Suwannee River to  $-445\text{‰}$  in the deep NE Pacific Ocean (Table S1). The Suwannee River DOM is primarily composed of recent C, evidenced by  $^{14}\text{C}$  enrichment due to atmospheric weapons testing, while BPCAs formed from Suwannee River BC are pre-bomb, likely less than a century old (Table 1). In contrast, the BPCAs formed from oceanic UDOM-BC were  $^{14}\text{C}$ -depleted. The  $\Delta^{14}\text{C}$  values of collected BPCAs co-vary with the BPCA distributions (Figure 1). That is, the younger BC (i.e., left side of Figure 1) exhibited a more condensed aromatic structure than the older BC (i.e., right side of Figure 1). The oldest BC, 20,100  $\pm$  3,000  $^{14}\text{C}$  years BP, was from 1000 m depth in the northeast Pacific Ocean. If the BC in the Amazon influenced sample is conservative with salinity (Table S1), a mass balance calculation reveals that the  $^{14}\text{C}$  age of BC exported from the river is modern ( $\Delta^{14}\text{C} \sim 0\text{‰}$ ).

#### 3.2. Distinction Between Riverine and Open Ocean BC

[10] Modern  $^{14}\text{C}$  ages of riverine and riverine-influenced BC suggests that a modern source of BC is exported from these rivers. The BPCA distributions of riverine and riverine-influenced BC resembles that of charred wood (Figure S2), which agrees with the findings that char is mobilized in watersheds [Hockaday *et al.*, 2007]. When this material reaches the ocean, it appears that the UDOM loses some of its aromatic character. This loss of aromaticity could be due to photochemical degradation. In estuaries the abundance of aromatic compounds exposed to ultraviolet radiation has been observed to decrease [Gonsior *et al.*, 2009] and/or undergo microbial utilization [Carlson, 2002]. Because BPCAs can only be formed from aromatic materials, the decreased aromatic character of BC in marine UDOM is not due to dilution with non-aromatic material.

[11] The BPCA distributions and  $\Delta^{14}\text{C}$  values of the marine samples suggest that BC cycling in the open ocean is distinct from the BC that is exported from the Suwannee and Amazon Rivers. If the BC exported from rivers remained unaltered in the UDOM pool, one would expect the chemical composition of BC from the Atlantic Ocean, which has four-times the input of river DOC per unit volume, to resemble terrestrial BC more than UDOM-BC from the Pacific Ocean. However, this is not the case. The  $\Delta^{14}\text{C}$  value and BPCA distribution of BC isolated from the Mid-Atlantic Bight and

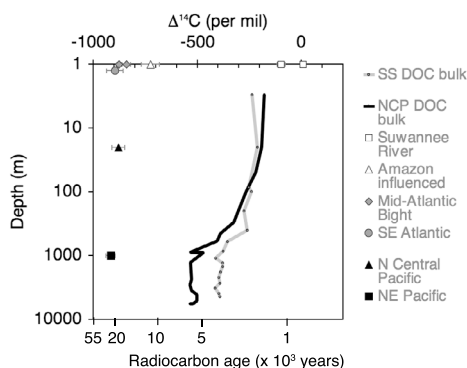
**Table 1.** Measurements of BC Isolated from UDOM<sup>a</sup>

	UCiD	$\Delta^{14}\text{C}_{\text{BC}}$ (‰)	$^{14}\text{C}_{\text{BC}}$ Age ( $^{14}\text{C}$ years BP)	[BC] in DOC <sup>b</sup>	$\Delta\Delta^{14}\text{C}^c$ (‰)
Suwannee River	11803,11804	$-49 \pm 33$	$410 \pm 280$	$29.4 \mu\text{M}$	-202
Amazon influenced	11956	$-727 \pm 44$	$10,400 \pm 1300$	$300 \text{ nM}$	-629
Mid-Atlantic Bight	10878, 11721	$-858 \pm 19$	$15,680 \pm 1100$	$560 \text{ nM}$	-861
SE Atlantic	11971	$-897 \pm 55$	$18,300 \pm 4300$	$330 \text{ nM}$	-807
N. Central Pacific	11958	$-880 \pm 38$	$17,000 \pm 2500$	$90 \text{ nM}$	-569
NE Pacific	11955	$-918 \pm 31$	$20,100 \pm 3000$	$330 \text{ nM}$	-473

<sup>a</sup> $\Delta^{14}\text{C}$  uncertainties are the propagated blank corrected values [Ziolkowski and Druffel, 2009]. See Table S1 for additional sample information.

<sup>b</sup>The estimation is an approximate minimum value of BC in DOC because ultra-filtered material was analyzed, which constitutes only a portion of the DOC pool, except Suwannee River.

<sup>c</sup> $\Delta\Delta^{14}\text{C} = \Delta^{14}\text{C}_{\text{UDOM}} - \Delta^{14}\text{C}_{\text{BC}}$ . ( $\Delta^{14}\text{C}_{\text{UDOM}}$  values are in Table S1)



**Figure 2.**  $\Delta^{14}\text{C}$  of black carbon and marine DOC as a function of depth. The depth profiles of DOC are from the Sargasso Sea (SS) and North Central Pacific (NCP) [Druffel *et al.*, 1992].

SE Atlantic do not appear to resemble the aromatically condensed modern  $^{14}\text{C}$  exported from the rivers. Additionally, the  $\Delta^{14}\text{C}$  values of BPCAs isolated from UDOM-BC from the Pacific were not significantly different from those of the Atlantic samples.

### 3.3. Source(s) of BC to the Open Ocean

[12] BPCAs extracted from UDOM-BC had lower  $\Delta^{14}\text{C}$  values ( $-858$  to  $-918\text{‰}$ ) than the bulk UDOM ( $+3$  to  $-445\text{‰}$ ), suggesting that BC is more recalcitrant or has much older sources compared to other components of bulk UDOM. The  $\Delta^{14}\text{C}$  offset between UDOM-BC and bulk UDOM is large ( $\Delta\Delta^{14}\text{C} = -202$  to  $-861\text{‰}$  (Table 1)), indicating that UDOM-BC cycles on much longer time scales than any chemical components of DOC identified to date. If BC was produced *in situ* (e.g., mid-water column production [Yamashita and Tanoue, 2008] or from bacterial production [Ogawa *et al.*, 2001]), the  $\Delta^{14}\text{C}$  of newly produced “BC” would reflect that of the consumed organic matter (e.g., DOC). However, little variation of the  $^{14}\text{C}$  ages of UDOM-BC is observed and it is consistently much older than bulk DOC (Figure 2). While the two river samples studied contained modern  $^{14}\text{C}$  levels and are condensed in aromatic character, it is possible that other river systems could export older BC-like material. Fossil material that chemically resembles black carbon, referred to as graphitic black carbon, is exported from some rivers and subsequently incorporated into shelf sediments [Dickens *et al.*, 2004]. It is unlikely that the UDOM-BC is graphitic BC because its structure is hypothesized to be sheets of aromatic material, which would form mostly fully substituted BPCAs (i.e., B5CA and B6CA).

[13] Our measurement of  $^{14}\text{C}$  in UDOM-BC from the deep NE Pacific Ocean revealed an age of  $20,100 \pm 3,000$   $^{14}\text{C}$  years. This residence time estimate assumes that the source(s) of BC to the ocean is  $^{14}\text{C}$  modern. Atmospheric BC  $\Delta^{14}\text{C}$  values are widely variable ( $-220$  to  $-600\text{‰}$ ), indicating a variety of sources [Eglinton *et al.*, 2002; Gustafsson *et al.*, 2009]. Amazon Basin atmospheric BC had a mean particle size of  $0.175 \mu\text{m}$  [Echalar *et al.*, 1998], smaller than the upper size cutoff for DOC, indicating that BC aerosols would be incorporated into UDOM. The observed UDOM-BC most closely resembles charred BC, formed at lower combustion temperatures. Unless soot is chemically solubilized via atmospheric oxidation, drastically changing its chemical

composition prior deposition to the surface ocean [Decesari *et al.*, 2002], it is unlikely that the isolated BC originated from recent soot emissions.

[14] Similarly, the observed UDOM-BC is unlikely to have originated from recent combustion of fossil fuel derived soot because the BPCAs formed from soot are predominantly B5CA and B6CA (Figure S2). With industrialization, fossil fuel combustion (soot) has increased the amount of  $^{14}\text{C}$ -depleted BC emissions [Bond *et al.*, 2004]. If BC from fossil fuel combustion was incorporated into the UDOM-BC, this would increase the  $^{14}\text{C}$  age. While stable carbon isotope ( $\delta^{13}\text{C}$ ) measurements of BPCAs extracted from UDOM-BC may help pinpoint the source of the BC, they are limited by a small dynamic range. Because the BPCA distribution of UDOM-BC does not resemble soot, it is unlikely that  $^{14}\text{C}$ -depleted soot is present in the old sample from the deep NE Pacific Ocean. If PAHs were complexed in DOC, it could produce the observed BPCA distributions, however it is unlikely that PAHs would be present in the UDOM fraction of the DOC because of their small size. This does not exclude the presence of other yet to be identified source(s) of  $^{14}\text{C}$ -depleted aromatic compounds resembling BC in UDOM.

### 3.4. BC and the Composition of DOM

[15] Typically UDOM isolated from bulk DOC represents 25 to 35% of the bulk DOC [Benner, 2002]. BC in our UDOM samples ranged from 0.5 to 3.5% C. This corresponds to minimum marine BC concentrations of 80–500 nM, compared to 36–90  $\mu\text{M}$  C in bulk DOC. The UDOM-BC samples studied here are likely macromolecules or smaller molecules that are complexed making them larger than the 1000 Da size cutoff. The low molecular weight (LMW) DOC would contain aromatic molecules ranging from PAHs to larger molecules such as fullerenes (e.g.,  $\text{C}_{60}$ ). If the abundance of BC in the DOC pool, as inferred by the observed BPCA distribution, is a function of  $^{14}\text{C}$  age, it is likely that the BC in the LMW fraction of DOC is even older ( $>20,100$   $^{14}\text{C}$  years) than the values presented here.

[16] From the age differences between BC and non-BC sedimentary organic carbon (SOC), Masiello and Druffel [1998] suggested that BC resides in the DOC pool from 2400 to 13,900  $^{14}\text{C}$  years before deposition. Based on these age differences, Masiello and Druffel [1998] assumed that if the average annual flux of pre-industrial BC to the world oceans is 0.01 Pg per year [Suman *et al.*, 1997] and a marine DOC pool of 685 Pg C [Hansell and Carlson, 1998], BC could be 4 to 22% of the total deep ocean DOC. The amount of DOC has since been reassessed to 662 Pg C [Hansell *et al.*, 2009], which would not change Masiello and Druffel’s [1998] estimate by more than 1%. Therefore 26–145 Pg of DOC could be BC, corresponding to a concentration of BC in marine DOC of 2–10  $\mu\text{M}$ . In the deep NE Pacific sample, we found that UDOM was 3.5% BC or 0.3  $\mu\text{M}$  (see Ziolkowski [2009] for calculation details). Thus, if DOC is 4 to 22% BC, then the lower molecular weight DOC contains a substantial proportion of BC (1.5–9  $\mu\text{M}$ ).

[17] BC isolated from UDOM has a much lower  $\Delta^{14}\text{C}$  value than DOC ( $-900\text{‰}$  versus  $-550\text{‰}$  for the deep NE Pacific Ocean). If BC is up to 22% of the deep DOC (i.e., 9  $\mu\text{M}$ ), then the remaining 78% (28.6  $\mu\text{M}$ ) would have an average  $\Delta^{14}\text{C}$  of  $-388\text{‰}$  (4000  $^{14}\text{C}$  years), which is significantly younger than the deep bulk DOC value (6000  $^{14}\text{C}$  years). It is likely that old smaller BC is in the LMW frac-

tion, which has been found to be significantly older than the UDOM fraction [Santschi *et al.*, 1995]. Molecular analysis of BC mobilized within a fire-impacted watershed had a peak mass to charge ratio of 400 [Hockaday *et al.*, 2007], which is equivalent to a five ring PAH and would be in the LMW fraction of DOC. Should it be demonstrated that there is a large pool of aged BC in the LMW fraction of DOC, then this would help to explain the enigma that has plagued our understanding of the BC cycle. That is, the sources of BC far outweigh the known sinks. However, marine DOC may be a temporary reservoir for BC, and processes that are responsible for its breakdown (e.g., photochemical oxidation, bacterial remineralization and/or physical removal to the sediments) warrant investigation.

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