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SPECIAL ISSUE-CURRENT EVIDENCE

Dissolved black carbon in aquatic ecosystems

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Scientific Significance Statement

Fire, both natural and anthropogenic, alters organic molecules into many chemical forms, all termed black carbon. Although well studied in soils and the atmosphere, black carbon in natural waters has only recently been identified as important. For example, 10% of dissolved organic carbon in rivers is in the form of dissolved black carbon. In this article, we present our emerging understanding of the chemistry, reactivity, fate, and ecological influence of dissolved black carbon in natural waters as well as the research challenges and opportunities.

Abstract

The incomplete combustion of organic molecules produces a chemically diverse suite of pyrogenic residues termed black carbon (BC). The significance of BC cycling on land has long been recognized, and the recognition of dissolved BC (DBC) as a major component of the aquatic carbon cycle is developing rapidly. As we seek a greater understanding of DBC cycling, our interpretation of environmental DBC concentrations and molecular composition should take into account both the formation conditions of charred residues, and the physico-chemical transformation of DBC that occurs during transit within aquatic systems. We present the current state of knowledge concerning sources, processing, and sinks of DBC in inland, coastal/estuarine, and ocean waters. We feature studies and new methodologies which focus specifically on the aquatic cycling of DBC, explore the relationship between particulate and dissolved BC, and highlight research gaps which should be targeted to advance our current knowledge of DBC biogeochemistry.

Fire has been an integral component of terrestrial ecosystems and biogeochemical cycles since the emergence of land plants some 420 million years ago (Bowman et al. 2009). Contemporary fire regimes are increasingly influenced by human activities, including the use of fire for agricultural practices, land management, vegetation control, and industry (Bowman et al. 2011). Black carbon (BC) is the organic residue formed during the incomplete combustion of organic matter, which occurs during both natural (wildfire) and anthropogenic (biomass burning, fossil fuel combustion) burning. Wildfires are the predominant source of BC to the environment and the vast majority of BC

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produced is deposited on the landscape, with other BC sources, such as fossil fuel combustion and biomass burning, providing minor contributions (Santín et al. 2015; Reisser et al. 2016). Aerosol BC is primarily sourced from fossil fuel burning and the annual flux of BC to the atmosphere is an order of magnitude smaller than the deposition of BC on land (Bird et al. 2015). BC is enriched in carbon relative to its unburned biomass source (Schneider et al. 2010), making BC burial an efficient means of carbon sequestration. Due to its structure and stoichiometry, the biogeochemical processing and environmental residence time of BC is different from that of its organic precursor material, which has major implications for global carbon cycling. Although BC deposited on land is largely retained within soils, it can be mobilized from the landscape in the form of dissolved and particulate BC (DBC and PBC, respectively), serving as a continuous source of pyrogenic carbon to inland, coastal, and oceanic waters (Jaffé et al. 2013; Santín et al. 2015). Research within the last 10 years has focused upon constraining the biogeochemical processes which control the reactivity and redistribution of this vast store of dissolved pyrogenic material across terrestrial and aquatic environments.

The first evidence of DBC in natural waters was offered by the identification of condensed aromatic ring structures via ultrahigh resolution mass spectrometry in volcanic ash soil humic acid (Kramer et al. 2004), soil pore waters (Hockaday et al. 2006), and the waters of the Rio Negro (Kim et al. 2004). Condensed aromatics were also identified in soil extracts as determined by NMR spectroscopy (Möller et al. 2000). These condensed aromatic structures were also found to be present in oceanic dissolved organic matter (Dittmar and Koch 2006). The transfer of DBC from the land to the ocean represents a major sink for terrestrial BC and a major source for marine DBC (Mannino and Harvey 2004; Preston and Schmidt 2006; Dittmar and Paeng 2009). Across fluvial systems, DBC comprises $\sim 10\%$ of bulk dissolved organic carbon (DOC), which equates to a global riverine DBC flux of ~ 27 Tg-C yr^{-1} (Jaffé et al. 2013) a flux which is over ten times the direct inputs of water soluble BC from global atmospheric deposition to the ocean (~ 1.8 Tg yr^{-1}; Bao et al. 2017). On land, soil BC constitutes ~ 200 Pg-C (Reisser et al. 2016). If fluvial DBC export is assumed to be the only mechanism that removes BC from soils, and we assume no additional BC inputs, the soil BC pool would be exhausted within ~ 7400 yr. However, 110–380 Tg-C of terrestrial BC is produced each year (Santín et al. 2015), providing continuous inputs that restock soil BC stores. Recent research has aimed to refine our understanding of the movement and biogeochemical processing of DBC in aquatic environments to better constrain the environmental cycling of fire-derived carbon.
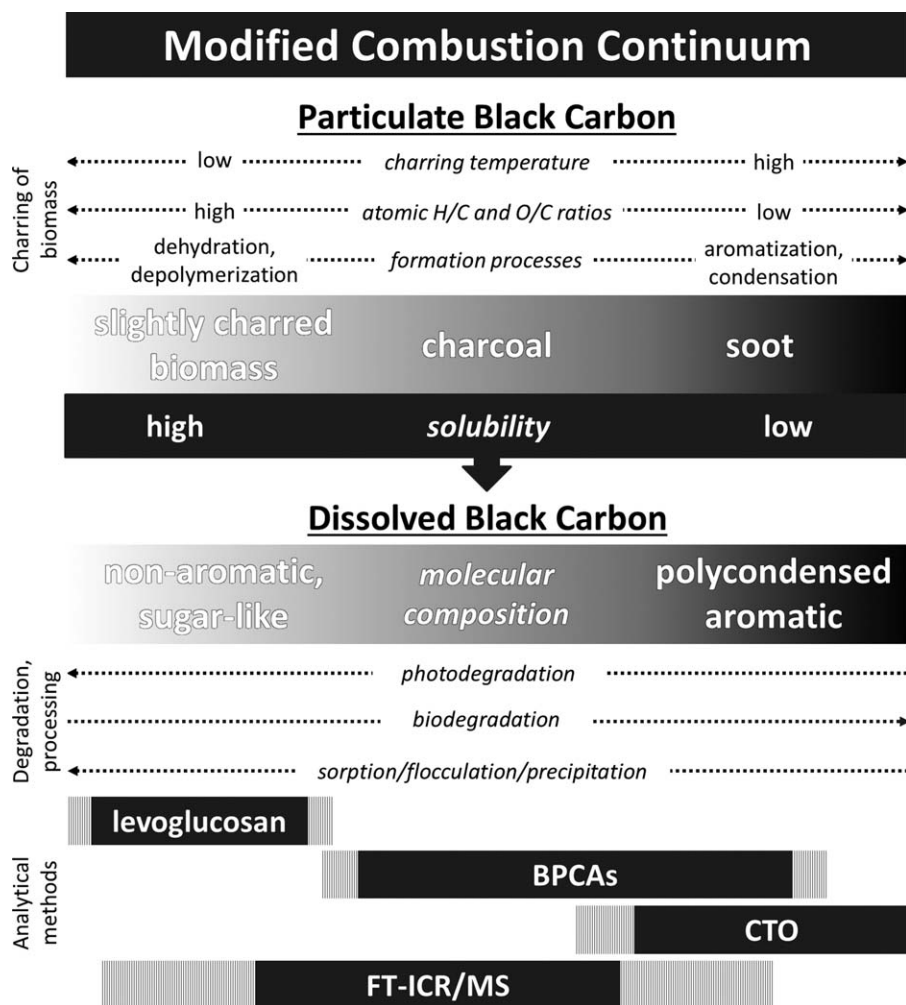
Although several reviews on BC exist (Masiello 2004; Czimczik and Masiello 2007; Bird et al. 2015; Santín et al. 2015), a detailed discussion on the environmental processes influencing the amount and quality of DBC is lacking. There is often an underlying assumption that chemical character, environmental patterns, and biogeochemical processes which apply to soil BC, also apply to DBC. However, the chemistry, reactivity, and fate of BC in soils differ from that of the DBC in natural waters. We also explore the relationship between DBC and PBC from a DBC-centric perspective, feature studies and new methodologies which focus specifically on the aquatic cycling of DBC, and highlight discrepancies and critical research gaps.

Black carbon formation: The chemistry of fire

The molecular composition of BC varies across the combustion continuum (Hedges et al. 2000; Masiello 2004) and controls the quality and quantity of DBC mobilized to aquatic environments. Therefore, understanding the "chemistry of fire" is essential to understanding DBC. The progressive heating of organic material generally (1) decreases H/C and O/C due to dehydration and losses of CO_2, (2) increases aromaticity and aryl carbon content, (3) reduces alkyl chain lengths, and (4) forms heterocyclic nitrogen functionalities (Baldock and Smernik 2002; Gonzalez-Perez et al. 2004; Knicker 2011). Vegetation-derived BC is produced from the charring of various biomolecules, including cellulose, a biopolymer consisting of linked glucose monomers, which comprises 20–50% of dry plant mass (Knicker 2007). At low charring temperatures (below 300°C), cellulose thermally decomposes into individual anhydrosugars, such as levoglucosan (Kuo et al. 2011), whereas furan- and aromatic-type structures form at higher temperatures ($> 300°C$; Baldock and Smernik 2002; Knicker et al. 2008). Lignin, which comprises 20–40% of wood biomass and $\sim 4\%$ of grassy biomass (Knicker 2007), undergoes dehydroxylation and cleavage of aryl ethers at temperatures $< 450°C$ with no net production of aromatic carbon (Sharma et al. 2004; Knicker et al. 2008). At temperatures $> 450°C$ lignin biopolymers are converted to condensed aromatic structures (Knicker 2010) and the pyrolysis of proteins and peptides results in the cyclization of organic nitrogen forming pyrrole-type moieties (Knicker 2010).

While the molecular composition of PBC is largely controlled by source material and charring temperature (Schimmelpfennig and Glaser 2012), the molecular composition of DBC is further modulated by the solubility of the specific BC compounds (Fig. 1). Once solubilized, DBC exists as a heterogeneous mixture of pyrogenic components ranging from non-aromatic, sugar-like compounds (e.g., levoglucosan) to polycondensed aromatic structures. This chemical diversity leads to a wide range in environmental reactivity (Fig. 1). Once in the water, photodegradation, biodegradation, sorption, and co-precipitation (Fig. 1), selectively alter DBC molecular composition. Consequently, the interpretation of quantitative and qualitative DBC data should consider both

Modified Combustion Continuum

Particulate Black Carbon

Charring of biomass

low ··········· *charring temperature* ··········· high

high ··········· *atomic H/C and O/C ratios* ··········· low

dehydration, depolymerization ··········· *formation processes* ··········· aromatization, condensation

slightly charred biomass | charcoal | soot

high | *solubility* | low

Dissolved Black Carbon

non-aromatic, sugar-like | *molecular composition* | polycondensed aromatic

Degradation, processing

········· *photodegradation* ·········

········· *biodegradation* ·········

········· *sorption/flocculation/precipitation* ·········

Analytical methods

levoglucosan

BPCAs

CTO

FT-ICR/MS

Fig. 1. Combustion continuum, modified from Masiello (2004), which incorporates the effects of solubility and reactivity/processing on the molecular composition of dissolved black carbon (DBC) and the interpretation of DBC data obtained from different analytical methodologies. The arrows associated with the degradation and processing of DBC indicates the direction in which the molecular composition of the DBC pool would shift if it underwent that particular biogeochemical process. For example, photodegradation preferentially removes polycondensed aromatic compounds, resulting in a pool of DBC molecules that is less aromatic.

the pyrogenic sources and subsequent environmental processing of DBC.

Chemical analysis

In the current review, BC is defined as comprising any organic molecule formed by incomplete combustion. Black carbon can be further defined from a chemical perspective based upon structural moieties, such as condensed aromatics (Glaser et al. 1998), or as specific molecular markers, such as levoglucosan (Kuo et al. 2011). Black carbon can be further classified by its pyrogenic origin (anthropogenic vs. natural wildfire-derived). While there is no single methodology which provides a comprehensive assessment of the entire pool of DBC molecules, several analytical techniques have come to the forefront in quantifying and characterizing DBC

along different regions of the combustion continuum (Masiello 2004; Fig. 1). Earlier reviews have contrasted various BC quantification methods as applied for soil and particulate BC (Schmidt and Noack 2000; Hammes et al. 2007; Roth et al. 2012), whereas we focus specifically upon methodologies used for DBC. These methods include analysis of benzenepolycarboxylic acids (BPCAs) and anhydrosugars, chemo-thermal oxidation, and ultrahigh resolution mass spectrometry.

The BPCA method was developed for BC measurement in soils (Glaser et al. 1998), and modified to quantify DBC (Dittmar 2008; Ziolkowski et al. 2011). The BPCA method converts condensed aromatics to individual benzene rings substituted with three, four, five, and six carboxylic acid groups (B3CA, B4CA, B5CA, and B6CA, respectively), and is a robust approach for measuring and characterizing the

condensed aromatic fraction of DBC (Dittmar 2008; Ziolkowski et al. 2011). The BPCA method has been applied to dissolved organic matter (DOM) from freeze-dried river water (Stubbins et al. 2015), ultrafiltered stream water (Jaffé et al. 2012), and solid phase extracted river and marine waters (Stubbins et al. 2012a; Ding et al. 2013; Wagner et al. 2015a; Coppola and Druffel 2016). Although BPCA oxidation patterns are not entirely predictable, molecules with larger condensed aromatic ring structures generally produce larger BPCAs (i.e., produce greater proportions of B5CA and B6CA; Ziolkowski et al. 2011). In soil and particulate chars, the relative distributions of individual BPCAs describe the overall degree of condensed aromaticity of BC (Glaser et al. 1998), which increases with charring temperature (Schneider et al. 2010). However, the relative distribution of BPCAs from BC in parent soils and chars differ significantly from the relative distribution of BPCAs in the DBC leached from those same soils and chars (Ding et al. 2015; Wagner et al. 2017b). Furthermore, BPCA composition can be altered via biogeochemical processing (e.g., via photodegradation; Stubbins et al. 2012a). Therefore, while the relative distribution of BPCAs is useful in qualitative comparisons of different pools of DBC, the observed discrepancies in BPCA distributions between particulate and dissolved BC highlight the uncertainty associated with using inferences from the particulate/soil BC literature to assess the sources of DBC based upon BPCA composition.

To better track BC in aquatic environments, compound-specific isotopic analysis of BPCAs has been developed. BPCA-specific radiocarbon (Δ^{14}C) measurements have revealed the apparent age and apparent residence times of oceanic DBC pools (Ziolkowski and Druffel 2010; Coppola and Druffel 2016). In natural waters, ^{14}C-enriched BPCAs signify DBC from contemporary biomass-derived pyrogenic material. However, BPCA-specific Δ^{14}C measurements cannot distinguish between contemporary inputs of ^{14}C-depleted DBC and the in situ aging of DBC. For example, the observed ^{14}C-depletion of oceanic DBC ($\sim$ 4800 to $\sim$ 23,000 ^{14}C years old; Coppola and Druffel 2016) could result from the long-term aging of DBC in the ocean or from recent inputs of pre-aged DBC sources (e.g., deposition of fossil fuel combustion products). Since radiocarbon signatures are not a conservative property of organic matter, BPCA-specific Δ^{14}C can be a poor indicator of DBC source. By contrast, the stable carbon isotopic signature (δ^{13}C) varies with organic matter source and is stable over time, assuming fractionation processes do not occur. Online quantification and isotopic characterization of BPCAs indicates that rivers and the ocean contain DBC with markedly different δ^{13}C signatures, suggesting ocean DBC may not be entirely derived from aged riverine DBC (Wagner et al. 2017a). While further work is needed to address fractionation effects which could alter BPCA-specific isotopic signatures, the combination of BPCA-specific δ^{13}C and Δ^{14}C would be a powerful approach in constraining the sources and cycling of DBC.

Conversion factors are used to estimate environmental DBC concentrations from BPCA abundances. In an early study, activated charcoal was used to derive a 2.27 conversion factor to estimate the amount of BC in soils and particulate charcoal samples from quantified BPCAs (Glaser et al. 1998). More recently, conversion factors have been derived from compounds which are a better representation of condensed aromatics within the DBC pool. The nitric acid oxidation of known polyaromatic hydrocarbon (PAH) structures yields, on average, 26% ± 7% BPCA-carbon (Ziolkowski et al. 2011). Therefore a conversion factor of 4 ± 1 (inverse of 26% ± 7%) has been used to convert from BPCA-carbon to DBC (Ziolkowski et al. 2011). In oceanic waters, condensed aromatics identified by ultrahigh resolution mass spectrometry contained an average of 7 aromatic rings and 33.4 carbon atoms (Dittmar and Koch 2006). Assuming 100% reaction efficiency, each of these condensed aromatic molecules would produce either one B6CA/B5CA marker or two B3CA/B4CA markers when oxidized (Dittmar 2008). Based upon these assumptions, concentrations of DBC (nM-C) were estimated from concentrations of BPCAs (nM-BPCA) in natural waters using the following equation: [DBC] = 33.4([B6CA] + [B5CA] + 0.5[B4CAs] + 0.5[B3CAs]) (Dittmar 2008). Since DBC concentrations (nM-C) were derived from BPCA concentrations (nM-BPCA), the conversion factor of 33.4 represents a conversion factor of $\sim$ 3 on a per carbon basis making it comparable to the conversion factors of 2.27 (Glaser et al. 1998) and 4 (Ziolkowski et al. 2011) developed by other groups. More recently, DBC concentrations have been derived from B5CA and B6CA only, as these two BPCAs have commercially available standards, are the most dominant and robustly measured BPCAs (Stubbins et al. 2012a), and have been suggested to be exclusively of pyrogenic origin (Kappenberg et al. 2016). A power function relationship was developed from an extensive environmental dataset to calculate DBC concentrations (μM-C) directly from B5CA and B6CA concentrations (nM-BPCA) in natural waters: [DBC] = 0.0891 × ([B5CA] + [B6CA])$^{0.9175}$ (Stubbins et al. 2015). The above-described conversion factors are derived from the measured and estimated oxidation patterns of condensed aromatic compounds, including PAHs. Therefore, the estimation of BPCA-DBC from BPCAs assumes the oxidation patterns for environmental dissolved condensed aromatics are similar to those of model compounds. Since representative standards for the functionalized condensed aromatics which comprise environmental BPCA-DBC do not exist, the accuracy of these conversion factors cannot be verified at present. As such, it is critical to report both DBC concentrations and the individual BPCA concentrations so the results of previous research can be best interpreted as the BPCA-DBC field continues to evolve.

The chemothermal oxidation (CTO) method was originally developed for the quantification of BC in sediments (Gustafsson et al. 1997, 2001) and is best suited for the measurement of the most condensed forms of BC, such as soot (Hammes et al. 2007). The CTO method includes pretreatment to remove inorganic carbon and minerals, followed by a 24-h oxidation, and subsequent quantification of residual BC by elemental analysis (Gustafsson et al. 1997, 2001). Chars produced at moderate temperatures (450°C) yield very little CTO-BC (Nguyen et al. 2004), therefore less condensed pyrogenic structures in DOM are underestimated using this technique (Hammes et al. 2007). CTO can also result in positive bias if samples char during analysis (Hammes et al. 2007). Therefore, the expected abundance of potentially interfering compounds and environmental matrix effects should be considered during analysis (Elmquist et al. 2006; Argawal and Bucheli 2011; Caria et al. 2011). To quantify soot-type CTO-BC in the dissolved phase, the CTO method has been performed on DOM isolated via ultrafiltration/lyophilization (Mannino and Harvey 2004) and solid-phase extraction (Wang et al. 2016; Xu et al. 2016).

Levoglucosan and its isomers, mannosan and galatosan, are thermal degradation products of cellulose and hemicellulose, and are molecular markers representative of DBC derived from the low temperature charring of biomass (LT-DBC; Kuo et al. 2011). Levoglucosan is isolated directly from pre-filtered water samples via solvent extraction, derivatized, and quantified using gas chromatography-mass spectrometry (GC-MS; Norwood et al. 2013). Measurements of levoglucosan isomers have been paired with measurements of lignin oxidation products for improved biomass source apportionment (Kuo et al. 2011). Ratios of syringyl to vanillyl and levoglucosan to mannosan differentiate between hardwood, grass, and softwood pyrogenic sources (Kuo et al. 2011; Myers-Pigg et al. 2015). LT-DBC, as quantified by the levoglucosan method, is highly biolabile in the aqueous phase, where the half-life of levoglucosan is 3–4 d (Norwood et al. 2013). As such, LT-DBC is expected to be rapidly removed via microbial degradation (Myers-Pigg et al. 2015).

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) can resolve complex mixtures and offers detailed compositional information concerning DOM and its subcomponents, including DBC (Sleighter and Hatcher 2007). The ultrahigh resolution of FT-ICR/MS allows for the assignment of molecular formulas to thousands of mass spectral peaks per DOM sample. Molecular formulas cannot inherently be linked to specific molecules, as each formula represents many possible isomeric structural arrangements. However, assigned molecular formulas can be categorized into compound classes by elemental ratios to better describe the overall molecular composition of DOM (Stubbins et al. 2010; Šantl-Temkiv et al. 2013). The modified aromaticity index (AI_{mod}) identifies molecular formulas with a high probability of being aromatic ($AI_{mod} > 0.5$) or condensed aromatic ($AI_{mod} \geq 0.67$; Koch and Dittmar 2006, 2016). Molecular formulas with modified aromaticity indices greater than 0.67 are considered part of the DBC pool (Koch and Dittmar 2006). The ionization efficiencies of individual DOM components have a strong influence on overall mass spectral composition and the overlap in analytical windows between FT-ICR/MS and the above-described quantitative methods is largely unknown. However, the reactivity patterns between DBC quantified by BPCAs, and characterized by FT-ICR/MS, are similar. For example, exposure of DOM to sunlight preferentially degrades B5CA and B6CA (Stubbins et al. 2012*a*) and FT-ICR/MS peaks which correspond with condensed aromatic structures (Stubbins et al. 2010), suggesting that both analytical methods are detecting highly photo-labile condensed aromatic DBC molecules.

In order to include the effects of solubility and reactivity/processing on the data obtained from the above-described analytical methodologies, we have modified the combustion continuum (Masiello 2004) as a visual aid in the interpretation of DBC information (Fig. 1). It should be mentioned that other techniques, such as analytical pyrolysis (Py-GC-MS; Kaal et al. 2016), are available for qualitative assessments of less condensed aromatic DBC components. In addition, a highly detailed DOM characterization study, using a combination of high field NMR, 2D-NMR, and FT-ICR/MS was able to further characterize condensed aromatic compounds as DBC containing both nitrogen and sulfur (Hertkorn et al. 2016) and advanced spectral editing NMR techniques revealed refractory deep ocean DOM to enriched in deprotonated (i.e., condensed) aromatic structures (Helms et al. 2015).

Questions remain regarding the physico-chemical interactions between DBC molecules and the larger organic/inorganic matrix they exist within. Near-edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy can determine the molecular speciation of soil BC (Singh et al. 2014). More recently, confocal laser scanning microscopy was paired with other spectroscopic methods to reveal mechanisms of BC stabilization in soils (Hernandez-Soriano et al. 2016). In the future, these spectroscopic techniques could be employed for the visualization of physico-chemical mechanisms which control the solubilization of DBC from soils into the water column.

Covariance between dissolved black carbon and total dissolved organic carbon

The solubilization and subsequent transport of BPCA-DBC via rivers is a major loss process of BC from terrestrial environments (Jaffé et al. 2013). Concentrations of BPCA-DBC and DOC correlate strongly on local (Ding et al. 2013, 2014) and global (Jaffé et al. 2013) scales. Similar correlative trends between LT-DBC and DOC were observed in Arctic rivers

Table 1. Published values of dissolved organic carbon (DOC) and dissolved black carbon (DBC) in rivers, estuarine/coastal environments, and the open ocean. The method used to quantify the reported DBC value is also listed. N.D. denotes values which were not determined.

Aquatic system	DOC (mg-C L^{-1})	DBC (mg-C L^{-1})	DBC : DOC (%)	Method	Ref.
Rivers					
Global rivers	0.7–17.5	0.018–1.7	2.5–12.2	BPCA	1
Glacial streams	0.4–1.0	0.0046–0.037	1.2–3.8	BPCA	1
Headwater streams	1.0–2.8	0.038–0.15	2.7–9.1	BPCA	1
Mid-sized rivers	1.6–20.7	0.0019–1.4	0.1–10.0	BPCA	1
Peat-influenced	6.9–21.9	1.2–2.8	12.7–17.4	BPCA	1
Wetland-influenced	1.4–15.5	0.046–0.90	3.0–13.6	BPCA	1
Arctic rivers	2.5–28.0	0.1–0.5	N.D.	levoglucosan	2
Huanghe, Changjiang rivers	1.4–3.4	0.028–0.34	1.2–13.0	CTO	3
Delaware River	2.3	0.13	5.4	CTO	4
Chesapeake Bay headwaters	2.2	0.28	12.7	CTO	4
Estuaries/coast					
Delaware River Estuary	2.4–3.2	0.19–0.45	8.0–14.0	CTO	4
Chesapeake Bay coast	1.7–2.3	0.094–0.16	5.5–7.1	CTO	4
East China Sea coast	0.9–1.7	0.031–0.048	2.9–4.1	CTO	3
Florida coastal everglades	3.3–20.4	0.080–3.2	1.9–19.3	BPCA	5
Tidal creek water column	2.8–7.3	0.096–0.49	2.9–7.1	BPCA	6
Gulf of Mexico coast	1.0–1.4	0.035–0.0072	0.7–3.3	BPCA	6
Tidal creek porewater	1.6–29.0	0.11–3.7	6.6–13.6	BPCA	7
Ocean					
Arctic Ocean	0.6–0.7	0.019–0.031	2.6–4.7	BPCA	8
Pacific Ocean	0.5–0.9	0.0010–0.0040	0.1–1.9	BPCA	8,9
Atlantic Ocean	0.7–1.1	0.0040–0.023	0.4–4.2	BPCA	8,9
Atlantic Deep Waters	0.5–0.6	0.013–0.014	2.1–2.9	BPCA	9,10

[1]Jaffé et al. (2013); [2]Myers-Pigg et al. (2015); [3]Wang et al. (2016); [4]Mannino and Harvey (2004); [5]Ding et al. (2014); [6]Dittmar et al. (2012*b*); [7]Seidel et al. (2004); [8]Coppola and Druffel (2014); [9]Ziolkowski and Druffel (2010); [10]Stubbins et al. (2012*a*).

(Myers-Pigg et al. 2015). However, the correlation between LT-DBC and DOC was not as strong as that between BPCA-DBC and DOC in the same region (Stubbins et al. 2015). The apparent coupling between DBC and DOC in natural waters (Table 1) suggests the biogeochemical mechanisms for their production, stabilization, and mobilization are similar and/or there is a physico-chemical affinity between DBC and DOC. In Arctic rivers, BPCA-DBC is strongly correlated with both DOC and chromophoric DOM (CDOM; Stubbins et al. 2015). CDOM is the optically active, aromatic-rich fraction of DOM (Weishaar et al. 2003). Since the DBC molecules which produce BPCAs are quantitatively the major identified fraction of the optically active, CDOM pool (i.e., they comprise ~ 9% of total DOC in large Arctic rivers; Stubbins et al. 2015), it is not surprising that BPCA-DBC concentrations correlate strongly with CDOM. In freshwater, BPCA-DBC was found to be associated predominantly with DOM in higher molecular weight size fractions (Wagner and Jaffé 2015). In light of supramolecular theory, in which DOM is proposed to exist as molecular assemblies of relatively small, heterogeneous molecules (Piccolo 2001; Simpson et al. 2002), BPCA-

DBC may be stabilized in solution by weak intermolecular forces between diverse forms of small organic molecules and cations, such as iron. Such interactions occur between DOM and PAHs (Perminova et al. 1999), resulting in the enhanced solubility of PAHs (Chin et al. 1997; Mitra and Dickhut 1999). Since the molecular structures of soluble compounds which comprise the bulk DBC pool and PAHs are similar (i.e., both contain condensed aromatic structures), it is likely that other dissolved organic molecules facilitate or enhance the solubility of both PAHs and the broader BPCA-DBC pool. This hypothesis was recently tested, via controlled leaching experiments, to determine whether the mobilization of BPCA-DBC from particulate soils and chars was enhanced in the presence of extraneous DOM (Wagner et al. 2017*b*). However, the apparent solubility of BPCA-DBC was shown to be primarily controlled by characteristics inherent to the individual soils and chars being leached, not by added DOM (Wagner et al. 2017*b*). As such, the physico-chemical drivers which control the transfer of BC to the dissolved phase require further study as we seek to unravel the environmental dynamics of DBC.

Sources of dissolved black carbon to aquatic environments

Aging of soil black carbon and the mobilization of terrestrial dissolved black carbon

Soils have been identified as an intermediate reservoir for BC prior to its transfer to the dissolved phase (Czimczik and Masiello 2007). Over time, BC in soils is partially oxidized via biotic and abiotic processes (Bruun et al. 2008; Zimmerman 2010). These oxidation processes result in the addition of polar functional groups to soil BC molecular structures, increasing the amount and degree of condensed aromaticity of BPCA-DBC solubilized from wood-derived charcoal (Abiven et al. 2011). Although the in-soil aging of BC plays an important role in the timing and amount of BPCA-DBC mobilized from the landscape, freshly produced charcoal can also leach considerable amounts of BPCA-DBC (Abiven et al. 2011; Wagner et al. 2017b). The production of BPCA-DBC from fresh charcoal suggests a pulse of BPCA-DBC may be released from fire-affected watersheds during the first rainfalls following a burn event. Following wildfires in Mediterranean watersheds, in-stream PAH concentrations increased initially, then dropped to backgrounds levels within a period of 15 months (Olivella et al. 2006; Vila-Escale et al. 2007). A similar pulse of BPCA-DBC may occur immediately post-burn. The unpredictability of both burn and rainfall events has hindered the temporally resolved capture of the export of freshly produced BPCA-DBC.

To date, temporally resolved studies have missed the first rains and have shown no relationship between fire recency/frequency and BPCA-DBC concentration (Ding et al. 2013; Wagner et al. 2015a) suggesting either the rapid release of fresh BPCA-DBC was missed or aging in soils is required for export. Further evidence of aging in situ comes from mass balance assessments that indicate BPCA-DBC in inland waters to be derived predominantly from soil BC produced by historic fires (Dittmar et al. 2012a). However, BPCA-specific radiocarbon measurements indicate that Suwannee River DBC is derived mainly from modern pyrogenic biomass ($F_m = 1.02$; Ziolkowski and Druffel 2010; Hanke et al. 2017). Further work is required to determine if this single example is representative of riverine BPCA-DBC age. Agriculture and/or urbanization can increase the mobilization of aged DOC to rivers (Butman et al. 2015). Therefore, the radiocarbon signature of BPCA-DBC may also vary with land disturbance. Looking forward, the application of BPCA-specific ^{14}C dating should be applied to determine the average and range of BPCA-DBC exported by rivers globally.

By contrast, LT-DBC formed from low temperature charring, is highly soluble when formed (Norwood et al. 2013). Therefore, the environmental release of LT-DBC from fire-impacted landscapes is expected to be largely controlled, not by aging and oxidation in soils, but instead by exposure of char particles to water. Further studies of LT-DBC release should therefore focus on capturing temporally resolved post-fire rainfall events to determine if they are the major hot-moments of LT-DBC export.

Hydrological controls on dissolved black carbon export

The export of DOC via rivers is disproportionately large during periods of high water discharge (Raymond et al. 2016). Hydrological events also serve as a significant process for the export of BPCA-DBC (Stubbins et al. 2015; Wagner et al. 2015a) and LT-DBC (Myers-Pigg et al. 2017). From the Paraíba do Sul River in Brazil, to high-latitude Arctic rivers, the greatest BPCA-DBC export occurs during highest discharge (Dittmar et al. 2012a; Stubbins et al. 2015). The export of LT-DBC (Myers-Pigg et al. 2017) also increases tenfold during the spring freshet in Arctic rivers, indicating that hydrology is an important control on the land-to-ocean flux of both LT and BPCA-DBC (Fig. 2a). Trends for BPCA-DBC in the Paraíba do Sul River and Arctic rivers can be explained by two-endmember mixing between low BPCA-DBC groundwater at base flow and high BPCA-DBC surface and soil runoff during high flow (Dittmar et al. 2012a; Stubbins et al. 2015). DBC quality also varies with discharge. At base flow, the BPCA-DBC pool is depleted in highly condensed aromatic structures, whereas at high flow, BPCA-DBC is enriched in such structures (Fig. 2b; Stubbins et al. 2015; Wagner et al. 2015a; Marques et al. 2017). As the increased degree of condensed aromaticity of BPCA-DBC with increasing discharge is not observed in all rivers (Stubbins et al. 2015), a more mechanistic understanding of these trends is warranted. In coastal environments, the export of BPCA-DBC to the ocean is further modulated by tidal hydrology. DBC concentrations in tidal creeks are highest in discharging porewater, which is then laterally transported during tidal pumping, providing an additional source of BPCA-DBC to the ocean (Dittmar et al. 2012b; Seidel et al. 2014).

Relationships between particulate and dissolved black carbon

Perturbation of the terrestrial landscape, through wildfire or anthropogenic activities, enhances erosion of surface soils and associated PBC. The mobilization of PBC from fire-impacted landscapes is an important loss factor for terrestrial BC (Foereid et al. 2011). Estuarine and coastal saltmarsh sediments contain stored records of PBC (Leorri et al. 2014; Hanke et al. 2016) and provide evidence that the transfer of PBC from the land represents a long-term source of pyrogenic material to coastal environments. However, the majority of soil eroded from the terrestrial landscape does not reach the coast and is instead re-deposited and stored within the watershed (Moody and Martin 2001). PBC from the landscape accumulates in alluvial deposits, where it can be stored for over 1000 yr (Cotrufo et al. 2016), representing a potential source of pre-aged DBC to inland waters. Sedimentary BC deposits could be a source of DBC through long-term, in-sediment solubilization mechanisms, as described above, or
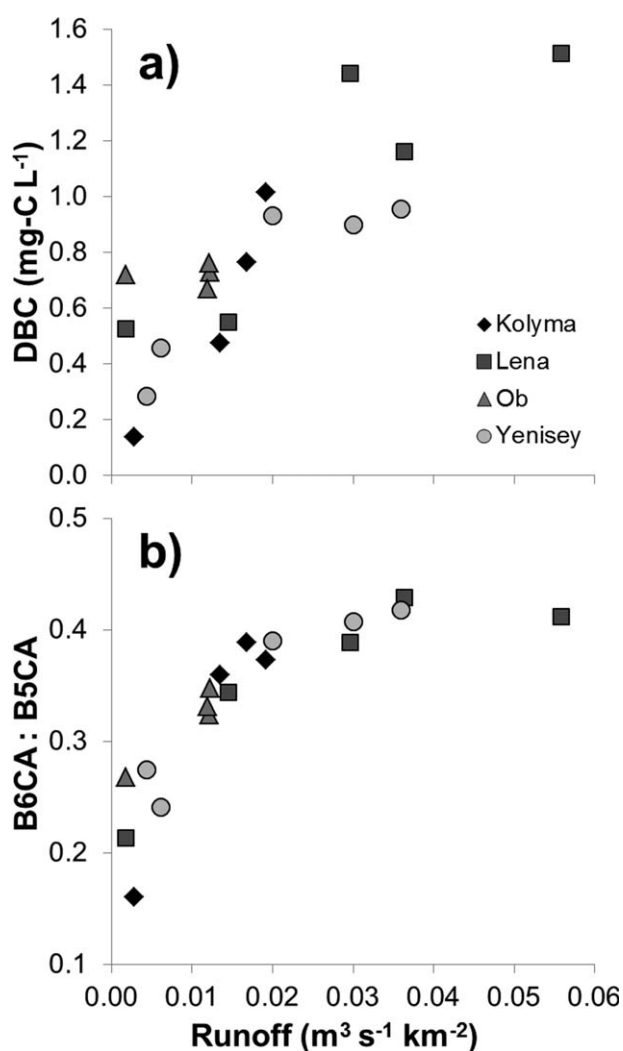
Fig. 2. (**a**) Dissolved black carbon (BPCA-DBC) concentrations vs. run-off and (**b**) benzenepolycarboxylic acid ratios (B6CA : B5CA) vs. runoff for Siberian Arctic rivers (Kolyma, Lena, Ob, and Yenisey). The BPCA ratio is a proxy for condensed aromaticity for BPCA-DBC. A higher B6CA : B5CA ratio represents a more condensed aromatic BPCA-DBC pool. These plots have been modified from Stubbins et al. (2015).

through sediment resuspension. When sediments are resuspended into the photic zone, exposure to sunlight can lead to photo-induced dissolution of particulate organic carbon (Estapa and Mayer 2010). This process is a significant source of DOC (Mayer et al. 2006; Pisani et al. 2011) and similar photo-dissolution processes apply to PBC (Roebuck et al. 2017), introducing a newly identified potential source of DBC to surface waters.

Considering the importance of land-to-river transfers of DBC and PBC, and the potential linkages between these two BC pools, tandem measurements of DBC and PBC have emerged as critical to research in BC cycling. While BPCA-DBC and LT-DBC concentrations are largely controlled by watershed hydrology (Dittmar et al. 2012*a*; Myers-Pigg et al.

2015; Stubbins et al. 2015), the mobilization processes of PBC and DBC from fire-impacted regions seem to be, in part, decoupled. For example, in an alpine watershed sampled 1 yr after an intense wildfire, the mobilization of BPCA-PBC occurred primarily during periods of overland flow (storm events, snowmelt), whereas BPCA-DBC fluxes were greatest during periods of high river discharge (Wagner et al. 2015*a*). The cumulative export of BPCA-PBC was fourfold greater than for BPCA-DBC during the sampling period (Wagner et al. 2015*a*). In the Huanghe River (China), the export of both particulate and dissolved CTO-BC was generally lowest in winter and highest in spring and summer (Wang et al. 2016). However, fluxes of CTO-PBC spiked dramatically higher than fluxes of CTO-DBC when the floodgates of an upstream dam were opened (Wang et al. 2016). These studies not only highlight decoupling in the mobilization of DBC and PBC in inland waters, but also suggest that PBC suspended in the water column can be sourced from the remobilization of alluvial sedimentary deposits.

The predominance of PBC over DBC is not consistent across all river systems. For example, the amount of DBC leached from subsoil pathways exceeded that of BC eroded from surface soils in river headwaters in East Africa (Güereña et al. 2016). In Arctic rivers, the export of BPCA-DBC and LT-DBC is 1–2 orders of magnitude larger than the export of PBC (Stubbins et al. 2015; Myers-Pigg et al. 2017). Since the mobilization mechanisms for pyrogenic carbon in the dissolved and particulate phases seem to be controlled by different hydrological, geomorphological, and physico-chemical drivers, the relationship between DBC and PBC in inland waters is expected to vary across aquatic ecosystems and requires further study.

Water soluble black carbon from deposited aerosols

The annual flux of the atmospheric deposition of BC to the ocean is $\sim$ 12 Tg-C yr^{-1}, where BC is primarily sourced from biomass burning and industrial emissions (Jurado et al. 2008). This estimate of total BC deposition is an order of magnitude greater than the estimated flux of water soluble BPCA-BC (i.e., the fraction of BPCA-quantifiable BC that can dissolve into seawater from deposited aerosols) to the ocean ($\sim$ 1.8 Tg-C yr^{-1}; Bao et al. 2017). Estimated lifetimes of atmospheric BC range from 40 h to 1 month (Ogren and Charlson 1983), allowing aerosol BC to be transported to even the most remote locations, such as the glaciers of the Himalayan-Tibetan Plateau (Xu et al. 2009; Li et al. 2016) and Antarctica (Khan et al. 2016). As with soil and dissolved forms of BC, aerosol BC represents a continuum of pyrogenic molecules, whose composition is largely dependent upon combustion efficiency, fuel type, and aging within the atmosphere (Bond et al. 2004; Venkataraman et al. 2005; Bao et al. 2017). Recent work has combined quantitative methods with radiocarbon isotopic analyses to better constrain the relative contributions of fossil fuel combustion

(^{14}C-dead) and burning of contemporary biomass (^{14}C-enriched) to atmospheric BC (Gustafsson et al. 2009; Mouteva et al. 2015). Other factors, such as geographic location, season, air mass source/trajectory, and even soil burn depth (as observed in boreal forest fires; Mouteva et al. 2015), contribute to the spatial and temporal heterogeneity of aerosol BC (Gustafsson et al. 2009), which ultimately influences the amount and composition of aerosol-derived DBC which enters aquatic systems.

Leaching experiments have shown BPCA-DBC solubilized from wood charcoal (Abiven et al. 2011) to be more polycondensed than BPCA-DBC solubilized from fossil fuel-derived aerosols (Ding et al. 2015). As such, the degree of condensed aromaticity, inferred from BPCA relative abundances, has been used to estimate sources of aerosol-derived BPCA-DBC. In cryospheric regions, the contribution of fossil fuel combustion and biomass burning to DBC is dependent upon environmental conditions and proximity to anthropogenic activity (Khan et al. 2017). For example, the composition of BPCA-DBC sequestered in the depths of Antarctic lakes indicates the historic, long-range transport of wildfire-derived aerosol BC to remote regions (Khan et al. 2016). However, it is important to note that the degree of condensed aromaticity of BPCA-DBC is significantly altered by photodegradative processes (Stubbins et al. 2012a; Wagner and Jaffé 2015). Therefore, the compositional variation of DBC across the cryosphere could, in part, be driven by its exposure to sunlight during transit and after deposition (Khan et al. 2017).

The contribution of aerosol BC to DBC in inland waters is dependent upon the rate of atmospheric deposition and watershed characteristics which determine its residence time on land prior to export. In glacier-fed streams, where DOM is not primarily sourced from soils or vascular plant material, DOM and associated DBC is mainly derived from anthropogenic aerosols (Stubbins et al. 2012b; Ding et al. 2015). Atmospheric deposition is as an important source of BC to temperate watersheds (Wozniak et al. 2011), however the contribution of aerosol-derived DBC is assumed to be negligible compared to soil-derived DBC in those river systems. This assumption is regionally dependent, as recent modeling efforts show atmospheric deposition of BC to the Paraíba do Sul River catchment to be a significant contributor to fluvial BC flux measurements (Jones et al. 2017).

Ocean dissolved black carbon

At the global scale, rivers are the single greatest quantified source of BPCA-DBC to the oceans ($\sim$ 27 Tg-C yr^{-1}; Jaffé et al. 2013) with the atmospheric deposition of water soluble BPCA-BC constituting a much smaller flux ($\sim$ 1.8 Tg-C yr^{-1}; Bao et al. 2017). However, aerosol BC may serve as a major source of DBC in open ocean regions which do not receive riverine inputs (Flores-Cervantes et al. 2009; Ding et al. 2015; Nakane et al. 2017). Based upon compound-specific radiocarbon measurements, BPCA-DBC is the oldest (most

[14]C-depleted) chemically defined compound class within the oceanic DOM pool, with an apparent age of $\sim$ 23,000 ^{14}C-years in the abyssal ocean (Ziolkowski and Druffel 2010; Coppola and Druffel 2016). The $\sim$ 14 Pg-C stored in the oceans as BPCA-DBC constitutes $\sim$ 2% of total oceanic DOC (Dittmar and Paeng 2009). The flux of BPCA-DBC from rivers could replace the standing stock of oceanic BPCA-DBC within $\sim$ 500 yr. This estimated turnover rate is 1–2 orders of magnitude shorter than the apparent age of oceanic BPCA-DBC (Coppola and Druffel 2016). Several explanations exist for this discrepancy between the estimated supply and apparent residence time of oceanic BPCA-DBC: (1) a strong sink removes most terrestrial BPCA-DBC (Stubbins et al. 2012a); (2) inputs of ^{14}C-depleted BPCA-DBC from atmospheric deposition of fossil fuels; and/or, (3) inputs of ^{14}C-depleted BPCA-DBC from soils or sediments.

Based upon FT-ICR/MS measurements, initial studies in marine DBC cycling reported elevated levels of condensed aromatics at depth, and suggested hydrothermal vents to be a potential source for DBC (Dittmar and Koch 2006). Recent work supports this hypothesis, showing condensed aromatics, as identified by FT-ICR/MS, to be enriched in some hydrothermal vent fluids (Rossel et al. 2017). However, refractory DOM (Hawkes et al. 2015), including BPCA-DBC (Niggemann 2016), was also shown to be consumed in vent fluids, pointing to hydrothermal systems as a potential long-term removal mechanism for DBC. Further work is required to determine if hydrothermal systems are a sink, source, or modifier of DBC in the abyssal ocean. Since a vast store of ancient BC is contained in marine sediments (Bird et al. 2015), the dissolution of DBC from PBC associated with resuspended sediments could add pre-aged DBC oceanic deep waters, however this contribution has yet to be constrained. Finally, the oceanic cycling of biolabile forms of DBC (LT-DBC) remains an unexplored research area.

Degradative processing and environmental sinks of dissolved black carbon

Photodegradation

The molecular composition and reactivity of DBC varies significantly along the combustion continuum (Fig. 1). The heterogeneous reactivity of high and low temperature pyrogenic organic matter indicates different fates for subcomponents of the bulk DBC pool. Condensed aromatic structures, as determined by FT-ICR/MS, are highly photosensitive and efficiently removed when exposed to sunlight, pointing to photodegradation as a major loss term for DBC in surface waters (Stubbins et al. 2010). The photo-reactivity of DBC varies across the DOM molecular size continuum, in which more polycondensed aromatic DBC structures, associated with high molecular weight fractions, are selectively photoremoved (Wagner and Jaffé 2015). The relative reactivity and biogeochemical impact of photo-altered DBC in natural

waters is not yet fully realized, however photodegradation of highly condensed aromatic molecules could transform them into more biologically labile forms of carbon. Studies have demonstrated the enhanced biodegradation of previously photo-altered terrestrial DOC (Obernosterer and Benner 2004; Chen and Jaffé 2014), which suggests similar processes may be possible for the photo-primed biolability of DBC in natural waters, further accelerating the environmental turnover rate of aromatic forms of DBC. However, some of the most biolabile forms of DOM can also be degraded by sunlight (Bittar et al. 2015), suggesting that photochemistry and microbes may compete for biolabile fractions of DBC.

Photochemistry is the main identified sink for marine DBC (Stubbins et al. 2012*a*) and offers an explanation for earlier observations in which condensed aromatics are depleted in oceanic surface waters relative to the deep sea (Dittmar and Koch 2006). Rates for the photochemical removal of DBC from oceanic surface waters remain poorly constrained. BPCA-DBC photodegradation rates have been estimated from photo-mineralization rates established for oceanic DOC (705–2680 Tg-DOC yr^{-1}; Mopper and Kieber 2002; Stubbins et al. 2006) and the changing ratio of DBC : DOC loss during the photochemical irradiation of North Atlantic Deep Water (3–18%; Stubbins et al. 2012*a*). Using this approach, global oceanic BPCA-DBC photo-mineralization rates were estimated to be between 20 Tg-C yr^{-1} and 490 Tg-C yr^{-1} (Stubbins et al. 2012*a,b*). Based upon these rates, the standing stock of ocean BPCA-DBC (14 Pg-C; Dittmar and Paeng 2009) could be removed via photodegradation within $\sim$ 770 yr (Stubbins et al. 2012*a,b*). Considering the photosensitivity of BPCA-DBC, its persistence in oceans for millennia may be driven by the slow pace of oceanic water mass turnover, which controls the supply of BPCA-DBC to photic surface waters (Stubbins et al. 2012*a*). Future work is needed to establish apparent quantum yields for BPCA photochemical loss and to couple models of photodegradation to those of ocean turnover to better quantify real world rates of oceanic DBC photochemical removal.

Photochemistry has also been implicated in the apparent photo-production of condensed aromatics from non-pyrogenic DOM (Chen et al. 2014; Waggoner et al. 2015) using photo-irradiation experiments for samples with very high DOC and high iron content. Iron appears to play an important role in the cycling of DBC (Riedel et al. 2012, 2013), and the presence of iron can induce photo-flocculation of terrestrial DOM (Helms et al. 2013; Sun and Mopper 2016). Therefore, the appearance of condensed aromatic structures in the particulate phase after photo-irradiation of highly aromatic, high iron samples (Chen et al. 2014) may have resulted from the photo-flocculation of DBC already present in the water sample rather than the net production of condensed aromatic compounds. These studies, based upon FT-ICR/MS characterization before and after photo-exposure, warrant further investigation using quantitative methods such as BPCA-DBC.

Biolability

To date, most aquatic DBC studies have utilized the BPCA-DBC method, which targets condensed aromatic DBC (Table 1). Therefore, the bulk DBC pool is commonly referred to as "biorefractory." However, microbial incubations of freshly produced charcoal leachates resulted in the removal of more than 50% of the total DBC (i.e., soluble BC) and almost all the levoglucosan and free lignin phenols (LT-DBC) within 1 month (Norwood et al. 2013). This suggests over half the bulk DBC pool and almost all LT-DBC could be consumed by bacteria in inland waters (Myers-Pigg et al. 2015). The apparent biolability of levoglucosan, and observed biorecalcitrance of condensed aromatics, may explain why the annual flux of BPCA-DBC is nearly an order of magnitude greater than the annual flux of LT-DBC in Arctic rivers (Myers-Pigg et al. 2015; Stubbins et al. 2015). While LT-DBC only comprises $\sim$ 2% of DOC in Arctic rivers (Myers-Pigg et al. 2015), this highly biolabile DBC component could be a contributor to local respired CO_2 fluxes and/or accelerate the remineralization of bulk DOC via "priming" processes during riverine transport (Bianchi 2011). Further research is needed to constrain the role of LT-DBC in global and regional biogeochemical cycles.

Although the biolability of BPCA-DBC has not been quantitatively assessed in natural waters, condensed aromatic compounds, as identified by FT-ICR/MS, were resistant to biodegradation (Spencer et al. 2015). However, the photo-alteration of DOC from natural waters (Stubbins et al. 2010, 2017) and charcoal leachates (Ward et al. 2014) changes the molecular composition of DOM, resulting in the simultaneous loss of condensed aromatics and production of aliphatic compounds with high H/C ratios. Aliphatic signatures in FT-ICR mass spectra, similar to those produced upon photodegradation of DOM, are highly biolabile in bio-incubations studies (Spencer et al. 2015). Therefore, the photo-alteration of condensed aromatic DBC may enhance DBC biolability. Dissolved aromatic compounds can also inhibit microbial utilization of otherwise biolabile DOC (Mann et al. 2014). As such, when studying the fate of DBC in aquatic systems, both the potential for the inhibitory influence of BPCA-DBC upon microbial utilization of LT-DBC and role of photochemistry in altering DBC chemistry should be considered.

In soils, the biodegradation of BC, as determined via nuclear magnetic resonance spectroscopy, is enhanced when charcoal is enriched in pyrogenic organic nitrogen (Knicker 2010; de la Rosa and Knicker 2011). This form of "black nitrogen" exists mainly in microbially accessible pyrrole-type moieties (de la Rosa and Knicker 2011). Black nitrogen is mobilized to the dissolved phase in aquatic systems (Maie et al. 2006; Ding et al. 2014), and exhibits similar pyrrole-type moieties as black nitrogen in soils (Wagner et al. 2015*b*). Qualitative analyses have provided preliminary evidence for the existence of dissolved black sulfur, in which condensed aromatic compounds exhibit sulfur-containing functionalities (Hertkorn et al. 2016; Poulin
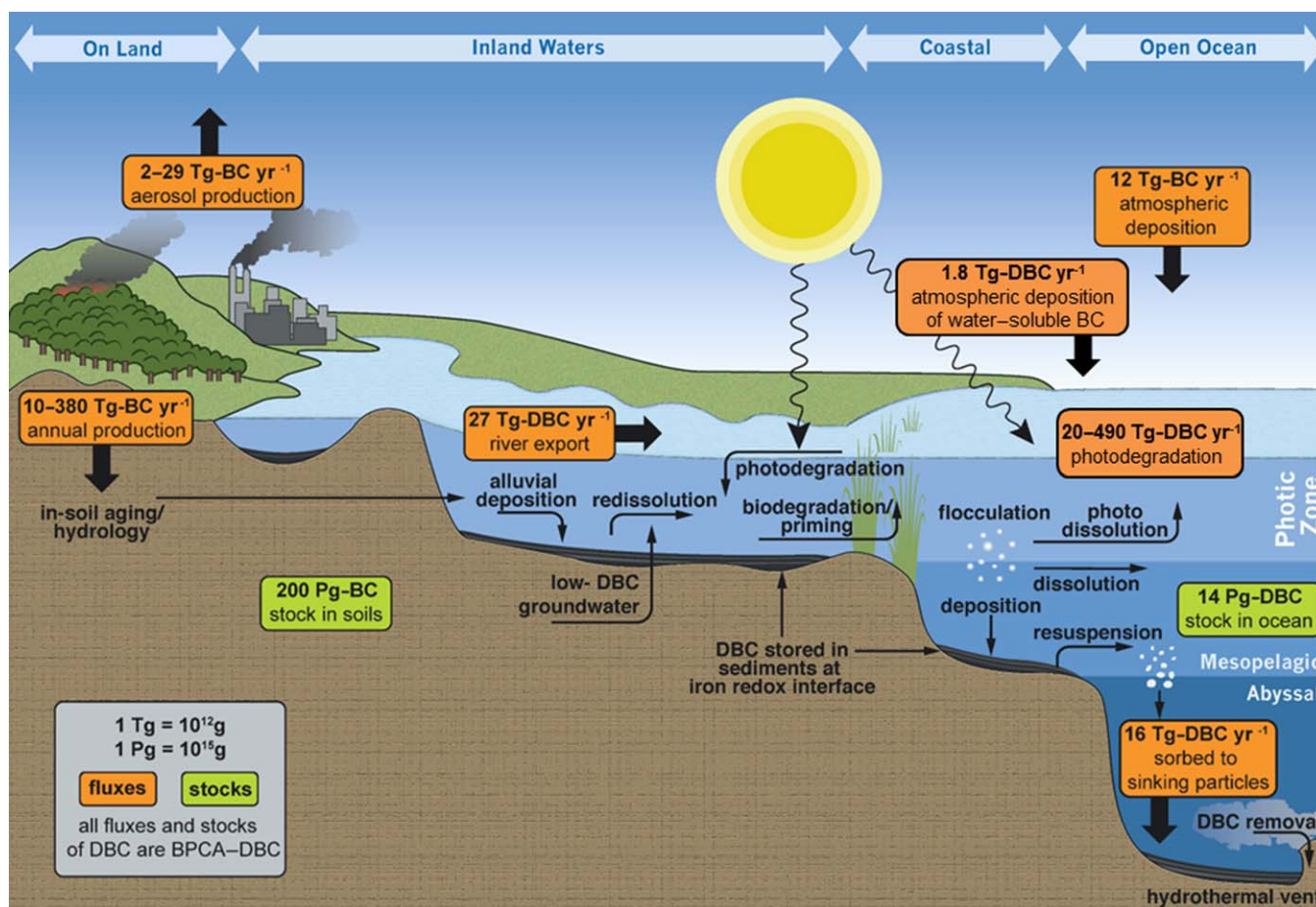
Fig. 3. Summary of DBC cycling from inland waters to the open ocean, modified from Santín et al. (2015). Known stocks and fluxes of BC and DBC are shown (Jurado et al. 2008; Dittmar and Paeng 2009; Stubbins et al. 2012*a*; Jaffé et al. 2013; Coppola and Druffel 2016; Reisser et al. 2016; Bao et al. 2017). Processes for which input/removal rates have yet to be quantitatively constrained are also included. It should be noted that processes, such as photodegradation, photodissolution, biodegradation, etc., can occur in waters across the freshwater-to-marine continuum.

et al. 2017). The bio and photo-lability of nitrogen- and sulfur-enriched DBC may differ from the lability of nitrogen- and sulfur-free DBC, but has yet to be assessed.

Flocculation, precipitation, and stabilization of dissolved black carbon in sediments

The stored records of BC in sediments provide historical evidence for the sedimentation and sequestration of combusted material in marine environments (Leorri et al. 2014; Hanke et al. 2016). Losses of terrigenous CDOM via flocculation and precipitation occur at low salinities (Asmala et al. 2014). As a component associated with the aromatic CDOM pool (Stubbins et al. 2015), it is possible that riverine BPCA-DBC could be removed from the water column via similar mechanisms and become incorporated into the sediment record. For example, the addition of metal salts to peatland waters promoted the flocculation and precipitation of condensed aromatic structures, resulting in residual DOM with a molecular composition similar to that of marine DOM

(Riedel et al. 2012). The sorption of BPCA-DBC to sinking particles relocates surface water BPCA-DBC to the deep ocean and marine sediments and is a significant removal process for oceanic BPCA-DBC (Coppola et al. 2014). Similar sorption processes could selectively remove BPCA-DBC from fresh and estuarine waters, but have yet to be verified. The photo-induced flocculation of DBC in low pH, high DOC, iron-enriched swamp waters further highlights the interplay between organic, inorganic, and degradative processes in DBC precipitation and sequestration (Chen et al. 2014). In sediments, the coupled cycling between iron and condensed aromatics at the sediment-water redox interface can trap a significant portion of DBC in anoxic porewaters of freshwater, estuarine, and marine sediments via co-precipitation (Riedel et al. 2013). Although LT-BC exits rivers in high enough quantities to accumulate in the coastal sedimentary record (Myers-Pigg et al. 2017) it is unclear if this biolabile form of DBC will persist once deposited.

Conclusions

Rivers transfer DBC from land to the ocean. Therefore, constraining the mobility, reactivity, and fate of DBC in rivers and other inland waters is critical in improving our fundamental understanding of global BC cycling. The DBC pool is molecularly diverse and its reactivity varies across the combustion continuum (Fig. 1). Much of the current understanding of DBC cycling draws upon data for BPCA-DBC, which represents a single, but well chemically characterized, fraction of the bulk DBC pool. Consequently, current estimates (Fig. 3) may underestimate the total pool, fluxes, reactivity, and ecological roles of DBC in aquatic systems. Parallel measurements of BPCA-DBC, LT-DBC, and CTO-DBC increase our appreciation of DBC cycling and refine global DBC budgets.

Since chemical composition drives environmental reactivity, we must define the molecular and structural diversity of DBC, which includes the other elements (e.g., nitrogen and sulfur) contained within dissolved pyrogenic matter. The development of new analytical approaches and techniques for the separation of DBC from bulk DOM would be useful in validating the interpretations of DBC described in this review. Despite significant advancements in DBC research, the identification of biogeochemical drivers which control the observed coupling between BPCA-DBC and DOC in fluvial systems remains elusive. The relationship between BPCA-DBC and DOC may result from the incorporation of BPCA-DBC compounds into molecular assemblies of DOM, or be controlled by similar biotic and abiotic processes for soil BPCA-DBC and DOC generation, stabilization, and mobilization.

Fire frequency and recency do not appear to significantly influence the export of BPCA-DBC to inland waters. From an analytical perspective, the apparent decoupling between the combustion signal in inland waters (e.g., BPCA-DBC concentrations) and fire disturbance is unsatisfying and counterintuitive. The delayed release of BPCA-DBC from catchments post-fire may be explained by the need for in-soil aging and oxidation of BC before it can be efficiently dissolved (Abiven et al. 2011) and exported as DBC. This delayed release concept is supported by mass balance approaches at regional scales that provide compelling evidence for the contemporary export of BPCA-DBC from historical forest clearing burn events (Dittmar et al. 2012a; Marques et al. 2017). Although the delayed release concept offers an explanation for the temporal decoupling of fire events from riverine export, other theoretical explanations exist. For instance, non-pyrogenic B5CAs and B6CAs are detected when the biogenic black pigment aspergillin is analyzed (Brodowski et al. 2005) suggesting non-pyrogenic sources of BPCA-DBC are possible. However, the contribution of aspergillin-derived BPCAs is negligible compared to pyrogenic BPCAs in soil (Brodowski et al. 2005). In addition, the apparent production of non-pyrogenic BC observed in soils (Glaser and Knorr 2008) was later found to have likely resulted from a methodological artifact (Kappenberg et al. 2016). It remains unclear whether additional, quantitatively significant non-pyrogenic sources of BPCAs exist. In order to rule out or identify potential non-pyrogenic sources of BPCA-DBC, the investigative analysis of other highly colored/aromatic biological material is warranted.

The ocean is presumed to be the ultimate repository for fluvial DBC, as evidenced by the ancient apparent age of deep ocean BPCA-DBC (Coppola and Druffel 2016). The groundbreaking work that revealed the ^{14}C-depletion of BPCA-DBC in the abyssal ocean needs to be applied to constrain the ages of BPCA-DBC in other reservoirs, such as soils, sediments, and inland waters. Previous studies have indicated that a fraction of riverine DOC is aged (Raymond and Bauer 2001; Butman et al. 2012), however the geochemical identity of this ^{14}C-depleted DOC, and whether it may include DBC, remains unknown. PBC stored in soils is older, by up to ~ 4000 ^{14}C-years, than bulk soil organic carbon (Schmidt et al. 2002) and is highly resistant to degradation (Kuzyakov et al. 2014). The long-term stability of terrestrial BC suggests that soils serve as an intermediate reservoir for BC aging, possibly for millennia, prior to its mobilization to fluvial systems. Since the apparent age of soil organic matter increases down depth profiles (Rodionov et al. 2010), the radiocarbon signature of riverine DBC would likely depend upon watershed hydrology (base flow vs. peak flow) and land use (forested vs. agriculture). Radiocarbon dating and constraining the apparent residence time of BC and DBC within different environmental compartments will allow us to better constrain global fluxes and budgets of fire-derived carbon in all aquatic systems.

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