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9

Black carbon in coastal and large river systems

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1. Introduction

Black carbon (BC) is defined as the highly condensed carbonaceous products of organic matter combustion (Novakov 1984; Goldberg 1985). It can be formed either via the condensation of combustion gases (i.e., soot), or as the residues of incomplete combustion of any type of biomass. BC in the environment has recently received increasing attention with the growing awareness of its potential importance to the short- and particularly the long-term C cycle and accompanying climate feedbacks. Although BC in the terrestrial environment has been extensively investigated, BC transport to and storage in aquatic environments has received far less attention. In this chapter, the evolution of BC is discussed, from its creation in watersheds to its fate in the oceans, with specific focus on its crossing of the terrestrial-aquatic interface.

The two major possible sources of BC to rivers or the ocean are from fossil fuel and biomass burning. Subsequent to its generation, BC may be transported to the ocean either by atmospheric deposition or after incorporation into soils and sediments, followed by its erosion and transport via fluvial systems (Fig. 9.1). Although these are important, examination and quantification of fluvial BC in large rivers is likely an important route for BC transfer to the oceans deserving further research attention for several reasons. First, despite the importance of BC and its fluvial discharge, there are a limited number of studies addressing BC discharge from the world's major rivers and limited measurements of BC in aquatic environments as a whole. Second, when measured, BC has been shown to comprise a substantial portion of sedimentary organic matter across different river systems and their coastal margins globally (Masiello and Druffel 2001; Mitra et al. 2002; Elmquist et al. 2008; Lohmann et al. 2009). Third, the quantity of BC identified in riverine particulate organic carbon (POC) is approximately twice the amount of BC calculated to be buried in ocean sediments (Druffel 2004), suggesting a missing sink, unidentified transformation processes, or uncertainty in the estimates associated with fluvial and coastal BC sources or oceanic sinks. Finally, as marine sedimentary rock is by far, the largest reservoir of organic matter on Earth (Hedges 1992), it might follow that it is also the largest reservoir for BC on the Earth. However, unlike other organic matter, BC is only created in the terrestrial sphere. Thus, quantifying the efficiency of the terrestrial-to-marine transfer of BC is particularly important toward understanding how biomass combustion is related to climate change and the C cycle. This is because, as a relatively refractory pool of carbon (e.g., Masiello 2004), the formation of BC from biomass combustion, followed by its deposition and burial,

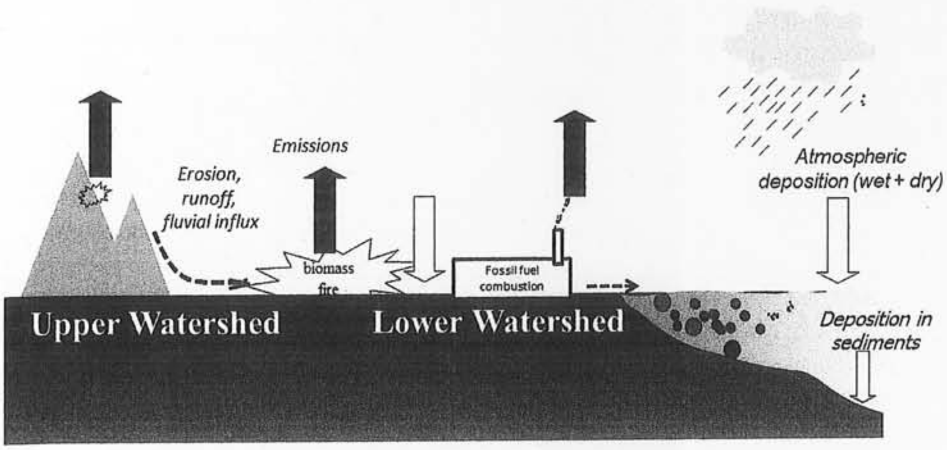

Figure 9.1. Conceptual model of reservoirs and fluxes of particulate black carbon in the terrestrial and aquatic environments. Large black arrows depict BC emissions processes, white arrows depict deposition processes. Small dashed arrow depicts erosion, runoff, and fluvial influx which may occur throughout a watershed.

represents a transfer of carbon from the short- to the long-term carbon cycling pools (i.e., long term sequestration – Fig. 9.2).

Different aspects of the biogeochemical cycling of BC have been reviewed previously (e.g., Schmidt and Noack 2000; Forbes et al. 2006; Preston and Schmidt 2006). The objective of this chapter is to provide a review of studies of BC sources, fluxes, and reservoirs, with emphasis on its fluvial transport and discharge into the ocean. It will be shown that, to the extent that can be determined, in many ways, the fluvial discharge of BC and its burial in the ocean is similar to that of terrestrial organic matter, which is discussed in other chapters of this book (Chapters 4 and 8); whereas in other respects, its cycling is quite distinct. Indeed, the result of the comparisons made in this chapter suggest that

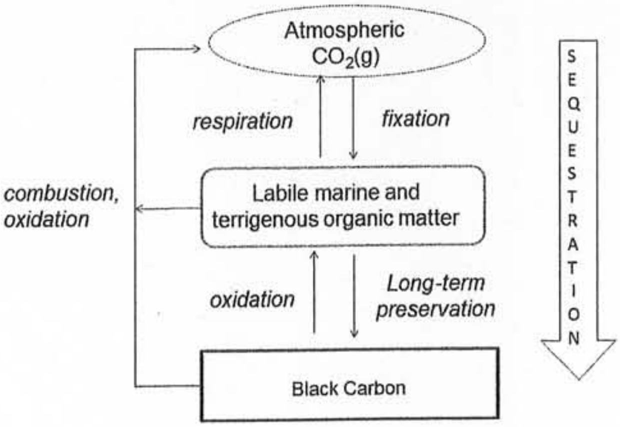

Figure 9.2. The relationship between biomass-derived BC and the global carbon cycle.

unlike bulk terrigenous organic matter, the riverine delivery of refractory BC, irrespective of isolation method used, may in fact be in balance with that found in marine sediments.

It is now widely recognized that atmospheric BC is an important driver of climate, only second or third in importance behind CO_2 in its atmosphere warming effect (Forster et al. 2007). And unlike CO_2 and methane, the reduction of BC emission to the atmosphere may be an easier goal to implement in efforts toward climate change mitigation (Jacobson 2001). Under future climate change scenarios, the threat of wildfires will increase (IPCC 2007) and, as society's dependence on fossil fuels continues to grow, concomitant increases in fossil fuel and aerosol BC emissions are expected. In addition, individuals and companies may soon intentionally produce BC (biochar) from waste biomass in large quantities in efforts to sequester C and improve soil fertility (e.g., Lehmann 2007). The fate of this increasing BC supply is not known, so knowledge of riverine fluxes and aquatic BC reservoir processes are needed now more than ever.

2. Sources of black carbon

The main sources of BC to the environment are fossil fuel (coal, oil, gasoline, and diesel) and biomass combustion. Except in the case of natural fires, these fluxes are driven largely by society's present and historical energy needs. Natural gas combustion is not a significant contributor to BC formation (Goldberg 1985); thus we do not consider it further in this chapter. Complete combustion of these organic materials results in the production of CO_2, an important greenhouse gas. However, the efficiency of combustion is dependent on several variables, including heating time, temperature, and type of fuel, but primarily the availability of oxygen. A sub-stoichiometric reaction of organic matter with oxygen, or what is known as pyrolysis, results in the formation of particulate, carbon rich, and O-H-S-N–poor compounds (Stanmore et al. 2001). For example, in the following equation,

$$C_mH_n + yO_2 = 2yCO + (n/2)H_2 + (m\text{-}2y)C \qquad (1)$$

BC will be formed when m exceeds the value of 2y (Goldberg 1985). It should be noted that kinetics of the reaction will often determine the ratio of m:2y.

Several terms have been used to identify the residuals (or subsets of the residuals) of incomplete combustion of organic matter, including char, biochar, charcoal, carbonaceous spherules, soot, fusain, elemental carbon, carbon black, oxidation resistant elemental carbon, and graphitic carbon. It may be best to conceptualize these types of BC as existing along a continuum of combustion, with the abundance of each of these products dependent on combustion conditions (Fig. 9.3) (Masiello 2004; Hammes et al. 2007). On the left side of this figure are the residues remaining from incomplete combustion of biomass, including slightly charred biomass and charcoal; these constitute the larger size class of pyrogenic BC. In contrast, soot and graphitized C, is a mix of amorphous microscopic particles that contain BC and other carbon and/or sulfur-containing products of incomplete combustion. During combustion, residual char and charcoal may form simultaneously with soot, depending on fuel composition and efficiency of combustion. For example, BC from diesel combustion has a higher proportion of soot compared to other incomplete combustion products. In contrast, smoke plumes from wildfires may appear brown, blue, or gray due to the reduced combustion efficiency of wildfires,

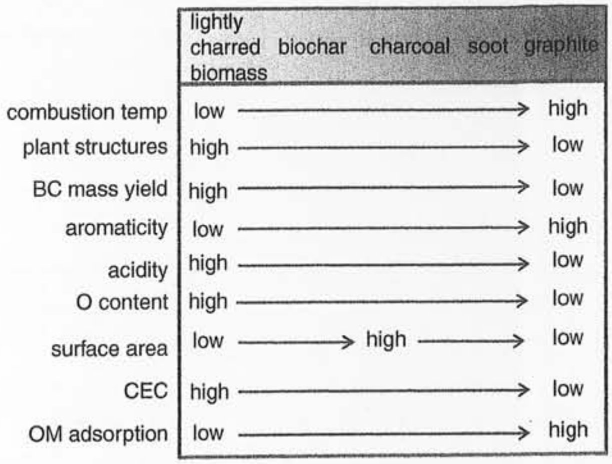

Figure 9.3. The combustion continuum. Modified from Masiello (2004) and Hedges et al. (2000).

which produce relatively greater amounts of non-condensed or partially-condensed organic carbon (sometimes called brown carbon) and other pyrolysis aerosols in comparison with soot (Bachmann 2009).

Laboratory charring experiments of individual components of wood (e.g., cellulose, lignin, pectin), as well as bulk wood and grass, offer some clues to understanding the controls on and variations in BC composition. In general, initial heating of organic matter results in dewatering and dehydration to phenols and aromatics. These are followed by additional chemical transformations that occur at higher temperatures and longer duration of heating leading to formation of more condensed refractory organic matter. For example, Czimczik et al. (2002) showed that at temperatures below 500 °C, BC formed via smoldering hardwood or softwood yielded small clusters of condensed C, lacking a high proportion of graphitic OM. Thus levels of condensed soot-type BC may be low in ecosystems dominated by low-temperature smoldering fires, especially when quantified by isolation methods that rely on detection of condensed aromatic structures (Czimczik and Schmidt 2002).

At formation temperatures beyond 450 °C, progressive depolymerization, loss of functional groups, aromatization, dehydrogenation reactions, and removal of substituents occurs, resulting in larger sheets of fused aromatic rings (Baldock and Smernik 2002; Knicker 2007; Arranz et al. 2009; Keiluweit et al. 2010; Zimmerman and Gao 2013). These condensed structures would likely be very resistant to biotic or abioitic degradation, as would the graphitic turbostatic crystallites that have been observed to form at temperatures >600 °C and in soot (Kercher and Nagle 2003; Keiluweit et al. 2010). In contrast to charcoal, which is irregularly shaped and larger, the basic units of soot are spherical or nearly spherical particles with diameters often in the range of 20–30 nanometers, corresponding to about one million carbon atoms (Haynes and Wagner 1981). Soot may be formed from the nucleation of gaseous carbonaceous species, such as acetylene and polycyclic aromatic hydrocarbons (PAHs) around uncharged radicals, which occur during intermolecular collisions. Subsequently, condensation reactions of gas phase species lead to the appearance of the first recognizable soot particles during the cooling process (Haynes and Wagner 1981). For some solid fuels, soot is also formed from the pyrolysis of tarry materials ejected during devolatilization. These gases then subsequently dehydrogenate and partially oxidize into soot spherules (Stanmore et al. 2001).

2.1. Atmospheric BC

The atmosphere is an important source of BC influx to rivers and the ocean. Moreover, the presence of BC aerosols in the atmosphere has been shown to affect hydrological cycles. For example, the radiative forcing of most aerosols is negative (i.e., leading to cooling of the Earth's atmosphere with increased concentrations) (Penner 2001), but BC aerosol's radiative forcing is positive as BC absorbs sunlight and warms the atmosphere and may enhance evaporation (Hansen et al. 2000; Jacobson 2001). These radiative effects have been shown to alter regional atmospheric stability and vertical circulation, while affecting large-scale circulation and hydrologic cycles, causing significant regional climate effects such as enhanced regional precipitation (Menon et al. 2002).

The aeolian transport of BC aerosols and their deposition on snow and ice are intimately linked via a positive feedback loop in the climate-carbon cycle. The long-range transport of BC aerosols to snow and ice in remote areas reduces albedo (Warren and Wiscombe 1979; Warren and Wiscombe 1981; Warren and Wiscombe 1985), resulting in increased ice melt in polar and boreal areas (Robock 1984; Clarke and Noone 1985; Barry 1996). For example, a concentration of 15 mg kg^{-1} of BC in snow reduced its albedo by 1% (Warren and Wiscombe 1980). In some cases, the BC remaining at the surface of glacier snow increased melting by 50% over areas of ice that were not impacted by BC deposition (Conway et al. 1996). Such BC-driven snow melting has been shown to contribute to historical rapid Tibetan glacier retreat, suggesting that BC deposition may significantly affect some of the world's largest freshwater supplies as well as sea level globally (Hansen and Nazarenko 2004; Xu et al. 2009). Furthermore, some recent studies have alluded to anthropogenic aerosols, rich in fossil carbon, contributing to much of the ancient organic matter in glacial runoff (Stubbins et al. 2012a). As a result, increased BC emission may ultimately enhance melting of ice from polar and boreal areas, leading to increased freshwater transport of BC into the oceans.

There are several factors that affect the concentration of BC aerosols in the atmosphere and their subsequent deposition. Geographically, modern day emissions of BC are highest in the tropics and East Asia (Ramanathan and Carmichael 2008), suggesting that watersheds and rivers in this area may be enriched in BC. Also, aerosol BC is found above both land and ocean, with concentrations being highest near urbanized areas and lowest above remote areas (Clarke et al. 1984). Present day estimates of annual global BC emission range from 6 to 24 Teragrams ($1\ Tg = 10^{12}$ g) BC from fossil fuel emission (Penner and Eddleman 1993; Novakov et al. 2003) and 50 to 260 Tg BC from biomass burning (Kuhlbusch and Crutzen 1995; Fernandes et al. 2007), suggesting both processes contribute to aerosol BC loading. However, another recent estimate of annual fossil fuel and biomass BC emission together (8 Tg y^{-1}; Bond et al. 2004), suggests that there is still some uncertainty in the scientific community regarding the amount of BC emitted into the atmosphere.

The residence time of BC aerosols in the atmosphere is determined by initial size distribution, concentration of ambient particles, frequency and duration of precipitation, and wind conditions (Ogren and Charlson 1983; Ogren et al. 1984). The largest BC particles are not likely to become or stay airborne and as such will deposit proximally to the source of combustion (Clark 1988). The majority of aerosol BC is found in the smaller 0.01–1.0 μm size fraction (Clarke et al. 2006) and will have atmosphere residence times of days to weeks (Clark 1988) (Fig. 9.3). Despite its importance locally and regionally, dry deposition does not contribute very much to the total atmospheric deposition of aerosol organic matter (Bidleman 1988). Additional studies at the regional level have shown that wet deposition accounted for 52–99% of aerosol BC deposition and thus is considered to be the most important deposition mechanism by which atmospheric BC enters the ocean (Suman et al. 1997). The most comprehensive estimate for atmospheric BC deposition to the ocean to date, suggests that dry and wet deposition of BC to the ocean are 2 and 10 TgC y^{-1}, respectively (Jurado et al. 2008). Next we address how this estimate compares with other BC sources into the ocean, namely that derived through soil erosion and fluvial influx.

2.2. Soil BC

Given that humans have been burning biomass since ~9 kya (Carcaillet et al. 2002), the widespread occurrence of natural fires (when unsuppressed), and the emission products associated with both processes, the occurrence of BC in nearly all soils is not surprising. Although there is still uncertainty regarding the most appropriate method to measure BC (see later section), calculation of pyrogenic OM contribution to soil organic carbon (SOC) using solid state ^{13}C nuclear magnetic resonance spectroscopy, acid potassium dichromate digestion, and benzenepolycarboxylic acid concentrations are becoming more common. Using these methods of determination, concentration of BC in most soils generally ranges 0.2–5 weight % of soil and represents between 2% and 15% of the soil TOC, with values of about 10% SOC most common (e.g., Bird et al. 1999; Hammes et al. 2007; Cusack et al. 2012). Soils thought to have anthropic inputs of pyrogenic OM such as Amazonan *terra preta* and higher latitude grassland OM-rich soils such as Chernozems and Mollisols have been found to have BC contents as great as 45% SOC (Chasar et al. 2000; Czimczik et al. 2002; Forster et al. 2007; Schmidt et al. 2002).

Much as for soil OM as a whole, there is considerable debate regarding the primary controls on soil BC concentrations. As with soil OM, the possible controls can be reduced to either input or preservation-related mechanisms. Although some studies have found soil BC stocks to be related to fire frequency or intensity, other studies have failed to find such relationships. For example, the BC content of an Andean volcanic agricultural soil that had yearly burns of wheat and barley residues was not different from one that had experienced no burning (Rivas et al. 2012). In contrast, a nearby forest with no recent burning had significantly less BC content (0.5% SOC) than the topsoil of a site affected by wildfire 3 years previously (7% SOC, Rivas et al. 2012). In studies of Siberian Scots pine forest soils, increases in BC of up to 40% were found in some soils and no lasting effect on others (Czimczik et al. 2003; Czimczik et al. 2005).

Despite all these uncertainties, wildfires have been estimated to produce approximately 0.04–0.2 Pg soil BC yr^{-1} (Preston and Schmidt 2006). Given these global estimates, as well as those for specific areas, workers have concluded that charcoal soil stocks should be several times greater than actually observed (Baldock et al. 2004; Ohlson and Tryterud 2000). Part of the difficulty in linking BC production to BC soil stocks is that BC may not be as fully inert as was previously assumed.

The observation of strong correlations between SOC and BC levels (Hammes et al. 2007; Cusack et al. 2012) suggests that similar processes may control their distribution and perhaps export, including degradation, translocation within soil, dissolution, and erosion. Both BC degradation and dissolution (soil as a dissolved BC source) are discussed further later.

Although horizontal and vertical movement of particulate soil BC by erosion and downward translocation, respectively, are infrequently quantified, there is a growing body of indirect evidence that these processes represent significant losses of soil BC at short timescales. First is the very presence of BC in aquatic environments, despite its exclusive production on land. Second, studies examining soil profiles in which the history of fire incidence is known have calculated wildly varying loss rates, leading many to conclude that process other than BC degradation, such as erosion, may play a dominant role (e.g., Nguyen et al. 2008; Zimmerman and Gao 2013). Finally, a few studies have attempted to follow all BC losses from a BC-amended soil in the field. Working in Colombia over two years, only a small portion of the BC losses could be accounted for, leading the researchers to conclude that 20–53% of the applied BC must have been lost by surface erosion (Major et al. 2010). Another study found that 7–55% of pyrogenic C added to the soil via a surficial grass fire was lost to erosion, and another 23–46% was moved vertically to greater soil depths (Rumpel et al. 2009). In addition, observations of low BC concentrations in upper layers of soils subject to frequent burning, but increased BC with depth, suggests mobility of BC within the soil profile (Dai et al. 2005; Dick et al. 2005; Knicker et al. 2012).

Perhaps it is not surprising that BC should make its way from soils into rivers, given that natural fires often occur on unstable slopes and may denude the landscape of erosion-deterring vegetation (Fig. 9.1). The passage of fire across soil can also lead to an increase in soil hydrophobicity and a concomitant decrease in water infiltration capacity, the net result of which is increased surface runoff and erosion, which are magnified in proportion to the intensity of the fire (Conedera et al. 2009). In addition, BC particles may be preferentially exported compared with other soil OM owing to their predominantly small size and low density (Skjemstad et al. 1999; Hammes et al. 2007). Exported BC was found to be most closely associated with the 20–50 μm soil fraction (Rumpel et al. 2009). Certainly, BC exported from soil versus storage or loss via other mechanisms will vary with such factors as climate, topography, soil type, and hydrological regime.

2.3. Dissolved BC

Despite the fact that fluvial BC has been typically regarded as particles found in suspended sediments or bedload, the recently proposed presence of BC in the dissolved phase is certainly reasonable. The definition of particulate versus dissolved classes of organic matter is operational, with POC often defined as organic material retained on filters with nominal size cutoffs (e.g., 0.45, 0.7, or 1 μm). Thus it is conceivable that microparticulate BC escapes the analytical window of what is defined as particulate material. Furthermore, material that passes through such filters may remain suspended in the water column for substantial periods of time, leading to the observed age offset between POC and BC (Masiello and Druffel 1998; Abiven et al. 2011). Also, desorption from soot BC aerosols at room temperature has yielded condensed aromatic molecules in the water soluble fraction, whereas oxidation of particulate BC causes it to become more water soluble (Chugtai et al. 1991;

Decesari et al. 2002; Wozniak et al. 2008). Thus leaching of carbon from the particulate to the dissolved phase, aided by chemical oxidation or biodegradation, may be significant.

Researchers have claimed to identify substantial amounts of pyrogenic substances in the dissolved phase of organic matter in rainwater, rivers, and the ocean (Kim et al. 2004; Mannino and Harvey 2004; Lee 2005; Hockaday et al. 2006; Dittmar 2008). Some of the recent studies that have detected the presence of BC in the sub-particulate phase are summarized in Table 9.1. What is clear from the comparison of these studies is that dissolved BC may comprise trace amounts up to 7% of the total DOC in an aquatic system. The studies in Table 9.1 suggest that a median value of ~5% is appropriate for the fraction of total DOC that is BC. Since DOC in the oceans is estimated at 7×10^5 Tg C (Hansell and Carlson 1998), the ocean's reservoir of dissolved BC can be approximated at 4×10^4 Tg. Using a value of 35,000 $\mathrm{km}^3\ \mathrm{y}^{-1}$ for the water discharged from all rivers to the ocean (Chapter 3), with a median concentration of all dissolved BC concentrations listed in Table 9.1 (10 μg L^{-1}), an estimate for the residence time of dissolved BC is calculated to be ~100,000 years. As the median age of bulk DOC has been measured to be far younger (~6,000 years; Williams and Druffel 1987), our simple calculations suggest that dissolved BC is certainly old enough to bias the age of bulk DOC. That said, several studies have found dissolved BC to be rapidly photooxidized (Stubbins et al. 2010; Stubbins et al. 2012b). It is likely that, as with particulate BC, dissolved BC is composed of materials with a continuum of compositions and labilities. Clearly, additional investigations into the chemical composition, age, and environmental fate of dissolved BC in the ocean are warranted.

3. Isolation, quantification, and source discrimination methods for black carbon

There are as many methods to isolate BC as there are BC practitioners. Furthermore, each method of BC isolation is often uniquely suited to the interests of the researcher. For example, the atmospheric community often quantifies BC by measurement of light transmittance or reflectance on filters as it is concerned about BC's radiative properties (Smith et al. 1975; Rosen and Novakov 1977; Novakov 1984; Horvath 1993; Liousse et al. 1993; Martins et al. 1998a; Martins et al. 1998b; Bond 2001; Currie et al. 2002; Moosmuller et al. 2009). But, isolation, quantification, and source discrimination methods for aquatic and sediment-associated BC fall into categories of visual/optical, oxidation-based (chemical and thermal), spectroscopic approaches, molecular proxy-based, and some combination of these. Specifically, quantification of BC after its isolation involves either direct optical methods (e.g., counting) or quantification of C by high temperature oxidation in the presence of a metal catalyst to CO_2. These BC isolation methods are briefly discussed later. The reader is also referred to several additional methodological review studies for further information (Schmidt and Noack 2000; Currie et al. 2002; Nguyen et al. 2004; Hammes et al. 2007).

The methods used to isolate BC in aquatic systems can result in large differences in the amount of BC quantified. Furthermore, each method for BC isolation has its inherent limitations based on the fact that each BC isolation method may be optimized for a specific portion of the BC continuum (Fig. 9.3). Also, there is no measure of accuracy for BC analysis. Methodological limitations can be attributed to (1) a lack of a common definition for BC, (2) failure to detect a broad range of pyrogenic carbonaceous residue, and (3) false-positive identification of non-BC carbonaceous substances such as soil geopolymers, kerogen, or other petrogenic carbon.

Table 9.1. *Compilation of dissolved or colloidal black carbon data measured in aquatic systems*

Geographical region	Isolation method	Comments on isolation method	Amount of BC in dissolved or colloidal phase (μg BC L^{-1})	Dissolved or colloidal BC/DOC (%)	Reference
Delaware Bay, Chesapeake Bay, USA	CTO-375 on HMW DOM	Some charring observed but not quantified	45–1,038	4–7	(Mannino and Harvey 2004)
Stream in New Jersey, USA	FT ICR-MS of aromatic compounds in DOC	Non-quantitative	NA	NA	(Kim et al. 2004)
Rio Negro, Amazon River, Brazil	FT ICR-MS on HMW DOM	Non-quantitative	NA	NA	(Kim et al. 2004)
River-to-ocean transect, north eastern Gulf of Mexico	Benzenepolycarboxylic acid quantification on cartridge isolated DOM via HPLC		9,600–44,000	0.9–2.6	(Dittmar 2008)
Southern Ocean	Benzenepolycarboxylic acid quantification on cartridge isolated DOM via HPLC	Functionality confirmed using FT ICR-MS	7.3–9.6	~2	(Dittmar and Paeng 2009)
Open Ocean (Sargasso Sea, North Central Pacific)	Radiocarbon age of benzenepolycarboxylic acid on cartridge-isolated DOM	Ultrafiltered material	0.96–6	0.5–3.5	(Ziolkowski and Druffel 2010)
North Atlantic Deep Water	Benzenepolycarboxylic acid quantification on cartridge isolated DOM	Functionality confirmed using FT ICR-MS	0.66–13	0.2–2.1	(Stubbins et al. 2012a)
Lake Tahoe, USA	SP2-FIA[1] on whole water	Restricted to ~60–400 nm particle size range	0.02–0.45	0.01–0.02	(Bisiaux et al. 2011)
Amazon River	Benzenepolycarboxylic acid quantification on cartridge isolated DOM	Aromaticity confirmed using FT ICR-MS	0–240	≤7	(Dittmar et al. 2012)

Notes:

[1] flow injection, ultrasonic nebulization, laser induced incandescence photometer.

NA – not available.

3.1. Visual methods for BC quantification

Paleoecological studies have benefited tremendously from quantification of the historical occurrence of fires made by enumeration and quantification on a per unit area basis of macroscopic or microscopic charcoal in the sedimentary record. Several recent studies that have comprehensively quantified historical charcoal deposition globally have suggested that both geographical and climatological differences contribute to BC loading (Carcaillet et al. 2002; Power et al. 2008; Bowman et al. 2009; Marlon et al. 2009a; Marlon et al. 2009b). Although light microscopy can identify larger particles that are clearly charcoal (i.e., jet black, opaque, angular) some particles can be challenging to identify due to their ambiguous color and/or shape (Patterson et al. 1987). Distinguishing between carbonized plant tissue and much smaller carbonaceous residue of combustion of fossil fuels and other sources is controversial, though important to climate studies. For example, using scanning electron microscopy, Kralovec et al. (2002) proposed that larger BC particles (>20 μm) isolated downcore in Lake Erie sediments were either (1) porous and spheroidal (oil-derived), (2) elongate with length-to-width ratios greater than three (wood-derived), or (3) irregular with a length to width ratio between 1 and 2 (coal-derived). An attempt to independently validate the BC isolation methods in that study using historical energy consumption data was only partially successful (Kralovec et al. 2002), suggesting that this approach may be limited in its application.

3.2. Chemical and thermal BC quantification methods

Quantification of BC in natural soils and sediments requires the ability to distinguish between inorganic carbon, non-pyrogenic OC and pyrogenic carbon. Chemical and thermal oxidation methods entail the removal of the former two, followed by quantification of residual carbon abundance. Prevalent chemical and thermal methods and their variables currently in use are noted in Table 1 of Nguyen et al. (2004). Subtle differences such as isolation temperature (Elmquist et al. 2006; Elmquist et al. 2004) or chemical oxidant reaction time (Masiello et al. 2002) can lead to substantial differences in BC yield for the same natural sample or reference material (Masiello et al. 2002; Elmquist et al. 2004; Elmquist et al. 2006). Thus it is critical that any BC isolation/quantification method be applied carefully and precisely. To that end, it is advisable to incorporate well-characterized available standard reference materials into any method of BC isolation such as those used in the BC Ring Trial (Hammes et al. 2007).

The thermal and chemical oxidation methods used most often for analysis of sedimentary BC are (1) acid-dichromate oxidation (AD) and (2) chemo-thermal oxidation at 375 °C (CTO-375). The AD technique involves thorough demineralization of a sample via hydrochloric acid (HCl) and hydrofluoric acid (HF), followed by a lengthy potassium dichromate (KCr_2O_7) and sulfuric acid oxidation of the demineralized residue (Wolbach and Anders 1989). The technique is based on the kinetics of the reduction reaction of an acidic solution of dichromate in conjunction with that solution's simultaneous oxidation of reduced organic matter. The dichromate in acid oxidizes labile and refractory carbon ranging from fresh biomass to kerogen and even labile BC, depending on the duration of oxidation time (Wolbach and Anders 1989). It is also assumed that each fraction of OM present in the sample responds differently to the oxidant, which is available in excess. The oxidation of carbon in the residue during the etching procedure is then modeled as a first-order exponential loss process, with a "fast" rate constant corresponding to labile non-BC, intermediate rate constants corresponding to kerogens, and a "slow" rate constant corresponding to BC (e.g., elemental carbon) (Wolbach and Anders 1989) with 400 hours being an adequate representation of the onset of the slower rate constant (Masiello 1999). It is commonly and incorrectly assumed in this approach, the BC can be approximated by carbon that is left in the residue after the oxidation reaction. However, that is not the case, as proper application of this technique relies on knowledge of the chemical kinetics of sample oxidation (Masiello et al. 2002). One criticism of wet-chemical methods is that they may underestimate BC as a result of losses during decantation or other transfers of the samples (Elmquist et al. 2004; Elmquist et al. 2006). However, other studies have not observed a difference in BC content of Standard Reference Material 1649a (urban dust) isolated by both the CTO-375 and the AD method (Mitra et al. 2009), suggesting that the BC losses during the washing and transfer steps can be minimized with careful handling. Although the AD method has been used to isolate fluvial BC in numerous studies (see Table 9.2), the toxicity of the reagents and the lengthy duration of the oxidation process are somewhat disadvantageous.

The CTO-375 technique for isolating BC has probably been the technique most widely applied to soils and sediments, owing to its ease of use. This method originally consisted of thermal oxidation of OC in the presence of excess air and was conducted at 375 °C followed by release of carbonates via in situ acidification in 1 M HCl (Gustafsson et al. 1997). The residual sedimentary carbon is then quantified by CHN elemental analysis (Gustafsson et al. 1997). Later testing of this technique indicated that this method only quantified soot BC (Nguyen et al. 2004). Several modifications have been made to this technique over the years. For example, the temperature as well as the point at which acidification should be done have both been modified since the initial study (Elmquist et al. 2004; Elmquist et al. 2006). One problem with thermal techniques is that they can yield false positives and overestimation of pyrogenic OM via charring. For example, nitrogen-rich macromolecules seem to be charred during thermal oxidation (Accardi-Dey 2003; Flores-Cervantes 2008), leading to quantities of soot BC in coastal planktonic organic matter isolates (Gelinas et al. 2001; Accardi-Dey 2003), bovine serum albumin (Flores-Cervantes 2008), and melanoidin (Hammes et al. 2007). It also appears that pollen is refractory to chemical and thermal treatment associated with the CTO-375 (Gustafsson et al. 1997). The reader is advised to carefully review the evolution of this procedure before proceeding and, in particular, evaluate its limitations alongside its simplicity. Several studies quantifying soot BC using the CTO technique are also listed in Table 9.2.

Recent advances in spectroscopic methods for identification of BC, which are based on molecular structure such as aromaticity, have yielded intriguing results about chemically and thermally isolated pools of BC. Spectroscopic methods such as ^{13}C nuclear magnetic resonance (NMR) and near-edge X-ray absorption fine structure (NEXAFS) have been used to demonstrate the presence of aromatic, graphitic, and amorphous moieties in chemically and thermally isolated BC (Lehmann et al. 2005; Dickens et al. 2006; Haberstroh et al. 2006). This suggests that material that is chemically or thermally isolated as BC may in fact be extremely heterogeneous in functional groups and composition.

3.3. Isolation of BC in the dissolved phase

Researchers have used a variety of techniques to isolate and quantify BC in the dissolved or colloidal phase in aquatic systems. For example, Mannino and Harvey (2004) quantified BC in

Table 9.2. *Values of particulate black carbon and organic carbon concurrently measured in river systems globally*

River	BC (mg/g)	TOC[1] (mg/g)	BC/TOC (%)	Type of BC[2]	Sample type	Reference
Santa Clara[3]	3.0	35.6	8.5	AD	Surface water TSS	(Masiello and Druffel 2001)
	7.1	16.0	44.3	AD		
	1.0	11.5	8.8	AD		
Ganges-Brahmaputra	2.9	5.7	50.9	AD	Surface water TSS	Mitra et al., unpublished
Mississippi	3.8	28.0	16.0	Soot	Surface water TSS	(Mitra et al. 2002)
	4.2	25.0	16.8	Soot	Bottom water TSS	
	0.5	32.0	1.5	Soot	Surface water TSS	
	0.8	25.0	3.0	Soot	Bottom water TSS	
AVERAGE BC IN TSS	2.9 ± 2.2	22.4 ± 10.3	18.7 ± 18.7			
Changjiang River	0.6	2.6	24.6	Soot	Surface sed (0–10cm)	(Kang et al. 2009)
	1.4	5.4	25.6	Soot		
	0.6	2.7	21.9	Soot		
	1.2	5.4	21.9	Soot		
	0.2	2.5	7.2	Soot		
	0.7	6.2	11.9	Soot		
	1.9	6.9	27.1	AD	Surface sed (0–2 cm)	(Li et al. 2012b)
	2.2	4.1	52.9	AD		
	2.2	4.7	46.2	AD		
	1.7	5.9	28.8	AD		
	2.2	6.3	34.1	AD		
	1.5	5.2	29.2	AD		
	2.3	6.7	34.0	AD		
Congo Fan	0.8	33.0	2.4	Soot	Surface sed (0–1 cm)	(Lohmann et al. 2009)
	0.9	20.2	4.5	Soot		
	0.9	13.3	6.8	Soot		
Amazon fan	1.2	3.7	32.4	Soot	Surface sed (0–1 cm)	(Lohmann et al. 2009)
	1.1	7.1	15.5	Soot		
	1.1	5.7	19.3	Soot		
	1.1	5.6	19.6	Soot		
Ob	0.5	9.2	5.1	Soot	Surface sed (0–2 cm)	(Elmquist et al. 2008)
Yenisey	1.2	19.4	6.2	Soot		
Lena	0.2	5.7	3.0	Soot		
Indigirka	1.4	18.1	7.7	Soot		

(continued)

Table 9.2 (*continued*)

River	BC (mg/g)	TOC[1] (mg/g)	BC/TOC (%)	Type of BC[2]	Sample Type	Reference
Kolyma	1.5	19.2	7.8	Soot		
Yukon	1.2	12.4	9.7	Soot		
Mackenzie	1.0	20.2	5.0	Soot		
AVERAGE BC IN SEABED SEDIMENTS[4]	1.2 ± 0.6	9.5 ± 7.5	18.9 ± 13.7			
OVERALL AVERAGE	1.6 ± 1.3	12.5 ± 9.7	18.9 ± 14.7			

Notes:

[1] TOC values correspond to the same time period as that of BC collection.

[2] Type of BC "AD" refers to isolation by acid-dichromate, "soot" refers to that isolated using CTO-375 or a similar chemothermal oxidation method. See original references for additional method details.

[3] Although not a large river, BC concentrations in the Santa Clara were included due to the overall paucity of information on BC in suspended sediments for large rivers globally.

[4] Although many stations were sampled within each of these studies, values of BC in seabed were only included if they were obtained directly at the mouth of that river system.

high-molecular-weight dissolved organic matter from the Delaware Bay using the CTO-375 method. However, quantities of BC in algal exudates, as well as the modern radiocarbon ages of the BC isolate (Mannino personal communication), suggest that their results were influenced by some charring of carbon during their sample processing. Indeed, the level of charring in the blanks used in that study created BC that was similar to the concentrations of BC estimated to exist in the open ocean (Mannino and Harvey 2004). As noted previously, selective charring of nitrogen-rich organic matter has been observed to occur via the CTO-375 technique (Gelinas et al. 2001; Accardi-Dey 2003). Thus, the thermal oxidation method may not be appropriate for isolating BC in coastal or oceanic DOM containing nitrogenous organic matter.

Evidence of BC in the dissolved phase is determined by the presence of condensed polyaromatic moieties in water, which has been revolutionized by Fourier Transform Ion Cyclotron Mass Spectrometry (FTICR-MS) (Kim et al. 2004; Hockaday et al. 2006; Koch and Dittmar 2006; Hockaday et al. 2007). This technique, although not quantitative, offers extremely high-mass resolving capacity of DOM (~200,000 mass units). To quantify dissolved BC, several researchers have relied on the fact that dissolved and unsubstituted PAHs can be oxidized in the lab with nitric acid into various benzenepolycarboxylic acids (BPCA). These BPCAs can then be quantified as a proxy for dissolved BC using liquid or gas chromatography (Glaser et al. 1998; Brodowski et al. 2005). However, it should be understood that the similarity of functionalized water-soluble condensed aromatics in natural waters to the degradative products of BC does not necessarily confirm their common origin. For example, functionalized polyaromatics such as those used as proxies for dissolved BC may originate from oil-weathering (Aeppli et al. 2012) or in situ thermogenic processes known to occur in hydrothermal seeps in the ocean (Dittmar and Paeng 2009). Furthermore, both improper laboratory acidification during the procedure and the presence of darker soil pigments have been shown to yield non-pyrogenic BPCA. Thus the use of BPCAs as a proxy for dissolved BC should also be done with caution.

One novel method of quantifying colloidal BC suspended in the water column involves using flow injection analysis (FIA) coupled to a single particle (SP) intercavity laser-induced incandescence photometer (Bisiaux et al. 2011). The FIA-SP2 method determines BC from the wavelength-resolved incandescent light emitted by individual BC particles heated to their boiling point (3,700–4,300 K) via laser. As a result, the method is free of positive interferences from humic acids, charcoal, mineral graphite, or PAHs and is insensitive to particle morphology. However, the method is restricted to a particle size range of ~60–400 nm, and thus larger colloidal BC would be omitted from being quantified.

3.4. Source discrimination of BC

Most BC quantification methods do not provide information about the BC parent material of mode of combustion. Nonetheless, this source information is useful in understanding BC's role in the global carbon cycle or effect on climate. Stable and radiogenic isotopes of BC as well as molecular proxies of combustion have been used to determine its sources. If minimal isotopic fractionation of the natural isotopes of carbon occurred during (1) combustion of fuel, (2) post combustion preservation, and (3) while carrying out a specific BC isolation technique, stable carbon isotopic signatures ($\delta^{13}C$) of residual BC might be used to distinguish BC from different sources. However, evidence suggests there is carbon isotopic fractionation of both fossil fuels and biomass, both during combustion as well as diagenesis. For example, the isotopic signature of fossil fuels is a function of their physical state (i.e., solid, liquid, or gas), and fractionation during combustion leads to isotopic depletion during the production of combustion gases, but is generally positive during the process of particle formation (Widory 2006). Similarly, isotopic shifts during the heating process of biomass resulted in fractionation of C-13 by as much as 2–4‰ (Gilhooly et al. 1996; Turekian et al. 1996). Also, up to 8‰ depletion in $\delta^{13}C$ was observed in C4-derived chars from natural burning without a similar isotopic change in chars from wood or C3 grasses, owing to the presence of occluded phytoliths in C4-derived chars (Krull et al. 2003). Residual BC may also contain some nitrogen, oxygen, hydrogen, and sulfur, in which case their isotopic signature may be used to fingerprint the source of BC. Because these elements comprise such a minor percentage of its composition, they are often not considered practical in BC source discrimination (Bird and Ascough 2012).

Radiocarbon (C-14) abundance can be used to elucidate the extent to which BC was produced from the combustion of fossil sources or modern biomass (Reddy et al. 2002; Gustafsson et al. 2009). Although living biomass incorporates C-14 from the atmosphere, it is deficient in ancient organic material. This method was applied in a most elegant manner to the infamous "brown cloud" or annual haze of combustion-derived aerosols over the Indian Ocean (Gustafsson et al. 2009). In that study, the C-14 value of aerosol BC was quantitatively used to conclude that 50% of the BC was derived from biomass combustion. Unfortunately, ancient petrogenic and paleosol carbon, which have been found in stream and river waters (Raymond and Bauer 2001), are also likely to be depleted in radiocarbon. Thus improper accounting for such recycled carbon may lead to overestimates of carbon sequestration in marine sediments. Although physical gravimetric separation conducted prior to oxidation may be effective in separating out some petrogenic material (Dickens et al. 2004b), more robust confirmation of BC source is generally necessary, as each source of carbon (fossil fuel or biomass) will have different net effects on the global carbon cycle.

Some of the uncertainties associated with chemical and thermal BC isolation methods of aquatic sediments have been overcome by quantifying trace organic chemical molecules cogenerated during combustion, such as selected polycyclic aromatic hydrocarbons (PAHs) (Gustafsson and Gschwend 1997; Louchouarn et al. 2007; Mitra et al. 2009) and levoglucosan, a byproduct of cellulose combustion (Elias et al. 2001; Kuo et al. 2011). Isomer ratios of high-molecular-weight and particle-reactive PAHs are often used to discriminate between sources of combustion (Yunker et al. 2002), but have also been used to corroborate the abundance and provenance of sedimentary BC (Mitra et al. 2002; Mitra et al. 2009). Another similar technique along these lines employs pyrene fluorescence quenching as a proxy for BC concentrations in natural sediments (Flores-Cervantes et al. 2009b). This method relies on the concept that BC has a high sorption affinity for PAHs such as pyrene and has yielded promising results for its quantification in coastal aquatic ecosystems (Flores-Cervantes et al. 2009b). In summary, it is recommended that any attempt at BC quantification should be coupled to multiple methods of its source discrimination.

4. Black carbon in large river systems

Despite the importance of the fluvial delivery of BC in the global carbon cycle as shown previously, only a few studies have characterized or quantified BC in the suspended river and coastal bed sediments associated with major rivers. The results of those studies are summarized in Table 9.2. Quantification of BC discharge from measurements of BC in riverine suspended sediments (e.g., Masiello and Druffel 2001; Mitra et al. 2002) are associated with uncertainties in that BC in suspended sediments can vary dramatically within and among river watersheds and likely vary with river size and discharge (Masiello and Druffel 2001). The amount of BC transported as bedload is also unknown. Additionally, erosion of soil from fire-affected areas can introduce non-BC soil-derived geopolymers, which may produce false-positive measurements of BC suspended in the water column. Other researchers have attempted to estimate BC discharge by quantifying BC in the seabed adjacent to major river systems (Elmquist et al. 2008; Lohmann et al. 2009) but this approach also has inherent limitations. For example, BC may be preferentially transported away from river deltas. And bed sediments adjacent to the mouth of large rivers have been termed "fluidized bed reactors," which are extremely efficient hot spots for remineralization of carbon (Aller 1998). As a result, quantities of BC in these areas may be disproportionately low and unrepresentative of global fluvial quantities entering the oceans.

4.1. Fluvial BC

Existing fluvial sedimentary BC concentration data were collected and parsed into estimates for BC in riverine suspended sediments as well as bed sediments (Table 9.2). In comparing these numbers, a few salient trends are apparent. First, irrespective of the isolation method used or geographic location, BC concentrations per mass of sediment are generally greater in suspended sediments than in bed

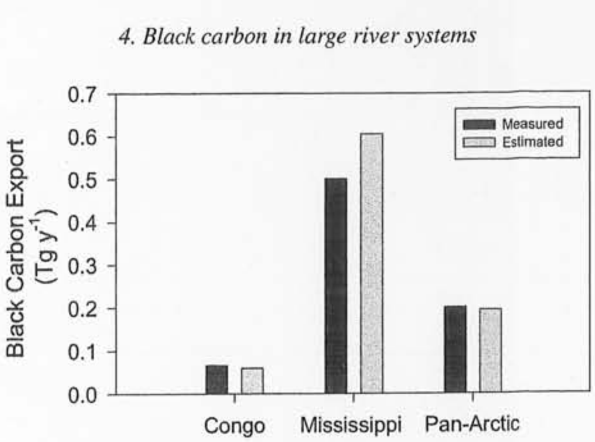

Figure 9.4. Measured and estimated BC exported from a selected subset of major river systems from Table 9.3. Measured values for the Congo, Mississippi, and Pan-Arctic Rivers are from Lohmann et al. 2009, Mitra et al. 2002, and Elmquist et al. 2008, respectively. Pan-Arctic rivers BC export is calculated as the sum of the well-studied Yenisey, Ob, Lena, and MacKenzie rivers.

sediments. Second, the concentration of POC, when quantified concurrently with BC, is significantly higher in suspended sediments than bed sediments. As a result, BC-to-TOC concentration ratios appear similar in all the fluvial systems in Table 9.2. This suggests that non-BC sedimentary organic carbon is transported, sorted, or degraded by similar processes as BC across coastal systems. For these reasons, we suggest that the average value of 1.6 mg BC per gram dry weight (gdw) of sediment (Table 9.2), integrated across suspended and bed sediments, be used as a convenient representative concentration of fluvial BC entering the oceans. To calculate global particulate BC exported from large rivers for which BC has not yet been quantified, the value of 1.6 mggdw^{-1} was multiplied by suspended sediment discharged from each large river listed in Table 9.3. A similar approach has been used to calculate global fluvial discharge of sedimentary POC (Burdige 2005). Estimated values of BC were then compared with known values of BC in a subset of the large river systems listed in Table 9.3, as determined by others. This comparison shows that estimated values of fluvial BC export are similar to experimentally-determined values of soot BC for the Congo, the Mississippi, and selected Pan-Arctic rivers (Fig. 9.4). Part of the reason that this estimation method agrees well with existing values of soot BC may be that averaging BC/TSS across different methods and across a larger number of rivers may eliminate differences owing to methodological artifacts. Alternatively, the comparison may be biased by the fact that most of the values and the 1.6 mg gdw^{-1} in Table 9.2 are derived from refractory BC, isolated using the AD and CTO-375 procedures.

The estimates for each river's BC discharge noted in Table 9.3 are graphically depicted in Figure 9.5, where the area of each arrow is proportional to the estimated annual BC discharge. It is apparent from Figure 9.5 that not only is the Amazon the dominant large river for BC discharge, but the BC discharge of the four major South American rivers (Amazon, Magdalena, Orinoco, and Paraná) is nearly equal to the total BC discharge of every other major river in the study combined (2.64 vs. 2.72 Tg y^{-1}, respectively). Perhaps this is due to the compound effects of residual widespread biomass burning (Dittmar et al. 2012) exacerbated by the lengthy watershed residence time of the basin, coupled with the sheer enormity of that river system's discharge. Nonetheless, the fluvial BC

Table 9.3. *Sediment, particulate organic carbon, black carbon, and polycyclic aromatic hydrocarbon discharge from large rivers*

River	Qs (T yr^{-1})	Qav (m^{-3}/s)	Yield (T km^{-2} yr^{-1})	TSS (kg m^{-3})	TSS (MT yr^{-1})	POC (mg L^{-1})	POC reference	BC discharged[1] (Tg y^{-1})	tPAH (ng g^{-1})	b[a]p (ng g^{-1})	b[a]p discharged (kg y^{-1})	PAH reference
Amazon	1.2×10^9	2.0×10^5	193	0.19	1190.4	2.83	(Richey et al. 1990)	1.91	701	NA		(Budzinski et al. 1997; Lohmann et al. 2009)
Mississippi	4.0×10^8	1.7×10^4	124	0.11	61.3	16.90	(Bianchi et al. 2007)	0.60	5300	372	22,817	(Maruya et al. 1997; Overton et al. 2004; Santschi et al. 2001)
Ganges-Brahmaputra	3.1×10^8	3.1×10^4	701	0.32	312.8	2.50	(Aucour et al. 2006)	0.47	2938	148	46,300	(Ahmad et al. 1996; Domìnguez et al. 2010)
Indus	2.5×10^8	3.2×10^3	261	1.05	105.0	8.82	(Ludwig et al. 1996)	0.38	NA	NA		
Magdalena	2.2×10^8	7.2×10^3	868	0.63	143.3	NA		0.33	NA	NA		
Orinoco	1.7×10^8	3.4×10^4	180	0.06	65.7	1.50	(Paolini 1995)	0.26	NA	NA		
Godavari	1.7×10^8	3.3×10^3	611	2.03	213.2	7.20	(Balakrishna and Probst 2005)	0.26	NA	NA		
Nile	1.2×10^8	3.5×10^3	43	1.4	153.8	3.85	(Ludwig et al. 1996)	0.18	1229	94	14,459	(Badawy and Emababy 2010)
Irrawaddy	1.1×10^8	1.4×10^4	614	0.26	111.2	3.59	(Bird et al. 2008)	0.17	133	0.6	67	(Chernova et al. 2001)
Yangtze	1.0×10^8	2.8×10^4	251	0.13	119.3	1.62	(Wang et al. 2012)	0.16	502	14.6	1,741	(Bouloubassi et al. 2001; Li et al. 2012a)

MacKenzie	1.0×10^8	1.0×10^4	58	0.39	128.0	6.36	(Macdonald et al. 1998)	0.15	1200	66	8,450	(Yunker et al. 1993; Yunker et al. 2011)
Mekong	9.8×10^7	1.7×10^4	123	0.08	44.2	2.01	(Ellis et al. 2012)	0.15	1379	30	1,326	(Keenan et al. 2010)
Paraná	9.0×10^7	1.5×10^4	31	0.18	82.3	1.69	(Ludwig et al. 1996)	0.14	2120	179	14,739	(Cataldo et al. 2001; Colombo et al. 2006)
Congo[2]	3.9×10^7	3.7×10^4	8.8	0.03	35.0	1.70	(Coynel et al. 2005)	0.06	227	NA		(Lohmann et al. 2009)
Huanghe	3.3×10^7	1.5×10^3	1122	2.52	117.7	15.26	(Wang et al. 2012)	0.05	5734	180	21,189	(Jiao et al. 2012; Ma et al. 2008; Wu et al. 2001; Xu et al. 2007)
Amur	2.4×10^7	1.1×10^4	28[3]	0.07	25.3	0.24	(Meybeck and Ragu 1997)	0.04	1100			(Nemirovskaya 2007)
Lena	2.0×10^7	1.7×10^4	8	0.02	10.8	0.99	(Lobbes et al. 2000)	0.03	97			(Elmquist et al. 2008)
Yenisey	4.9×10^6	1.8×10^4	5[3]	0.008	5.0	0.98	(Unger et al. 2005)	0.01	636	4.3	22	(Fernandes and Sicre 1999); (Dahle et al. 2003)
Ob	3.5×10^6	1.3×10^4	6.4[3]	0.009	3.8	0.66	(Unger et al. 2005)	0.01	376	6.9	26	(Fernandes and Sicre 1999); (Dahle et al. 2003)

Notes:

[1] A value of 5.4 Tg y^{-1} is estimated as the sum of BC discharged.

[2] Although the Congo's POC load is low, its expansive watershed is in an area subject to high biomass burning (Cachier and Ducret 1991; Delmas et al. 1991), and 2–7% of its POC is made up of soot BC.

[3] Milliman and Meade 1983.

Unless otherwise noted, physical variables for rivers are from Syvitski and Saito (2007). Qs: suspended load, Qav: average discharge Yield, TSS: total suspended sediments, POC: particulate organic carbon, BC: black carbon, b[a]p: benzo[a]pyrene. NA – not available.

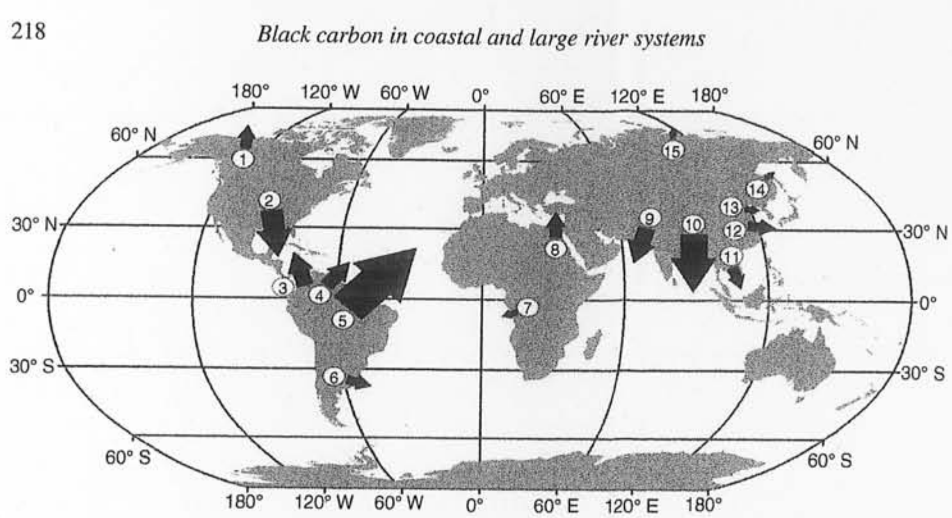

Figure 9.5. World map with arrows depicting fluvial BC discharge from major rivers noted in Table 9.3. Names of rivers are: (1) Mackenzie, (2) Mississippi, (3) Magdalena, (4) Orinoco, (5) Amazon, (6) Parana, (7) Congo, (8) Nile, (9) Indus, (10) Ganges – Brahmaputra, Irrawaddy, and Godavari, (11) Mekong, (12) Yangtze, (13) Huanghe, (14) Amur, and (15) Lena, Ob, and Yenisey.

discharged from South America seems to supersede that of any other continent. However, as we note in another section later, the quantities of BC measured in the seabed adjacent to the Amazon River are surprisingly low.

Although quantifying fluvial BC discharge is not a straightforward process, the BC discharge of some large river systems as determined with our simple BC discharge model agree well with the measured values (Fig. 9.3). As noted in other chapters of this book, the large rivers listed in Table 9.3 are viewed as some of the most influential ones globally in terms of either water or sediment discharge (e.g., see Chapter 3). Thus we assume their collective contribution to BC discharge to the ocean to be the most important, globally.

Although collectively, small mountainous high-yield river systems (SMR) provide 40–70% of the global sedimentary delivery to the ocean (Milliman and Syvitski 1992; Leithold et al. 2006), they are not included in the global BC discharge estimates in Table 9.3. This may be justified given that their watersheds are smaller. Nonetheless, we do discuss their potential role in fluvial BC discharge later.

4.2. Global pyrogenic PAH discharge and comparison with BC

As noted earlier, PAHs co-evolve with BC during combustion (Lima et al. 2005). During biomass and fuel combustion, the liberation of hydrogen associated with fuel combustion en route to its formation of BC produces aromatic molecules (Chakraborty and Long 1967). Several researchers have isolated PAHs concurrently with BC in an attempt to confirm the pyrogenic origin of BC quantified (Mitra et al. 2002; Louchouarn et al. 2007; Kuo et al. 2008; Flores-Cervantes et al. 2009b). Here we attempt to validate our approach for calculating global BC discharge for the river systems listed in Table 9.3 by making a comparison between the discharge of benzo[*a*]pyrene (a high-molecular-weight particle-reactive PAH) and the estimated values of large river BC discharge depicted in Fig. 9.5. The

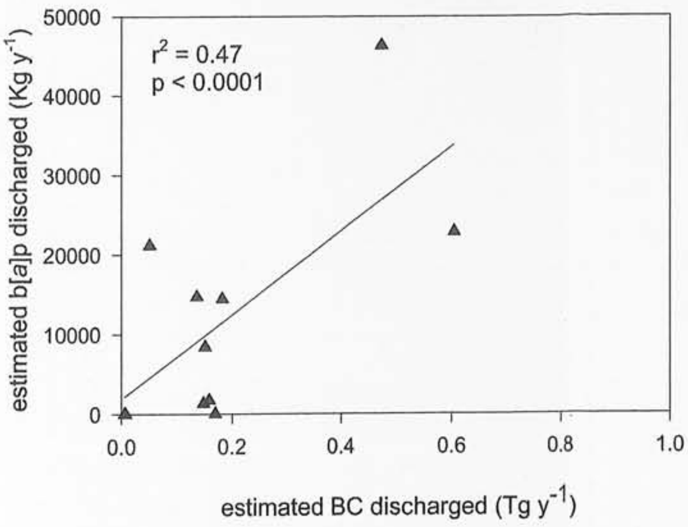

Figure 9.6. Relationship between estimated values of benzo[*a*]pyrene and black carbon discharged in rivers listed in Table 9.3. Estimated values are the product of benzo[*a*]pyrene and black carbon concentrations in sediment multiplied by total suspended sediment discharged for each river system.

significant correlation between the two values ($r^2 = 0.47$; $p < 0.005$ – Fig. 9.6) suggests that the fluvial particulate BC estimated using our approach is pyrogenic and not substantially influenced by non-pyrogenic refractory material (e.g., petrogenic C or soil-derived polymers). In contrast, river discharge of total PAH and BC was not significantly correlated ($r^2 < 0.01$), which is a reasonable result, because not all PAHs are pyrogenic. For example, low-molecular-weight and alkylated PAHs would not be expected to be coeval with combustion-derived BC (Lima et al. 2005).

The global sources and sinks of BC to the ocean can be summarized as follows. First, the most recent estimate of atmospheric BC deposition to the ocean was combined with our estimated fluvial discharge summary (Table 9.3). It was assumed that the most recent value for atmospheric deposition of BC into the world's oceans (12 Tg y^{-1}) is also the most reliable (Jurado et al. 2008), because it is similar in magnitude to the most updated and comprehensive estimate of the amount of fossil fuel and biomass BC emitted annually throughout the world (8 Tg y^{-1}; Bond et al. 2004). This value for annual BC emission globally is much lower than the often cited 50–270 Tg y^{-1} for atmospheric BC emission strictly attributed to biomass burning (Kuhlbusch et al. 1996). Use of the larger range for BC emission calculated by Kuhlbusch et al. (1996) has yielded higher and perhaps erroneous estimates for the magnitude of BC introduced into the ocean compared with the lower amounts found in ocean sediments (Druffel 2004; Masiello 2004).

The value for the global estimate for large river delivery of BC into the ocean calculated above is 5.4 Tg y^{-1} (sum of BC discharged column in Table 9.3). If this fluvial estimate is increased by 40% to incorporate SMR contributions, the total influx of particulate BC to the oceans from rivers may be as high as 8 Tg y^{-1}. This value is comparable to the 12 Tg y^{-1} supplied by atmospheric deposition (Jurado et al. 2008) and implies a total flux of ~20 Tg y^{-1} BC to the ocean. It should be noted, however, that these estimates pertain mainly to more refractory BC (e.g., soot) and may not include other more labile portions of the BC continuum such as charcoal.

5. Fate of black carbon

Despite efforts to understand the short- and long-term cycling of BC derived from both natural and anthropogenic sources, the role of the coastal zone in sequestering fluvial BC is still uncertain. As noted earlier, long-term burial of biomass-derived BC in sediments is a net long-term sink for atmospheric CO_2. In contrast, deposition of fossil fuel BC amounts to reburial of ancient carbon and does not promote net carbon sequestration. It is important to note that understanding of the role of BC in the carbon cycle is confounded by the timescales of the records in which it is quantified in various reservoirs. For example, variations in aeolian BC production and deposition have been observed at seasonal-to-annual time scales, whereas the marine sedimentary record can only be reconstructed at decadal or longer resolution. Consequently, in many areas of the open ocean where sedimentation is low (mm 1,000 y^{-1}) variations in BC will be dominated by BC derived from natural forest fire sources as opposed to modern anthropogenic sources. In contrast, coastal areas with higher sedimentation rates are more likely to record BC inputs from both anthropic fossil fuel and biomass combustion. Next, we discuss sedimentary BC after it leaves a river and consider its fate both on continental margins as well as the deep ocean.

5.1. Storage BC in the ocean

Globally, continental margins (shelf, slope and rise), estimated to be responsible for about 80–90% of the ocean's OC storage (Berner 1982; Hedges and Keil 1995), are the largest reservoirs of marine OC. This is likely to be true for the majority of sedimentary BC as well, which is thought to be deposited in continental shelf regions where water depths are less than 200 m (Suman et al. 1997). The amount and ultimate fate of sedimentary BC on continental margins will vary as a function of the concentration and flux of delivered BC, climate, tectonics, biological and physical mixing, and geomorphology of the margin. Additionally, throughout the Quaternary, there is evidence that stochastic events such as large storms may be drivers of the geochemical record in coastal environments (Goni et al. 2007; Rogers and Goodbred 2010). Most of these drivers have not been comprehensively addressed in existing studies of bulk sedimentary carbon, let alone in BC studies.

We address this data gap by compiling existing estimates of BC deposition in coastal and open ocean sediments (Table 9.4) to determine whether any salient trends can be attributed to any of the state variables noted previously. Furthermore, this compendium may help determine whether there is imbalance in BC delivery and deposition in the ocean. The data in Table 9.4 are listed geographically from high-to-low latitude. What is particularly striking is that the highest concentrations and largest fluxes of BC to coastal sediments do not seem to be related to either latitude or to proximity to large river mouths. And, once again, there does not appear to be a trend in BC concentrations or fluxes related to its quantification method. Rather, the highest fluxes of sedimentary BC listed in Table 9.4 (Swedish Continental Shelf, Chesapeake Bay, coastal East China Sea, and the Palos Verdes Shelf) are

Table 9.4. *Deposition of BC in coastal and open ocean sediments*

Geographical region	Isolation method	BC concentration in sediments ($mg\ g^{-1}$)	BC Flux ($\mu g\ cm^{-2}\ y^{-1}$)	Reference[1]
Coastal Areas				
Saanich Inlet,BC, Canada	Chemical treatment, IR spectrometry	0.55	74	(Griffin and Goldberg 1975)
Pan Arctic Shelf	CTO – 375	0.5–1.5	0.13–5.6	(Elmquist et al. 2008)
Swedish Continental Shelf	CTO – 375	2–2.8	270–8100	(Sanchez-Garcia et al. 2012)
Gulf of Maine, USA	CTO-375, pyrene fluorescence quenching	0.11–0.17; 0.1–15[2]	100–200; 80–170	(Flores-Cervantes et al. 2009a; Gustafsson and Gschwend 1998)
Puget Sound, Washington, USA	GBC[3]	0.1–0.3	30–1,040	(Kuo et al. 2011)
Washington Coast, USA	GBC[3]	0.14–0.71	1.2–3.1	(Dickens et al. 2004a)
Chesapeake Bay, USA	AD	1.1–7.5	760–5,400	(Mitra et al. 2009)
Coastal East China Sea	AD	1.5–2.2	210–1300	(Li et al. 2012b)
Santa Barbara Basin	Chemical treatment, IR spectrometry; AD	0.29; 2.2	26; 35	(Griffin and Goldberg 1975, Masiello and Druffel 2003)
Gulf of Panama	Chemical treatment, IR spectrometry	NQ	109–354	(Suman 1986)
Continental rise adjacent to Nicaragua	Chemical treatment, IR spectrometry	NQ	23–135	(Suman 1986)
Eastern South Atlantic Shelf	CTO-375	0.8–1.6	0.5–7.8	(Lohmann et al. 2009)
Western South Atlantic Shelf	CTO -375	0.4–1.7	0.6–2.6	(Lohmann et al. 2009)
Palos Verdes Shelf	CTO -375	1.2–1.4	700–1000	(Gustafsson and Gschwend 1998)
Open Ocean				
South China Sea	AD	0.01–1.9	NQ	(Jia et al. 2003)
Pelagic Pacificand Atlantic	Chemical treatment, IR spectrometry	0.01–1	0.002–0.2	(Smith et al. 1973)
Pelagic Pacific	Chemical treatment, IR spectrometry	0.44	0.057	(Griffin and Goldberg 1975)
Pelagic Pacific	Chemical treatment, IR spectrometry	0.001–3	<0.0014–3.6	(Herring 1985)
Equatorial Pacific	GBC[3]	0.092	0.05	(Dickens et al. 2004a)

Notes:

[1] The following studies of BC in the deep ocean sediments were reviewed but were not included in the table because neither concentration nor sediment mass flux were provided: (Bird and Cali 1998; Masiello and Druffel 1998; Thevenon et al. 2004).

[2] Concentrations in $\mu g\ L^{-1}$.

[3] The GBC (graphitic black carbon) technique is a thermal oxidation technique with additional organic acid pretreatment specifically designed to minimize charring of occluded organic matter (Gelinas et al. 2001).

NQ – unable to be quantified.

adjacent to fluvial systems affected by urbanization within their watershed, suggesting that fossil fuel combustion primarily drives the bulk of sedimentary BC influx into coastal margins today. Without higher temporal or spatially resolved data, little more can be said about the additional controls on the BC in the coastal sedimentary record.

Based on the calculations discussed in Section 4.2, the global flux of BC to the ocean is estimated at ~20 Tg y^{-1}, with the reasonable assumption that 40% of this is contributed by rivers and 60% by the atmosphere. Although there exists the methodological issue of whether this estimate is mainly for soot or includes all BC, we have shown that estimates don't vary greatly across detection methods that employ chemical and thermal oxidation (Tables 9.2 and 9.4). Assuming a figure of about 90% of total seaward flux of particulate BC to be deposited on continental margins (Suman et al. 1997), BC storage in these regions can be estimated to be 18 Tg y^{-1}. This leads to a delivery estimate of ~2 Tg of BC y^{-1} deposited annually in the deep ocean at water depths greater than 200 m. Assuming the deep ocean has an area of 3.34×10^8 km^2 (Suman et al. 1997), we calculate an expected average BC flux of 0.60 μg cm^{-2} y^{-1}. This falls within the range of measured open ocean flux values from 0.001 to 3.6 μg cm^{-2} y^{-1} (Table 9.4). Using a similar approach, 18 Tg y^{-1} delivered to continental shelves globally can be scaled to the total area of continental shelves (2.75×10^7 km^2) to yield an expected average flux of 65 μg cm^{-2} y^{-1}, which is on the lower end, but within the range of values for BC burial flux in coastal regions globally that are listed in Table 9.4. In summary, our compilation of data for the annual budget of refractory BC suggests that its atmosphere and riverine delivery and deposition to surface sediments in the coastal and deep ocean are in balance. However, our estimates are not able to provide an evaluation of the role of labile pools of BC in the global carbon cycle. In light of recent studies quantifying BC degradation in the environment, data on the production, transport, and fate of these labile pools such as char and charcoal are sorely needed.

5.2. Degradation of BC

There is a growing awareness that, although BC is a relatively refractory OM form, it is not completely inert in the environment. There are a number of lines of evidence that suggest that some pools of BC degrade via abiotic and biotic processes. Physical processes that may enhance BC degradation include UV exposure, leaching/solubilization, volatilization and consumption by later fires, erosion, resuspension and transport in the seabed, and biological processes that include bioturbation and ingestion by macrofauna or remineralization by microbes.

The first type of evidence showing BC oxidation comes from studies measuring CO_2 efflux during in vitro laboratory incubations of laboratory-produced pyrogenic OM. These experiments have recorded pyrogenic C losses ranging about 0.5–5% over a few months to a few years, with some larger losses for materials produced at lower temperatures (<400 °C, Baldock and Smernik 2002; Hamer et al. 2004; Nguyen and Lehmann 2009; Nguyen et al. 2010; Zimmerman 2010; Cross and Sohi 2011; Bruun et al. 2012). About half of these losses can be attributed to abiotic mechanisms (Zimmerman 2010), and greater losses have been observed in the presence of labile sources of OM (so-called positive priming; Cross and Sohi 2011; Zimmerman et al. 2011). These observed losses translate to half-lives of 10 to several hundred years. However, exponential decreases in rates of C loss over time suggest that the power model of OM decomposition (Middleburg 1989) might be more appropriately applied, leading to the calculation of BC half-lives in the thousand to million year range (Zimmerman 2010).

Second, measurements of BC distributions in soil profiles with known pyrogenic OM input histories lead to calculations of apparent BC field loss rates ranging from zero loss (completely stable) to BC half-lives of 3 years. Discrepancies among these studies are likely due to uncertainties that include (1) the likelihood that BC particles are mobile in the soil column and lost via erosion, (2) differing BC degradation rates in different climates and soil types, (3) poorly known BC input rates, and (4) differing BC quantification methods. Only a few studies have examined BC in marine sediment columns, and none of these show progressive BC losses with time of burial (Masiello and Druffel 1998; Middleburg et al. 1999; Masiello and Druffel 2003). However, observations of 64% greater BC contents in abyssal plain sediments exposed to oxygen over 10–20 thousand years versus anoxic sediments suggest BC half-lives of ~10 ky (Middleburg et al. 1999). In addition, smaller BC-nonBC OM ^{14}C-age offsets in oxygenated versus anoxic Santa Monica Basin sediments (Masiello and Druffel 2003) also indicate that sedimentary remineralization of BC does occur, at least in the presence of oxygen.

Next, mass balance considerations suggest the occurrence of large-scale BC remineralization at some location between its production and final marine burial. For example, given estimated BC production rates, over the past 7,000 years, soil OC would become 25–125% BC in just 20,000 years (Masiello and Druffel, 2003). Calculations presented in this chapter also suggest losses between soils and coastal deposition. For example, globally averaged BC concentration in TSS of 2.9 mg g^{-1} versus 1.2 mg g^{-1} in deltaic sediment beds suggest about half the BC is lost during transport (although this could also result from preferential transport processes). This is despite the fact that many of these estimates are based on BC measurement by chemical and thermal oxidation methods that isolate relatively refractory BC, perhaps only soot. However, at this time, estimates of BC production, river export, and sediment sink fluxes within the same geographical area are too few and too widely ranging to use for predicting global BC mineralization rates.

One area where BC may be readily degraded is on broad continental shelves. These environments, which are often physically dynamic due to periodic resuspension, contain sediments frequently subjected to redox oscillations, which have been shown to enhance BC degradation (Nguyen and Lehmann 2009). These areas have been termed "fluidized bed reactors" (Aller 1998) and have been shown to be hot spots of terrestrial OM remineralization. In addition, continuous addition of labile planktonic debris may co-metabolize the degradation of OM, which has also been shown to enhance BC degradation (i.e., positive priming; Hamer et al. 2004; Zimmerman et al. 2011). This may explain the seemingly contradictory observations of large amounts of BC export by the Amazon and other South American rivers (calculated in this chapter) and relatively low concentrations of BC in Amazon shelf sediments (Lohmann et al. 2009).

Finally, losses to BC may occur by solubilization or leaching either in the soil or as part of the suspended or deposited sediment. Although laboratory leaching experiments have recorded only small losses of BC ranging from 0.04% to 1% (Hammes et al. 2007; Abiven et al. 2011; Katsoyiannis et al. 2011; Zimmerman and Gao 2013), aged charcoals seem to exhibit leach C rates similar to those of fresh ones, and detection of mobilized BC in rivers draining Brazil's Atlantic forest even 40 years after widespread burning (Dittmar et al. 2012) suggests C losses that occur by this method may be continuous. And there is evidence from both laboratory microbial incubations showing up to 70% C loss over 1 year (Zimmerman and Gao 2013) and photo-degradation experiments showing a 20-fold decrease in coastal and North Atlantic deepwater dissolved BC (Stubbins et al. 2012b; Stubbins et al. 2010) that losses via leaching followed by mineralization may be a primary sink for BC.

6. Conclusions

Many recently developed analytical techniques show great promise toward identification and quantification of pyrogenic carbon. Yet, even with the advent of these techniques, further study of BC in the environment is warranted to fully understand it from a source-to-sink perspective. This is because several important questions about the global cycling of BC still remain. For example, how long does BC remain in soil, and what processes move it to river systems? Does BC spend very little or a substantial amount of time in transit through river systems and how is BC transformed there? To what extent does BC comprise the bedload versus suspended load of a river system? As there are few studies of the transport and fate of BC within river systems, these questions cannot yet be answered. Because few studies concurrently measure charred OM charcoal, and refractory BC, questions also remain about the fate and transport of labile pools of BC shown in the left side of Figure 9.3. Also, the presence of dissolved BC in rainwater as well as in fluvial and ocean systems begs the question, "What are the mechanisms by which dissolved BC cycles in the ocean?" Lastly, although it seems clear that continental margins are repositories for the bulk of sedimentary BC, a comprehensive understanding of BC fate and degradation in these areas is lacking. With ever-increasing changes in land use and anthropic impacts to climate, now more than ever, it is necessary to address these data gaps in order to understand the role of BC in the global carbon cycle and its possible use for climate mitigation.

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