The black carbon cycle and its role in the Earth system

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Abstract:

Black carbon (BC) is produced by incomplete combustion of biomass by wildfires and burning of fossil fuels. BC is environmentally persistent over centuries to millennia, sequestering carbon in marine and terrestrial environments. However, its production, storage, and dynamics are underrepresented in Earth system models. In this Review, we discuss BC cycling in the land-to-ocean continuum. Wildfires are the main source of BC, producing 128±84 Tg year^{-1}. Negative climate–BC feedbacks could arise as wildfire increases with anthropogenic warming, producing more BC, which in turn sequesters carbon, but the magnitude of these effects are unknown. Most BC is stored in terrestrial systems with some transported to the ocean via rivers and the atmosphere. However, the oceanic BC budget is not balanced, with known BC removal fluxes exceeding BC inputs. These observed inconsistencies are demonstrated with a simple ocean box model, which highlights key areas for future research. Measurements of BC mineralisation and export rates along the land-to-ocean continuum and quantification of previously unexplored sources of oceanic BC are needed to close the global BC budget.

[H1] Introduction

Wildfires and fossil fuel combustion produce substantial amounts pyrogenic organic materials, including black carbon **[G]** (BC)[1]. Globally, fires produce about 128±84 Tg BC year^{-1} (Ref[2])where most is left behind on the landscape as part of charcoal, ash, and other charred plant residues. A smaller fraction (2-11 Tg of BC year^{-1}) is emitted to the atmosphere as soot[3,4]. Fossil fuel burning emits an additional 5-13 Tg aerosol BC year^{-1} (Ref[4]). As these processes convert relatively labile **[G]** biomass carbon to more environmentally persistent **[G]**, more slowly cycling BC, they modify rates of turnover in the global carbon cycle. Omitting BC production from assessments of fire impacts on the carbon cycle leads to overestimation of the strength of positive feedbacks[5] between climate change and wildfire emissions[2,6].

The precise definition of BC varies, but generally refers to the carbonaceous, polycondensed aromatic product (>60% organic carbon) derived from the incomplete combustion of biomass and fossil fuels[7]. BC is part of an incomplete combustion continuum consisting mainly of polycyclic aromatic structures of high molecular diversity, whose size, configuration, and functionality is driven by formation temperature, heating duration, oxygen availability, and fuel materials (**Figure 1**)[8]. It is operationally divided into dissolved BC **[G]** (DBC), which passes through a filter (usually 0.1 to 0.7 μm), and particulate BC **[G]** (PBC), which is retained on a filter. These operational definitions are inherited from the oceanography community, in which dissolved organic carbon **[G]** (DOC) and particulate organic carbon **[G]** (POC) are traditionally divided based on filtration. In reality, however, the range from DOC to POC is a size continuum that includes monomers, polymers, colloids and gel particles[9] (**Figure 1**), and DBC and PBC occur along a continuum of size and phase.

In the environment, BC persists on timescales of centuries to millennia. This stability and longevity is related to its condensed aromatic chemical structure, which is resistant to microbial decomposition[10,7]. The reactivity of BC is further constrained by ecosystem properties including microbial populations, enzyme kinetics, environmental conditions, and matrix protection[10,11]. As a result, BC is the oldest and most abundant molecularly characterized component of the modern carbon cycle[12,13].

In this Review, we describe the occurrence, cycling, and persistence of BC in the environment. We focus on BC, rather than all fire-derived pyrogenic residues, because the BC fraction is the longest-lived[10], giving it relevance for carbon sequestration in a changing climate. The broader implications of BC production are discussed as a possible long-term feedback mechanism, which is underrepresented in Earth system models (ESMs) modern global BC budget for all major components of the Earth System is then presented. We next describe inconsistencies between apparent ages of oceanic BC determined via geochemical methods and BC turnover rates inferred by mass balance equations and highlight areas of the global BC budget that exhibit the highest degrees of uncertainty. Explanations of the observed inconsistencies in the oceanic BC budget are explored using simple ocean box model. Finally, we define major research activities that must be prioritized in the coming years to close the knowledge gaps and minimize uncertainties in the global BC cycle.

[H1] BC Climate Feedbacks

Open biomass fires, including wildfires, deforestation fires, and other land use fires, are the dominant source of BC. Changing wildfire occurrence relates strongly to climate and has the potential to invoke feedbacks to climate change via emission of CO_2 and production of BC. Climate change has increased global wildfire risks globally by increasing the frequency of fire-prone weather conditions[14,15]. In some regions, particularly in temperate and boreal forests, increased weather-related fire risks have translated into rising wildfire activity[16] Globally, fires have widespread impacts on the carbon cycle, directly emitting ~2.2 (2-3) Pg C year^{-1} mainly in the form of CO_2 (Ref[17]). In turn, post-fire vegetation regrowth re-captures ~1.8 Pg C year^{-1} (Ref[17,18]). Much of the remaining ~0.4 Pg C year^{-1} is emitted by deforestation and peatland fires and is lost indefinitely to the atmosphere[17]; however, changing wildfire frequencies in some regions are also leading to an imbalance between the fire emissions and post-fire recovery fluxes and net loss of C to the atmosphere[6,19,20]. While large declines in burned area have been observed in savannahs during the past two decades, forest burned area has synchronously increased and so global CO_2 emissions from fire have remained approximately stable or increased slightly[16,21].

The biogeochemical feedbacks between anthropogenic climate change and fire emissions are positive (**Figure 2**), with a warmer climate leading to increased fire activity, ecosystem disturbance and CO_2 emission. For example, increased fire frequency has already been observed to reduce boreal forest carbon stocks and release carbon to the atmosphere[19]. Taken together, the magnitude of the positive feedback from fire emissions and climate change has been modelled to be on the order of 6 ppm of CO_2 in in the atmosphere per degree of warming[5].

Whereas the positive feedback between climate change and increased fire CO_2 emissions has been studied widely, increased fire activity also leads to an understudied enhancement of BC production and storage with potential to invoke a negative feedback[6,22,23](**Figure 2**). As the turnover of BC is considerably slower than that of unburned biomass carbon[24], the distinction between these two pools is critical to modeling the carbon balance in the decades to centuries following a fire. Unlike positive feedbacks between climate change and fire CO_2 emissions, fire-enabled ESMs do not consider the production of BC. Consequently, ESMs are biased towards positive fire-driven feedbacks under a warming climate. The plausible magnitude of this bias is on the order of 10-20% of the positive feedback based on rates of BC production[22,23]. Overall, omitting the BC cycle from ESMs limits the accurate quantification of the role of fire in the global carbon cycle under climate change.

[H1] BC stocks, ages, and losses

Following its production during wildfires and fossil fuel combustion, the first interactions between BC and the soil surface and water influence its fate. PBC can be incorporated into the soil matrix where it slowly degrades, or transferred via water or wind erosion to aquatic systems[26]. PBC can also physically disaggregate and be transformed through microbial or abiotic activity into submicron particles or DBC, which are transported via surface water or groundwater flows. This section describes BC cycling and export to the ocean.

[H2] BC in the atmosphere

BC aerosol emission inventories suggest that biomass burning and fossil fuel combustion emit 2–11 Tg BC year^{-1} and 4.5–12.6 Tg BC year^{-1}, respectively[4]. BC aerosol is initially emitted as soot in the $PM_{2.5}$ **[G]** class**,** but over time it ages, photo-degrades and coagulates with hydrophilic aerosol species leading to its solubility in rain droplets[183]. Submicron BC can remain airborne for up to 14 days[27], indicating BC aerosols can be deposited far from the fire source. BC leaves the atmosphere by either dry deposition (falls from suspension in the atmosphere) or wet deposition (deposition with falling rain droplets) to the land or surface ocean[27].

Aerosol BC deposited to river catchments represents a secondary source of BC to rivers. Indeed, regional BC aerosols can contribute 5-22% of riverine DBC fluxes[28,29]. For example, in some tributaries of the Amazon River, local sources of fossil fuel emissions from cities along rivers reveal a low- DBC ^{14}C signature but are effectively removed further downstream[30].

Aerosol BC deposition on the surface ocean can be a substantial BC source to the global ocean, with a global flux estimates ranging from 1.8 ± 0.83 Tg year^{-1} (Ref[31]), wet deposition only) to around 12 Tg year^{-1} (Ref[27], wet and dry deposition). In the western North Pacific and South China seas, for example, atmospheric deposition of aerosols from fossil fuel combustion is likely the major source of DBC in the surface ocean[32-34]. In fire-affected coastal areas of the western United States, direct inputs of DBC from atmospherically deposited ash and smoke appeared to be negligible[35]. However, under experimental conditions, leaching of wildfire ash in seawater released a substantial amount of DBC[35]. Taken together, these observations suggest that the deposition of BC aerosols from wildfires could be an important, transient source of fire-derived material to marine surface waters.

[H2] BC in soils and terrestrial intermediate reservoirs

Although BC aerosol fluxes are important, most BC produced during wildfires is retained on-site (128±84 Tg BC year^{-1})[2], mostly from tropical savannas, forests, and peatlands[36]. BC accumulation in soils is determined by BC production rates minus losses via mobilization, degradation, or re-combustion. BC in soils comprises 160-200 Pg C globally, or 13% of the total soil organic carbon on average[13,37]. Higher soil clay content, greater soil depth, higher wildfire temperatures, lower pH, and lower soil cation exchange apparently enhances the retention of BC in soils[13,38,39].

Soil BC is degraded and lost via multiple biotic and abiotic pathways. BC in soil can be microbially oxidized[40-42], which reduces the hydrophobicity of the condensed aromatic structures, thereby increasing solubility and mobilization by leaching and enhancing accessibility for further microbial degradation[43]. Photooxidation and sorption of DBC to minerals or other particulates is an important DBC loss mechanism[44,45], but in situ rates for photodegradation and sorption processes have not yet been robustly quantified. There is also little understanding of how mobility varies across DBC and PBC, as mobility can depend on many factors, including parent materials, fire temperature and behavior, soil type, climate, and topography[37,46].

In-situ mineralization, erosion and solubilization via water, and wind-driven transport are key loss mechanisms for soil PBC[47-49]. Most research has focused on microbial decomposition[39,50-52], with physical degradation and mobilization studied less[53]. Starkly different residence times have been estimated for soil BC. Field-based approaches and long-term laboratory incubation experiments have estimated the soil residence time of BC to be 88 - 870 years (Ref[54]). Conversely, mass balance assessments (annual global BC production minus riverine BC export) suggest that soil BC turnover occurs within 2,400±2,100 years, which is consistent with some incubation experiments that indicate BC is stable in soils for millennia[55].

Once mobilized from production sites, BC can be physically retained in intermediate reservoirs on land prior to riverine export. For example, BC contributes up to 20% of the soil organic carbon in mollic horizons of European floodplains[56] and to around 10-30% in surface sediments in restored Chinese wetlands[57]. Deposition in lakes and other fresh water sediments could be a key but understudied BC retention mechanism, as lake sediments store twice the amount of macroscopic BC than surface soils in boreal forest watersheds[58]. Groundwater could also contain BC, although the magnitude of this pool as well as the flux to the ocean is unknown[59,60]. Therefore, despite the potential relevance of intermediate reservoirs like waterlogged soils, sediments, and groundwaters, the depositional and decomposition rates and storage of BC in these areas are not sufficiently constrained, which prevents a comprehensive understanding of their role in the global BC cycle.

[H2] BC transport in rivers

Rivers transport 43±15 Tg BC year^{-1} (Ref[2]), which equates to ~34±26% of the BC produced annually by wildfires. Globally, riverine DBC and PBC are exported in similar proportions (18±4 Tg DBC year^{-1} and 17-37 Tg PBC year^{-1}, respectively). These estimates are based on datasets with global-scale coverage, and the fluxes are well constrained in comparison to other elements of the aquatic BC cycle[2,61] (**Figure 3**). Compared to other soil particles, PBC is preferentially transported by water erosion and is therefore prone to rapid lateral transfer from hillslopes to the hydrological system during water erosion events, particularly within the first few years post-fire[47,62]. In contrast, the release of DBC from soils to streams is driven by the solubilisation of soil BC by biotic or abiotic mechanisms followed by export with soil pore water to river channels[63,64]. Relative to PBC export, DBC export occurs over longer time periods, after the slow aging and oxidation of soil BC to functionalized condensed aromatic molecules for enhanced solubility in water[43]. The continual export of DBC from historically fire-affected watersheds[65] further supports the hypothesis that aging of condensed aromatic structures is a prerequisite to their solubilization in soils.

The different transport and transformation mechanisms of DBC and PBC are reflected in their apparent radiocarbon ages. In rivers, DBC age is highly variable, but generally modern (contemporary), whereas PBC can be up to several thousand years old[29,61] (**Figure 3**). This age discrepancy between DBC and PBC is also observed in both bulk organic carbon and other compound-specific fractions[66,67]. The apparent lag in PBC mobilization and in-stream export might be explained by the PBC physicochemical properties that enhance its long-term stability and aging in intermediate reservoirs. Freshly produced charcoal and ash can leach considerable amounts of DBC[35,49,63], which suggests terrestrial wildfires produce a stock of readily soluble BC with a younger radiocarbon age than PBC (**Box 1**). Based upon their established transport mechanisms, we might expect the apparent radiocarbon age of DBC (slow leaching over time) to be older than that of PBC (rapid erosion soon after fire). This observation runs counter to what has been measured for BC in rivers (Figure 3). This discrepancy may be driven, in part, by the general lack of spatiotemporal radiocarbon data for BC in rivers globally. Submicron-scale BC soot aerosols deposited within river basins also contribute a minor fraction of riverine DBC[2,28], on the order of 5-20% with wide variation across regions [29,68,69].

Riverine DBC fluxes are usually highest at peak discharge and lowest during baseflow [64,65,69-71]. This coupling between DBC concentration and discharge results from DBC mobilization from upper organic soil horizons during heavy rainfalls[44]. The concentration and radiocarbon age of DBC and dissolved organic carbon (DOC) is often coupled, presumably because both forms of carbon share a soil source[72,73]. However, the DBC content in bulk riverine DOC can vary between 2 and 15% depending upon biome, latitude, climate, soil type, and land cover[46,74] (**Figure 3**). Moreover, DBC and DOC export are largely decoupled in some locations, such as the Amazon River and other channels in Brazil[30,46,68,] where variable soil properties, rainfall and aerosol deposition affect DBC mobilization. Decoupling of DOC and DBC concentrations might also result from variation in the timing of rainfall events with respect to stages of soil pore water replenishment with DOC and DBC (pore water DOC stocks are likely replenished more quickly than pore water DBC following prior rainfall events due to the greater recalcitrance of soil BC)[46,75]. Freshly burned watersheds can have higher in-stream concentrations of DBC that can persist for years after the fire event[76,77]. However, some studies have shown that watershed fire history has little to no effect on in-stream DBC concentrations, which suggests that other environmental factors, such as topography, soil type, climate, fire and vegetation characteristics are also important[64,78,79]. With changes in watershed properties, mainly due to agricultural activities, shifts in molecular composition and reactivity of DBC can be expected[80,81] with yet unknown consequences for the fate of riverine export of DBC.

Like DBC, PBC inputs to rivers are elevated during precipitation events and periods of overland flow[61], as the lateral transfer of charcoal from hillslope to stream channels is primarily controlled by physical erosion. However, riverine PBC is not exclusively sourced from contemporary wildfires. In temperate river systems, around 90% of PBC has been retained in catchment soils for millennia prior to export and deposition in aquatic sediments[82]. In addition, PBC deposited within the stream corridor can be resuspended during periods of high discharge[64,73]. This successive hydrological redistribution of river-transported material within stream channels and alluvial plains[47,83] causes an observed lag between fire occurrence and sedimentary charcoal deposition in coastal basins[84]. Therefore, the weighted average age of riverine PBC is 3,700±400 ^{14}C years, which reflects enhanced residence times and some degree of storage within intermediate reservoirs[61], including locations where environmental conditions favor both preservation or mineralization. In several high-latitude rivers[61], the apparent age of PBC was as high as 17,000 ^{14}C years (**Figure 3**). The ratio of PBC to particulate organic carbon (POC) varies in smaller watersheds and at high temporal resolution, reflecting local geomorphological and hydrological effects of fire and associated charcoal inputs[64] (**Figure 3**). However, the PBC to POC ratio in global rivers is roughly constant (15.8±0.9%) (**Figure 4a**), regardless of environmental conditions or watershed characteristics[61], which permits scaling of PBC fluxes.

[H2] BC processing in rivers

Rivers are not passive pipes that conservatively transfer organic materials from land to the ocean. A substantial amount of riverine organic carbon is lost as CO_2 during transit due to biogeochemical processes, such as photodegradation and biodegradation[85,86], specifically in two loops carrying carbon from land to inland waters, then from tidal wetlands to the ocean ocean[87]. In situ rates for BC degradation and remineralization are not well constrained but can be inferred from known removal mechanisms for bulk organic carbon. Like organic carbon, BC losses could be focused in areas where water masses with different physicochemical properties mix, such as at river confluences, along estuaries, within river plumes, and in the coastal ocean[88]. However, coastal zones are not only potential hotspots of BC turnover, but can be sources of DBC to the ocean themselves, especially in areas with high tidal water exchange[89]. The addition of bio-labile substrates (for example, algal biomass and exudates) might enhance the decomposition of environmentally persistent organic matter such as BC[90]. This priming effect, which has been well-studied in soils [55], is an emerging research topic in aquatic environments[91,92], but has yet to be meaningfully explored within the context of BC degradation.

Photochemical degradation is a major loss and alteration pathway for DBC in aquatic environments[93,94]. For example, DBC leached from grass and oak chars is highly photolabile (>75% removal in 5 days) under experimental conditions[45]. The photo-lability of DBC is mainly controlled by the abundance of polycyclic aromatic structures, with larger condensed structures being more susceptible to photooxidation than less condensed structural features[45]. In laboratory experiments, the photochemical half-life of polycyclic aromatic structures is one to two days and as such much shorter than the typical riverine transit time to the ocean[95]. However, the DBC content is relatively high in most rivers mouths (12±5% of DOC)[2], despite a portion of the DBC undergoing river transit. Therefore, factors such as turbidity, shading, and protection by mineral associations[96] with suspended matter might protect dissolved organic matter from photodegradation[97] and explain why DBC is largely conserved in river waters despite high photodegradation rates in laboratory experiments. It is also hypothesized that constant inputs from the surrounding landscape and smaller tributaries maintain relatively constant levels and compositions of dissolved organic matter along the mainstem of large rivers until they reach the sea, despite high rates of remineralization[98].

Microbial remineralization at river–ocean interfaces is another BC loss process. In contrast to photodegradation, lower molecular weight DBC is mineralized by microbes first[52], whereas high molecular weight DBC is comparably resistant[45]. Microbial remineralization and photodegradation are likely coupled, in which photo-exposure breaks down the condensed aromatic structures, thereby potentially increasing the bioavailability of DBC[45,52,99]. The overall balance between the two processes in the environment is unknown, though. In the Amazon River, for example, DOC photo-mineralization rates are seven times greater than microbial remineralization. However, when intergraded over the entire water column, microbial remineralization is likely the dominant organic matter removal process because it is not restricted to surface waters such as photo-mineralization[97]. There is currently no global estimate for losses of DBC via microbial degradation at aquatic interfaces.

[H1] Sources and Fates of Oceanic BC

After transport from rivers and other sources, PBC is thought to be primarily buried in coastal shelf and marine sediments and sequestered on long-term and potentially geologic timescales[100,101]. Semi-enclosed basins act as a trap for riverine PBC burial[102], where PBC storage could be related to oxygen conditions[103]. However, burial and retention of PBC in marine sediments remains largely unconstrained on a global scale[104-106].

The fraction of DBC that escapes mineralization at the river-ocean interface becomes part of the 662 Pg C marine DOC pool[44,107] (**Figure 4a**). DBC accounts for about 2-6% of oceanic DOC, which corresponds to a 12-14 Pg C standing stock of DBC in the global oceans [12,108](Table 1). River DBC mainly enters the deep ocean at the deep-water formation sites in the North Atlantic. It takes decades to centuries for DBC to travel at the sea surface from the discharge sites at the river mouths to the North Atlantic where surface water masses sink down to thousands of meters of water depths[12]. Therefore, loss processes such as photodegradation and microbial degradation along this long pathway could be important for altering and removing DBC[45,52,109].

At the basin scale, DBC behaves largely conservatively on time-scale of decades to centuries in the absence of photodegradation[44,109,110]. Sorption onto sinking particles is potentially the dominant removal mechanism for DBC in the dark ocean and explains the decrease in DBC concentration along deep-ocean meridional circulation[69]. The global removal flux of DBC to abyssal sediments via sorption to sinking particles has been estimated as 40-85 Tg C year^{-1}[69,100], which is larger than the estimated global inputs of

DBC via rivers and atmospheric deposition. This mismatch in the mass balance reflects major uncertainties of estimated rates and pools, but it could also indicate other substantial, yet unidentified sources of DBC in the ocean and or unknown losses of DBC. For example, hadal zones are an apparently important, but long unrecognized sink of BC, removing 1.0± 0.5 Tg BC year^{-1} due to higher accumulation rates in these zones[111].

There are a number of major uncertainties in the BC cycle, including the fate of DBC. Riverine DBC fluxes (18±4 Tg C year^{-1}) are sufficient to sustain the turnover of the entire oceanic DBC pool in just 500 years (based on simply dividing the marine stock by the riverine discharge)[12]. This value suggests the apparent ^{14}C ages of oceanic DBC should be young. However, apparent ^{14}C ages of oceanic DBC are on average 4800±620^{14}C years in the surface ocean (though with large range likely due to variable inputs of modern DBC through rivers and aerosols)[12,35,112]. In the deep ocean, apparent ages are >20,000 ^{14}C years (**Figure 4b; Table 1**) [12]. Calculating the residence times of abyssal oceanic DBC on the basis of estimated removal fluxes and pool sizes results in much younger (2,100–4,100 years) DBC ages than the measured apparent ^{14}C age of DBC in the deep ocean[69]. Thus, despite its expected recalcitrance, most BC delivered by rivers is not accumulating in the ocean.

This conundrum highlights the gaps in our understanding of DBC losses in the ocean, which include UV oxidation in the surface ocean, sorption of DBC onto sinking POC, burial of DBC in hadal zones, and (potentially) loss of DBC by bursting bubble plumes (Figure 5). For example, the high degree of uncertainty associated with first order estimates of DBC removal via photodegradation[93] could be preventing the closure of ocean BC budgets. The turnover of DBC in the ocean is apparently related to the rate at which DBC is cycled through the photic zone[93]. The entire oceanic DBC pool could, in principle, be photodegraded in approximately 30-800 years[93], yet DBC persists in the ocean for up to 23,000 ^{14}C years in the deep[112]. Therefore, a realistic and scalable rate for the photo-oxidation of DBC is still needed. For instance, the current understanding of marine DBC photodegradation rates does not consider light fields or quantum yields, which makes it difficult to accurately scale these loss rates globally.

Additional processes must be considered when using the current, published photodegradation rates. A notable process is the co-occurrence of DBC removal from the photic zone via sorption to sinking particles, which has been identified as a major loss process in the western South China Sea and the western Arctic Ocean[34,113]. Primary marine aerosols produced by bursting bubble plumes in the surface ocean and its subsequent photo-oxidation is a major removal pathway for old DOC from ocean. Around 2-20 Tg of aged DOC is removed annually by this mechanism, of which 19 to 40% of freshly produced primary marine aerosols contained aged DOC[114]. Because DBC is an aged component of DOC, and assuming DBC is 6% of DOC[12], this un-measured loss could represent 0.02-0.48 Tg BC year^{-1}. However, the actual amount of BC lost by primary marine aerosol formation is unknown[114].

While there remain many unknowns in how DBC is lost from the ocean, there are also questions about the sources of DBC. Rivers are the largest known source of DBC to the ocean, but the stable carbon isotopic composition ($\delta^{13}C$) of DBC in the ocean is inconsistent with a terrestrial source from C3 plants, pointing to a large contribution of C4 plant combustion to fire-derived BC in the oceans or to an autochthonous, marine source of oceanic DBC[115](Supplementary Figure 1). This observation is surprising for two reasons. First, it implies the almost complete removal of riverine and aerosol-derived DBC at the sea surface, prior to deep water formation at high latitudes. Second, it implies there is another major source of DBC in the ocean, but the main source of riverine DBC (fire) would not be expected underwater. However, condensed aromatic molecules can be produced from other thermogenic processes.

In the deep sea—mainly at mid-ocean ridges—hydrothermal processing of marine debris might produce molecular structures resembling those produced during charring of terrestrial biomass. Therefore, hydrothermal marine sediments could be a source of DBC to the ocean[110,115]. Indeed, BC structures have been identified in petroleum[116-118] and abiotic synthesis of graphite occurs in marine hydrothermal vents[119]. However, deep-sea dissolved organic matter, including the condensed aromatic fraction, is almost entirely destroyed in hydrothermal systems[120,121]. Whether organic matter rich hydrothermal sediments or petrogenic processes release DBC to the water column remains unknown. Autochthonous biotic sources of condensed aromatic material that is characterized as DBC and PBC are also possible, as anaerobic methanotrophs are capable of synthesizing elemental carbon[122].

A newly identified, allochthonous source of DBC to oceanic surface waters[123] is the large input of polyaromatic hydrocarbons and other semi-volatile aromatic-like compounds by diffusive air–water exchange. This source could contribute to the $\delta^{13}C$ signatures observed for oceanic DBC, but the isotopic composition of these semi-volatile aromatic-like compounds is unknown. Overall, the sources of the DBC's $\delta^{13}C$ signature and their relative contributions are highly uncertain.

[H1] Insights into the age of oceanic DBC

The conundrum associated with measured radiocarbon ages[12,115], stable carbon isotopic signatures of oceanic DBC, and the inconsistent mass balance of DBC demonstrate that input fluxes and losses of DBC are not well constrained[69]. It also might suggest the input fluxes of radiocarbon-depleted and stable-carbon enriched DBC, potentially from an autochthonous source within the ocean, are equally important to riverine DBC in maintaining the oceanic DBC pool[69]. Here, we incorporate current known losses, stocks, ages, and fluxes (Table 1, Supplementary Table 1) with an oceanic box model with seven boxes and a simplified overturning circulation[124,125] (Supplementary Material). Although the box model is a strong simplification of the ocean, it serves to set known sources and sinks into a common context and allows for a first approximation on gaps in the marine DBC budget (Supplementary Figure 1).

Consistent with previous work, the radiocarbon age of the marine DBC pool cannot be matched with existing DBC $\Delta^{14}C$ observations in our model. This mismatch implies that it is not possible to represent DBC as a homogenous pool with a single $\Delta^{14}C$ value using a box model (Supplementary Figure 2a-2b). Instead, there are at least two components of DBC: a modern component from rivers (+58 ± 207‰) added to an aged background DBC pool (-945±5‰)[12]. Moreover, DBC might have two distinct molecular constituents – one that is old, abundant, and recalcitrant; and another young, sparse and labile. Having these constituents would suggest that DBC follows the same mixing processes as bulk oceanic DOC[126] with modern and aged components.

One proposed explanation for the puzzling carbon isotope data is that marine DBC contains aged fossil fuel-derived BC. However, fossil fuel derived BC input fluxes from land to the oceanic DBC pool are considered minor for several reasons. First, the annual production of biomass-derived (contemporary) BC (128 ± 84 Tg $year^{-1}$)[22] substantially outweighs the input of fossil-fuel derived BC because fossil fuel combustion is a recent phenomenon (since ~1750). Secondly, as soil formation rates span centuries to millennia, the vast majority of DBC eroded from soils pre-dates the beginning of the industrial revolution, and thus must be predominantly biomass-derived., riverine DOC globally is more modern ($\Delta^{14}C$ = +22 to +46‰)[127] than riverine POC. Based on these assumptions, fossil-fuel derived inputs of BC to the oceanic DBC pool are not high enough to influence oceanic DBC $\Delta^{14}C$ values.

A second explanation for the old age of DBC in the ocean is the presence of condensed aromatic carbon of lithogenic origin deriving from hydrothermal systems or petroleum, rather than pyrogenic sources. Hydrothermal vents are considered sinks for DBC, as they are for recalcitrant DOC[121]. However, the hydrothermal processing of sedimentary organic matter in some systems could produce condensed aromatic structures as part of DOC[128], representing a deep ocean source of DBC. Indeed, natural asphalt seep samples released water-soluble DBC in a laboratory incubation experiment, suggesting that natural petroleum seeps could represent a deep ocean source of DBC. Based on a conservative, first-order estimate upscaled from an asphalt volcano in the Gulf of Mexico, about 3.3- 5.0 × 106 g (0.000005 Tg) DBC can be released from petroleum seepages per year[190].

To assess the role of hydrothermal carbon input, an estimated input from the seafloor of 0.12 to 1.2 Tg $year^{-1}$ of DBC (with a ^{14}C fossil age of 50,000 years) was used. These values are based on DOC inputs by hydrothermal vents of pre-aged hydrothermal DOC (1.2–5 Tg $year^{-1}$)[129] and methane seeps (0.2–20 Tg $year^{-1}$)[130]. Assuming hydrothermal DBC content in DOC is present at the upper limit of DBC% of marine DOC (based on DBC% in marine DOC ranging from 2-6%)[12,110], then hydrothermal DBC fluxes would cover a range of 0.012-1.2 Tg DBC $year^{-1}$ by pre-aged hydrothermal sources. Using the smaller input of 0.012 Tg DBC $year^{-1}$, pre-aged sediment input better reconciles the budgets, but the overall modelled age range between surface (~7,000 years) and subsurface (~11,000 years) remains too narrow. A 10x higher sediment source (1.2 Tg $year^{-1}$) would increase the subsurface age to >20,000years, but overestimates bulk DBC concentrations (Supplementary Figure 2e-f). This gap indicates that there could be other missing sources of old material and/or unknown bulk DBC sinks, and reinforces the need for a direct study of the amount of DBC originating from lithogenic materials present in the ocean. This modeling exercise suggests that hydrothermal DBC is a possible source that might explain the age of DBC. However, a sink of DBC is also missing, in addition to the known losses in hadal zones[100,111,131] that are needed to reconcile the low concentrations in the ocean.

A third proposed explanation is that the oceanic stocks of DBC experience pre-aging on land before transport to the ocean[82,132]. Although DBC in rivers is generally modern, aged PBC from rivers might solubilize to the DBC fraction at river-ocean interfaces[9]. Riverine PBC experiences long periods of aging in intermediate terrestrial reservoirs (estimating 1,500-3,000 ^{14}C years), such as in alluvial fans[83]. If solubilized to DBC, the PBC could potentially act as an aged DBC source[61,82]. However, taking these values into account does not conclusively reconcile the BC budget (Supplementary Figure 2g-2h). The input of pre-aged material increases the overall age in the box model simulation, especially in the deep ocean (~24,000 years, closer to the measured values), but the resulting surface ocean BC age is too old (~17,000 years). Increasing the amount of sediment DBC input would require the adjustment of sink terms to balance simulated concentrations, violating the turnover times given[12] to match observed DBC concentrations. This synthesis underlines that the currently known sources and sinks of marine DBC are incomplete, and work is urgently needed to identify the enigmatic source of the large marine DBC pool.

[H1] Summary and Future Perspectives

In summary, BC is environmentally persistent[7] and represents a mechanism for long-term carbon sequestration over centuries to millennia[133,134]. It is clear that rivers transport substantial amounts of BC from wildfires to the ocean. Ultimately, most of the BC on Earth is stored in ocean sediments. However, there are outstanding gaps in our understanding of BC cycling. For example, residence times of BC in soils are poorly constrained and vary considerably across studies [54,55]. Likewise, the modelled ocean BC concentrations versus observation-based age profiles do not agree, based on the current expected sources and sinks of marine DBC. Reconciliation of BC budgets is essential for a comprehensive understanding of the global BC budget, and also to support Earth System modelling of the BC cycle and enable the quantitative assessment of the negative feedback to climate change.

Future research should target a refined framework for understanding the chemical identity of BC, improved measurement of BC decomposition across all pools of the Earth system (but particularly in soils, floodplains and inland water bodies), and improved identification and quantification of BC sources to the ocean. Rates of BC degradation and transfer between pools, and coupled processes that influence its fate, in particular are needed to incorporate BC feedbacks into ESMs.

Here, we discuss the major open questions and challenges that the BC research community should address in the years to come in support of model development (Figure 5, Table 2). We also highlight judicious observations that are likely to provide critical constraints on understanding the role of BC in the Earth System as a potential negative carbon feedback.

[H2] Chemical identity of BC

Isolating BC from other organic components in an environmental matrix (soil, sediment, water, air) is still a challenge (**Box 1**), and contributes to inconsistency amongst research on BC in different environments. Future improvements in both techniques and reporting are needed, and there must be consistency when reporting BC amounts and isotopic signatures across a large suite of environmental standards and across analytical approaches[135]. A cross-laboratory comparison that incorporates multiple methods measuring a larger range of BC reference materials with isotopic measurements[136,137] would facilitate direct linkages between BC reactivity, source, and apparent residence time. For example, Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry can identify the ionizable fraction of DBC based its molecular formulas[80,138,139]. Atomic Force Microscopy can also quantify and characterize DBC structures based on visualization of polycondensed aromatics[140]. Combining approaches like these could address method biases associated with different analytical measurements[30,80,138] and improve our understanding of BC itself.

Other known sources of non-pyrogenic condensed aromatic carbon should be included in the next phase of method inter-comparisons, such as petrogenic and lithogenic lignite, coal, and petroleum[136,141]. Recoveries of BC for coal, oil and lignite samples have been already reported[141], and these are present in negligible amounts in the rocks eroded in the global river catchments[61], but potentially important condensed aromatic carbon contributions are not yet explored. For example, Green River Shale as a reference standard is a good analogue of riverine petrogenic carbon, yet only had very low BC recoveries (see Text Box)[136]. Other more common shales and lithogenic carbon which might also interfere should be tested. For instance, kerogen, the main organic component of sedimentary rocks, incorporates highly aromatic structures[142]. Other potential sources of condensed organic matter derived from composting[143] and degraded lignin products[144] should also be considered. At the moment, there are no quantitative constraints on non-pyrogenic sources of BC in the ocean, but their contributions are likely.

DBC and PBC fractions should be analyzed synchronously, as BC cycling occurs along a size continuum[145,146](**Figure 1**). As POC (3 Pg) is only a small fraction of oceanic OC (DOC is 700 Pg)[107], it is assumed that that most observed oceanic DBC are due to the dissolved fraction but not particles. However, high PBC concentrations might enhance the transfer of carbon from dissolved to particulate phases by DOC absorption and aggregation[69,100,147]. In rivers, BC is unequally distributed across operationally defined dissolved, colloidal, and particulate size fractions[81] and within the DOC pool[148]. Therefore, BC might also be unequally distributed within the oceanic DBC and PBC pools, requiring the routine quantification of both pools.

[H2] Rates across the Earth system

Increased observations of decomposition rates and transport flows are required to constrain rates of transformation and turnover, and therefore the global BC budget in ESMs. Soil decomposition rates are the largest source of uncertainty in the global BC cycle in absolute terms. Widespread field campaigns are needed to assess decomposition rates across diverse environments, climates, soil types and landscape positions (for example, uplands, slopes, depositional environments). In particular, decomposition rates in lakes, reservoirs and other inland water bodies are virtually unknown, and pioneering measurements are required to construct an initial understanding of BC dynamics in these environments. Sampling at high resolution across hydrological gradients will help to constrain when and under what conditions BC is mobilized or decomposed in terrestrial environments, and provide valuable insights for process-based representation of BC decomposition and transport for use in global modelling applications.

Immediate research is required to quantify the role of intermediate reservoirs and coastal areas in transforming BC, and might be key to understanding the mismatch between observed and modeled DBC ages in the ocean. Encouragingly, some work has started to address processes occurring at the interface of different ecosystems along the land-ocean continuum[30,44,138]. At present, although well-represented in the China Sea[101,105,106,149,150] and the North western Pacific[69,151] corresponding global observations of DBC and PBC are extremely sparse in the coastal domain.

Dedicated studies of the processes leading to BC decomposition in oceans are also required to constrain the oceanic BC balance. For example, rates of loss by photodegradation are very poorly constrained. Expanding a mechanistic understanding of processes that drive BC transformation and stability across aquatic interfaces[87] requires new research targeting coupled processes occurring in aqueous and solid phases. For example, priming effects[90,152] and BC-mineral interactions[153,154] could affect BC reactivity.

[H2] DBC sources in the ocean

The lack of explanation for the old DBC in the ocean highlights the uncertainty around its source, fate, and cycling in marine environments. Rivers are the main source of marine BC, but there is an incomplete understanding of the composition, concentration, and timing of material export out of watersheds immediately in the short term (hours to a few years) following a burn event. The first-year post-burn is a critical time for the mobilization and redistribution of carbon, as wildfires substantially alter landscapes by changing the hydrology and geomorphology of the burned area[155]. Sampling and monitoring should take place at the beginning of the window of wildfire disturbance through initial system recovery (at least a year), and ideally longer. Given the complex nature of BC production and timing of subsequent transport to the deposition sites, charcoal calibration studies are essential for relating sedimentary charcoal records to regional fire activity[156-158]. Thus, modern data coupled with calibrated sedimentary records will enable the community to better model and predict future fire-hydrology interactions.

Increasing the spatial coverage of concentration and radiocarbon age measurements in the ocean is required to constrain large-scale processes such as the turnover times on decadal and longer time scales. It will also inform models to better address how future changes to BC production rates may influence the carbon cycle[23]. Box models such as the one trialed here are useful for rough assessments, but a higher resolution spatial model with localized river and atmospheric sources is required to further constrain processes and fate of marine DBC[125]. Future modelling approaches would benefit from increased spatial coverage of PBC and DBC concentration and radiocarbon age measurements across different water masses in the ocean. Measurements along water masses of different ages will further constrain net production or consumption rates of DBC[131]. Targeting potential sources of DBC in the ocean will help identify if there are other BC sources to oceanic DBC, explaining the stable isotope differences between oceanic and riverine DBC[115].

Currently, the time, effort and expense of sample collection and processing is hindering progress in measuring ocean BC, as is often the case for oceanic measurements more broadly. Establishing optical or other easy to measure proxies is a promising way forward for collecting proxy data, such as by utilizing remote sensing data[159] to track post-fire riverine DBC export through estuaries using links between DBC molecular markers and chromophoric properties of DOC and at a higher spatiotemporal resolution[160]. Using absorbance data, it is possible to track DBC photodegradation from soil sources to the marine environment using an index of condensed aromatic carbon as an indicator of aromatic BC cluster size[45]. As part of ocean observing systems, gliders equipped with fluorescence sensors targeting polycyclic aromatic hydrocarbons can potentially increase the coverage of deep open ocean environments that are not accessible by satellites[161,162]. Also, biosensors can be engineered to detect the presence of BC in soils and waters, as initial research on this topic seems very promising[163,164]. Lastly, establishing regional or global correlations between BC concentrations and high resolution or remote sensing measurements (such as discharge, absorbance data from satellites) can scale land-based assessments through time and space.

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Author Contributions

A.I.C, M.W.J and C.S. started the first conceptualization of the review. A.I.C. was responsible for writing and project administration. S.L., A.I.C, M.W.J., and M.S. contributed in the box model conceptualization for oceanic black carbon, and S.L. applied box model simulations using published rates. All authors contributed equally to writing in the original draft, review and editing.

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Supplementary information

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Data availability

The fluxes of PBC, radiocarbon ages of PBC and mapped river basins derive from Ref. [61]. The fluxes of DBC within latitudinal ranges derive from Ref.[2]. The magnitude of the global stocks, fluxes, and radiocarbon ages of BC shown in figure 4 derive from the studies cited in table 1.

Key Points:

1. Black carbon (BC) is produced from incomplete combustion of biomass and fossil fuels and persists on the order of centuries to millennia in the environment.
2. BC production is expected to increase with increasing fire activity under anthropogenic warming, and could act as a negative feedback ~~on~~ to climate change.
3. BC is often divided into particulate and dissolved black carbon, which can have different environmental transport mechanisms, residence times, and fates.
4. The largest BC pool is in the soil (160-200 Pg C globally). Rivers transport 43±15 Tg BC year^{-1}; BC is cycled in other inland aquatic systems, but the global relevance of these processes is unknown.
5. Oceans store 12-14 Pg C of dissolved BC. The observed age of this BC (4800 ± 620^{14}C years in the surface ocean, >20,000 ^{14}C years in the deep) does not match expected ages based on mass balance estimates.
6. Future research must further explore the possibility that some of the dissolved black carbon in marine waters is not derived from terrestrial fires.

Display items

Table 1| BC and OC stocks and fluxes. Values were used to construct Figure 4 and the marine box model. Standard deviations included where applicable. BC: black carbon; DBC: dissolved black carbon; DOC: dissolved organic carbon; OC: organic carbon; PBC: particulate black carbon; POC: particulate organic carbon.

Pools and processes	Radiocarbon	BC content (%) of Organic carbon	Value of BC fluxes (Tg year^{-1}) or stocks (Pg)	Reference
Fluxes (Tg year^{-1})				
Production of BC in post-fire residues (charcoal, charred plant material)	-	Assumed 50 (± 30) %	128 ± 84	2, 22
Production of BC as aerosol through biomass burning	-	-	2-11	4
Production of BC as aerosol through fossil fuel combustion	-	-	4.5-12.6	4
Atmospheric deposition	Fossil fuel: -885‰ Biomass: +131±52‰ (mean biomass age of 20 years)	2.8	Globally variable: 2–10 Tg year^{-1} To ocean DOC pool: 1.8±.83 Tg year^{-1}	27, 31, 179, 184, 185
River PBC	Variable between rivers Average age: 3,700±400 years	15.8±9	17-37 Tg year^{-1}	61

River DBC	Modern Yangtze River: −60 ± 30‰ Yellow River: −140 ± 20‰ Pearl River: −91 ± 3‰,	12±5	18±4 Tg year^{-1}	2, 29, 68
Leaching DBC from soils to rivers	-	-	203 Tg year^{-1}	37
Biodegradation at river-ocean interfaces	-	-	Unknown	-
Marine Sinking PBC	-	-	40-85 Tg year^{-1}	100, 131
Transport to hadal zones	-	-	1.0-0.5 Tg year^{-1}	111
Loss by primary aerosol formation	-	-	Unknown	114
UV loss	-	-	2-4 Tg year^{-1}	93
Coastal sedimentation	-	-	Unknown	-
Pre-aged hydrothermal fluxes from DOC	-	-	Unknown Pre-aged hydrothermal DOC in range of 1.2–5 Tg year^{-1} Methane seep DOC inputs to the deep ocean of 0.2–20 Tg year^{-1} Pre-aged natural petroleum DBC seepage 0.000003-0.000005 Tg year^{-1} (3.3 × 10^{6} to 5.0 × 10^{6} g)	129, 130, 190
Pools (Pg)				
Terrestrial Soils	Variable surface age; modern to millennia	13% on average in the top 2 m of soil	160 - 200 Pg	13, 54, 55
Oceanic DBC	Variable surface DBC age; average 4,500±1,200 years Deep: 23,100±300 years	2-6%	12 – 14 Pg Surface: 3 Pg Deep: 14±2 Pg	12, 108
Oceanic PBC	1,700±200 years	Upper 100 m: 0.5–2.5% Below 100 m depth: 6%	40-85 Pg	100, 131, 179, 186, 187
Oceanic Sediments	Surface: 6,000±800 years Deep: 24,000±520 years	4-22% of ocean sediment organic carbon pool	Global coastal zones: 480–1140 Pg Global open ocean: 80–240 Pg	100, 132, 188

Table 2| Assessment of the level of BC process understanding required for incorporation into models. The number of stars (*) indicates the level of understanding of these terms related to the proportion of the research effort and number of studies, as used in Ref. 189. *limited understanding; **emerging understanding; ***ready understanding; ****applied knowledge. BC: black carbon; DBC: dissolved black carbon; ES: Earth system; PBC: particulate black carbon.

ES component	Process	Knowledge or research effort needed
Atmosphere	*Water soluble aromatic carbon deposition onto the ocean surface	Quantify BC present as water soluble aromatic carbon
	*Loss of BC through injecting primary aerosol formation	Quantify removal pathway at surface ocean for DBC, amounts and isotopic values
Soil BC	****Storage in soils	Collect data from underrepresented soils
	*Microbial loss in soils	Quantify long-term (decades to centuries) mineralisation rates
	****Biotic transformation in soils	Field-based studies, incubations, mesocosm experiments and upscaling
	***Abiotic transformation in soils	Description, quantification and modeling, mesocosm experiments
	***Movement within and from soils	Quantify and model at landscape and larger scales
Rivers		
Underground waters	*Storage and transport of PBC and DBC	Description, quantification and modeling
Riverine fluxes of DBC	***Solubilization in soils and river fluxes	Characterize chemical composition of BC post-fire; in-situ mechanistic studies; regional studies
Riverine fluxes of PBC	***Slope erosion and riverine export of PBC	Characterize chemical composition of BC post-fire; in-situ mechanistic studies; regional studies
Aquatic continuum	*In channel decomposition of DBC and PBC	Quantify DBC budgets and mass balances; incubation studies; in-situ labeled studies
	*Biodegradation at river–ocean interfaces	Establish bio-degradation rates under key conditions; measure flocculation and dissolution along salinity transect
	**Sedimentation at coastal shelves	Establish rates under key conditions; quantify large-scale rates; evaluate the seasonal variability, residence timescale in seawater, and settling flux
	**Photodegradation losses	Establish photo-degradation rates under key conditions; measure flocculation and dissolution along salinity transect
	*Transfer between DBC and PBC pools	Regional studies of pristine vs anthropogenically impacted locations
	**Fractionation of DBC δ13C	Measure DBC δ13C across aquatic continuum
Models	*Modeling land-to-ocean transfers	Collect globally relevant flux and stock data (continue measuring and publishing data along terrestrial-aquatic continuum)
Freshwater sediments	*Storage in intermediate reservoirs	Evaluate using field studies in all major reservoirs and upscale
	*Decomposition in intermediate reservoirs	In-situ lab incubations and field studies
Oceans		
Oceanic DBC	***Turnover rates and ages in marine DOC inferred by mass balance	Identify and quantify new sources and fluxes of marine DBC
	**Patterns in concentration and isotopes across biogeochemical and physical regimes	Compare river outlets; compare up- and down-welling regions (to address photo-and bio-activity, respectively)

	**Photodegradation of DBC	Establish photo-degradation rates in situ or in the laboratory under key environmental conditions
	****Storage in DOC	Measure global marine DBC concentration; large spatial-scale and multi-season and multi-layer seawater sampling campaign; sample localized sources
	****Decomposition estimates inferred by mass balance	In-situ measurements
	****Turnover and ages inferred by 14C	Global marine DBC ∆14C measurements
Oceanic PBC	**Storage in marine POC	Spatiotemporal measurements, global estimates of fluxes, and 14C measurements
	*Transfer between POC and DOC pools	Laboratory DOM-particle studies, oceanic observations (particle traps)
Oceanic sediments	***Deposition to sediments	Evaluate global sinking POC time series, global evaluation of sediment cores in coastal and abyssal locations
	*Hadal zone sinks of BC	Update current conservative estimate by including episodic events such as earthquakes
	***Storage in ocean sediments	Global evaluations
	*Decomposition in ocean sediments	Measure rates over long and short timescales
	*Hydrothermal vent fluxes	Measure pore water to determine if a DBC source
Models	*Global ocean modeling	Build BC into a more complex and spatially-resolved ocean biogeochemistry model with water mass circulation verify that data produced from different methods is comparable; correlate BC concentrations and remote sensing measurements

Figure 1. **BC characteristics.** Pyrogenic material is chemically heterogenous and includes a continuum from char to soot. The amount of recognizable plant structures and solubility of charred material depends on the formation temperature, fuel type and duration of incomplete combustion. Black carbon (BC) is formed at high charring temperatures and is characterized as having a condensed aromatic structure. BC is present in both dissolved organic carbon (DOC) and particulate organic carbon (POC), which are operationally defined based on pore size during filtration of water. Thus, DBC, which is a part of bulk DOC, can include colloidal, truly dissolved, macromolecular, and nanoparticulate forms of BC. Note, the position of labels along combustion continuum does not directly correspond to the size continuum.

Figure 2. Climate-carbon cycle feedbacks involving fire. The role of wildfire in the terrestrial carbon cycle as it is typically conceptualized and represented in Earth System Models (ESMs) is in yellow. Wildfire leads to large near-term emissions of CO_2 that can be re-captured through subsequent vegetation recovery in the longer term. As wildfire frequency increases under climate change, rates of CO_2 emission also increase and an imbalance can emerge versus post-fire recovery, leading to net reduction in the carbon stored in vegetation and a corresponding increase in CO_2 in the atmosphere. A positive feedback to climate change results because increases in atmospheric CO_2 concentration contribute to further global warming, which in turn elevates the risk of wildfire occurrence. However, about 5-30% of burned biomass is transformed into BC (shown in blue), which can persist in the environment for thousands of years. BC cycles slowly in the terrestrial soils and sediments, and when rivers transfer BC to the global oceans (far right blue arrow), BC degradation is further slowed. Increases in fire activity lead to more BC production and storage, invoking a negative feedback to climate change by sequestering carbon. ESMs omit the BC cycle and associated negative feedback. Consequently, these models over-estimate the magnitude of positive feedbacks to climate change.

Figure 3 Black carbon in terrestrial systems. Riverine particulate black carbon (PBC) $\Delta^{14}C$ values, shown by basin on the map. Fluxes of particulate black carbon (PBC) are shown in the bar graph[61]. Horizontal arrows indicate the global flux of dissolved black carbon (DBC) from each 30° latitude range (Tg C year^{-1}), based on values in Ref[2]. DBC $\Delta^{14}C$ signatures are generally modern, whereas PBC is older. Figure adapted from Ref 61, Springer Nature Limited.

Figure 4. Global dynamics of the BC cycle. a| The relative size of the stocks (circles) and fluxes (triangles) of organic carbon and black carbon (BC) in soils, sediments, dissolved organic carbon (DOC) and suspended particulate organic carbon (POC)[2]. Where relevant, stocks and transfers of BC (in black) are shown as a proportion of total organic carbon (lighter shades), with the BC to organic carbon ratios shown as percentages. b| Estimates of BC Δ ^{14}C values (darker reds indicate older ^{14}C ages). Values of stocks, fluxes, and BC ages in Table 1. DOC dissolved organic carbon, DBC dissolved black carbon, POC particulate organic carbon, PBC, particulate black carbon. The largest stocks and fluxes of BC are observed on land as wildfire is the main BC source. Most BC remains on the burned site following a fire and is incorporated into soils. Rivers transport BC from soil stocks to the oceans in dissolved and particular forms, while atmospheric circulation can also redistribute some emitted aerosols to the ocean surface. BC is a relatively large component of oceanic DOC and POC stocks due to its conservative behavior

during transport to the oceans. Eventually, some BC is deposited to the deep ocean bed where it enters the geological stores. Figure adapted from Ref 61 and Ref 2, Springer Nature Limited.

Figure 5. BC processes across the Earth System.
Key processes along the land-river-ocean continuum are highlighted, and processes with major unknowns are noted with question marks. Atmospheric black carbon (BC) is best understood, followed by marine BC. There is an emerging understanding of riverine and soil BC, but large gaps in understanding and quantifying storage, transformation, and transportation remain be addressed. Intermediate reservoirs are poorly understood, and both field and laboratory-based investigations are needed to understand their role in BC cycling. Figure adapted with permission from ref 1, Wiley.

Box 1| **Measuring BC**

The use of consistent scientific language and methods to describe BC (and fire-derived carbon generally) promotes efficient communication within and among disciplines. It is also important to clearly articulate the specific methodological techniques and associated analytical windows used to assess BC, as these each have biases and artifacts that should be considered in results comparison and interpretation[135]. The main approaches used by various disciplines are described here.

[bH1] Atmospheric sciences

Aerosol BC (soot) is quantified using optical approaches that detect particles with highly absorptive properties that are characteristic of BC[167,168]. Optical methods fundamentally differ from other BC observation approaches, and methodological intercomparisons have been small in scale[168,169], but optical methods are generally thought to identify only the most persistent forms of fire-derived carbon [136,167,169,170].

[bH1] Soil science

BC is commonly measured using benzene-polycarboxylic acid molecular markers. Bulk organic material is thermally digested in acid, after which benzenepolycarboxylic acid molecular markers (presumed to originate solely from condensed aromatic compounds) are separated and quantified chromatographically [171-173]. ^{13}C nuclear magnetic resonance spectroscopy (NMR) is also used to identify polycyclic aromatic structures in soils. ^{13}C NMR yields different but complementary information about the aromaticity and condensation of BC. Hydrogen pyrolysis eliminates labile organic carbon from total organic carbon using thermochemical decomposition into gases in the absence of oxygen [174], isolating samples for stable and radiocarbon analysis[175]. The weak nitric acid method isolates and quantifies the BC fraction in mineral soil samples[176].

[bH1] Oceanography

In the oceanography community, two methodologies have emerged for the determination of BC. The first approach involves chemothermal oxidation of bulk organic material to reductively eliminate chemically reactive organic compounds, leaving behind a BC residue that is then quantified via elemental analysis[177-179]. This method is suitable for coastal sediments and other matrices with a relatively high content of BC, but it is less suited for environmental samples with low BC content. For open-ocean applications, the benzenepolycarboxylic acid molecular marker approach is most often applied for molecular level determination of DBC[180]. A correction factor accounts for the conversion efficiency of DBC into benzenepolycarboxylic acids during the analytic digestion method [180]. For consistency, BC data should be published before and after these corrections[113,135].

Since the 2010s, radiocarbon ($\Delta^{14}C$) and stable carbon ($\delta^{13}C$) isotopic analysis of chemothermal BC residues[68] and BC-derived benzenepolycarboxylic acids[166,181,182] have enabled unprecedented insight into potential sources and environmental residence times of BC in the earth system.

Glossary Terms: [G]

Black Carbon: a carbonaceous, polycondensed aromatic product (>60% organic carbon) derived from the incomplete combustion of biomass and fossil fuels, with greater environmental persistence than its unburned biomass source

Dissolved Organic Carbon: Organic carbon dissolved in water that passes through a filter, usually with a 0.1 to 0.7 µm pore size

Dissolved Black Carbon: The black carbon fraction measured within dissolved organic carbon.

Particulate Organic Carbon: Organic carbon suspended in water that is retained on a filter, usually with a 0.1 to 0.7 µm pore size

Particulate Black Carbon: The black carbon fraction in solid environmental matrices, like particulate organic carbon, soils, and sediments

Environmentally persistent: compounds that resist rapid microbial degradation, accumulating on land and in the ocean for centuries to millennia

Labile: compounds that experience rapid turnover within hours to days of release and do not accumulate

$PM_{2.5}$: as fine particle matter 2.5 µm or smaller in size

Table of Contents Summary:

Black carbon is produced by wildfire and fossil fuel burning, and persists in the environment over centuries to millennia. This Review describes black carbon sources and budgets, discusses its transport along the land-to-ocean continuum, and highlights its enigmatic cycling in the ocean.