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, and therefore its role in the broader carbon cycling during global change, are poorly understood. In this Review, we discuss BC cycling across the land-to-ocean continuum. Wildfires are the main source of BC, producing 128 ± 84 teragrams per year. Negative climate–BC feedbacks could arise as wildfire increases with anthropogenic warming, producing more BC, which in turn will sequester 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. We demonstrate these observed inconsistencies using a simple ocean box model, which highlights key areas of future research. Measurements of BC mineralization 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.

Wildfires and fossil fuel combustion produce substantial amounts of charred pyrogenic organic materials, including black carbon (BC)[1]. Globally, fires produce about 128 ± 84 teragrams (Tg) BC per year[2], of which most is left behind on the landscape as part of charcoal, ash and other charred plant residues. A smaller fraction (2–11 Tg BC per year) is emitted to the atmosphere as soot[3,4]. Fossil fuel burning emits an additional 5–13 Tg aerosol BC per year[4]. Because these processes convert relatively labile biomass carbon to more environmentally persistent, 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[2,6,7].

The precise definition of BC varies depending on discipline, but the BC term used in this Review refers to the carbonaceous, polycondensed aromatic product (>60% organic carbon) derived from the incomplete combustion of biomass and fossil fuels[8] since first described in 1985. 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[9] (FIG. 1). It is operationally divided into dissolved black carbon (DBC), which passes through a filter (usually 0.1–0.7 µm), and particulate black carbon (PBC), which is retained on a filter. These operational definitions are inherited from the oceanography community, in which dissolved organic carbon (DOC) and particulate organic carbon (POC) are traditionally divided on the basis of filtration. In reality, however, the range from DOC to POC is a size continuum that includes monomers, polymers, colloids and gel particles[10] (FIG. 1), and DBC and PBC can 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[8,11]. The reactivity of BC is further constrained by ecosystem properties including microbial populations, enzyme kinetics, environmental conditions and matrix protection[11,12]. As a result, BC is the oldest and most abundant molecularly characterized component of the modern carbon cycle[13,14].

In this Review, we describe the occurrence, cycling and persistence of BC in the environment. We focus on BC, rather than on all fire-derived pyrogenic residues, because the BC fraction is the longest-lived[11], making it relevant for carbon sequestration in a changing climate. The implications of BC production, in which fast cycling biomass carbon is converted to environmentally persistent BC, are reviewed as a long-term feedback

Black carbon
(BC). 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.

Labile
Compounds that experience rapid turnover within hours to days of release and do not accumulate.

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

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Key points

- Black carbon (BC) is produced from incomplete combustion of biomass and fossil fuels and persists for centuries to millennia in the environment.
- BC production is expected to increase with increasing fire activity under anthropogenic warming and could act as a negative feedback to climate change.
- BC is often divided into particulate and dissolved BC, which can have different environmental transport mechanisms, residence times and fates.
- The largest BC pool is in the soil (160–200 petagrams (Pg) C globally). Rivers transport 43 ± 15 teragrams (Tg) BC per year; BC is cycled in other inland aquatic systems, but the global relevance of these processes is unknown.
- Oceans store 12–14 Pg C of dissolved BC. The observed age of this BC (4,800 ± 620 ^{14}C years in the surface ocean, >20,000 ^{14}C years in the deep ocean) does not match expected ages based on mass balance estimates.
- Future research must further explore the possibility that some of the dissolved BC in marine waters is not derived from terrestrial fires.

Dissolved black carbon (DBC). The black carbon fraction measured within dissolved organic carbon.

Particulate black carbon (PBC). The black carbon fraction in solid environmental matrices, such as particulate organic carbon, soils and sediments.

Dissolved organic carbon (DOC). Organic carbon dissolved in water that passes through a filter, usually with a pore size of 0.1 to 0.7 μm.

Particulate organic carbon (POC). Organic carbon suspended in water that is retained on a filter, usually with a pore size of 0.1 to 0.7 μm.

mechanism, which is currently under-represented in Earth system models (ESMs). The 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 a simple ocean box model. Finally, we define major research activities that must be prioritized in the coming years to close knowledge gaps and minimize uncertainties in the global BC cycle.

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 wildfire risks globally by increasing the frequency of fire-prone weather conditions[15,16]. In some regions, particularly in temperate and boreal forests, increased weather-related fire risks have translated into rising wildfire activity[17]. Globally, fires have widespread impacts on the carbon cycle, directly emitting around 2.2 (2–3) petagrams (Pg) C per year, mainly in the form of CO_2 (REF. 18). In turn, post-fire vegetation regrowth recaptures about 1.8 Pg C per year[18,19]. Much of the remaining 0.4 Pg C per year is emitted by deforestation and peatland fires and is further lost indefinitely to the atmosphere[18]. However, changing wildfire frequencies in some regions are also leading to an imbalance between fire emissions and post-fire recovery fluxes and net loss of C to the atmosphere[6,20,21]. 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[17,22].

The biogeochemical feedbacks between anthropogenic climate change and fire emissions are positive (FIG. 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[20]. 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 the atmosphere per degree of warming[5].

The positive feedback between climate change and increased fire CO_2 emissions has been studied widely, but increased fire activity also leads to an understudied enhancement of BC production and storage, with the potential to invoke a negative feedback[6,7,23] (FIG. 2). Because the turnover of BC is considerably slower than that of unburned biomass carbon[24], the distinction between these fire feedbacks are critical to modelling the carbon balance in the decades to centuries following a fire. Moreover, methane emission from peatlands could be suppressed by the presence of BC, acting as a negative feedback by partially offsetting increased emissions of greenhouse gases from warming peatlands relative to the scenario in which no BC production is considered[25]. Although this effect has thus far only been reported by one laboratory-based study, it appears that further investigation of the role of BC in the peatland methane cycle is warranted[25]. 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 of the order of 10–20% of the positive feedback, based on rates of BC production[7,23]. Overall, omitting the BC cycle from ESMs limits the accurate quantification of the role of fire in the global carbon cycle under climate change.

BC stocks, ages and losses

Following its production during wildfires and fossil fuel combustion, the first interactions between BC and water influence its fate in the environment. BC can be incorporated into the soil matrix, where it slowly degrades, or is transferred via water or wind erosion to aquatic systems[26]. BC in soils can also physically disaggregate and be transformed through microbial or abiotic activity into submicrometre-sized particles or DBC, which are

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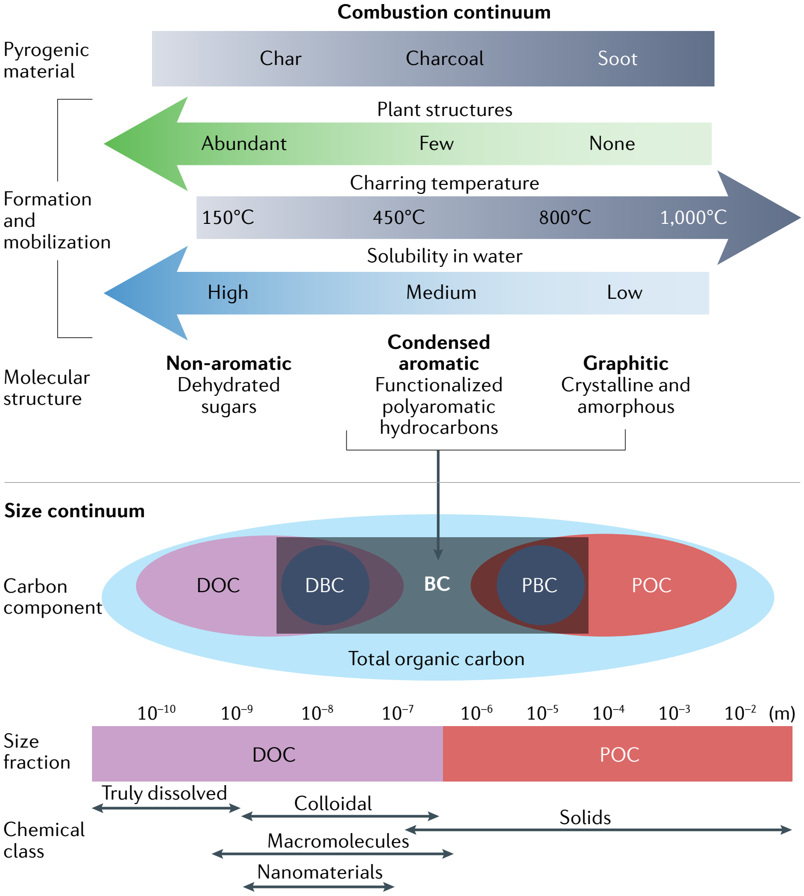


Fig. 1 | **BC characteristics.** Pyrogenic material is chemically heterogeneous and is best described as a continuum from char to soot[9,138,171]. The amount of recognizable plant structures and solubility of charred material depends on the formation temperature, fuel type and duration of incomplete 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 on the basis of pore size during filtration of water. Thus, dissolved black carbon (DBC), which is a part of bulk DOC, can include colloidal, truly dissolved, macromolecular and nanoparticulate forms of BC. We note that the position of labels along the combustion continuum does not necessarily correspond directly to the size continuum. PBC, particulate black carbon.

transported via surface water or groundwater flows. This section describes BC cycling and export to the ocean.

BC in the atmosphere. BC aerosol emission inventories suggest that biomass burning and fossil fuel combustion emit 2–11 Tg BC per year and 4.5–12.6 Tg BC per year, respectively[4]. BC aerosol is initially emitted as soot in the $PM_{2.5}$ size-class, but over time it ages, photodegrades and coagulates with hydrophilic aerosol species, leading to its solubility in rain droplets[27]. Submicrometre-sized BC can remain airborne for up to 14 days[28], indicating that BC aerosols can be deposited far from the fire source. BC leaves the atmosphere by either dry deposition (falling from suspension in the atmosphere) or wet deposition (deposition with falling rain droplets) to the land or surface ocean[28].

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[29,30]. 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[31].

Aerosol BC deposition on the surface ocean can be a BC source to the global ocean, with global flux estimates in the range 1.8 ± 0.83 Tg per year[32] for wet deposition only, up to around 12 Tg per year[28] for wet and dry deposition. In the western North Pacific Ocean and South China Sea, for example, atmospheric deposition of aerosols from fossil fuel combustion is probably the major source of DBC in the surface ocean[33–35]. In fire-affected coastal areas of the western USA, direct inputs of DBC from atmospherically deposited ash and smoke appear to be negligible[36]. However, under experimental conditions, leaching of wildfire ash in seawater released a substantial amount of DBC[36]. 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.

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 per year)[2], in tropical savannas, forests and peatlands[37]. 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[14,38]. Higher soil clay content, greater soil depth, higher wildfire temperatures, lower pH and lower soil cation exchange apparently enhance the retention of BC in soils[14,39,40].

Soil BC is degraded and lost by multiple biotic and abiotic pathways. BC in soil can be microbially oxidized[41–43], which reduces the hydrophobicity of the condensed aromatic structures, thereby increasing solubility and mobilization by leaching and enhancing accessibility for further microbial degradation[44]. Photo-oxidation and sorption of DBC to minerals or other particulates is an important DBC loss mechanism[45,46], 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 behaviour, soil type, climate and topography[38,47].

In situ mineralization, erosion and solubilization via water, and wind-driven transport are key loss mechanisms for soil BC[48–50]. Most research has focused on microbial decomposition[40,51–53], with physical degradation and mobilization studied less[54]. Very 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[55]. 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 to be stable in soils for millennia[56].

Once mobilized from production sites, BC can be physically retained in intermediate reservoirs on land

$PM_{2.5}$
Fine particle matter 2.5 μm or smaller in size.

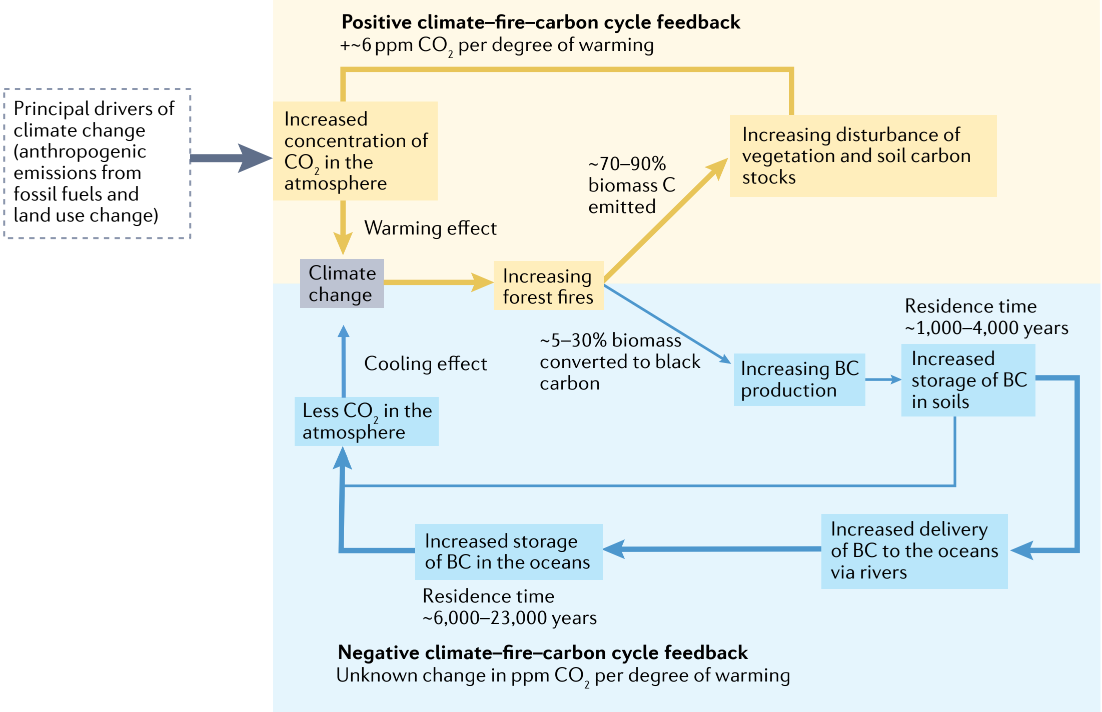


Fig. 2 | **Climate–carbon cycle feedbacks involving fire.** The role of wildfire in the terrestrial carbon cycle as it is typically conceptualized and represented in Earth system models (ESMs) is shown in yellow. Wildfire leads to large emissions of CO_2 that can be recaptured through subsequent vegetation recovery in the longer term. However, as wildfire frequency increases under climate change, rates of CO_2 emission from fires also increase and a carbon imbalance can emerge even after post-fire recovery regrowth. This leads to a 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 more wildfires. However, about 5–30% of burned biomass is transformed into black carbon (BC; shown in blue), which can persist in the environment for centuries to millenia. BC cycles slowly in the terrestrial soils (centuries) and sediments, and when rivers transfer BC to the global oceans (blue arrow at far right), BC degradation is further slowed to millenia timescales. Increases in fire activity lead to more BC production and storage, producing a negative feedback to climate change by sequestering carbon as this environmentally persistent form of BC. ESMs omit the BC cycle and associated negative feedback. Consequently, these models overestimate the magnitude of positive feedbacks to climate change.

prior to riverine export. For example, BC contributes up to 20% of the soil organic carbon in mollic horizons of European floodplains[57] and to around 10–30% in surface sediments in restored Chinese wetlands[58]. Deposition in lakes and other fresh water deltaic sediments could be a key but understudied BC retention mechanism, because lake sediments store twice the amount of macroscopic BC than surface soils in boreal forest watersheds do[59]. Groundwater could also contain BC, although the magnitude of this pool as well as the flux to the ocean is unknown[60,61]. 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.

BC transport in rivers. Rivers transport 43 ± 15 Tg BC per year[2], which equates to approximately 34 ± 26% of the BC produced annually by wildfires. Globally, riverine DBC and PBC are exported in similar proportions (18 ± 4 Tg DBC per year and 17–37 Tg PBC per year, respectively). These estimates are based on data sets with global-scale coverage, and the fluxes are well constrained in comparison to other elements of the aquatic BC cycle[2,62] (FIG. 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 days to few years post-fire[26,48,63]. By contrast, the release of DBC from soils to streams is driven by the solubilization of soil BC by biotic or abiotic mechanisms, followed by export with soil pore water to river channels[64,65]. Relative to PBC export, DBC export occurs over longer time periods, after the slow ageing and oxidation of soil BC to functionalized condensed aromatic molecules for enhanced solubility in water[44]. The continual export of DBC from historically fire-affected watersheds[66] further supports the hypothesis that ageing of condensed aromatic structures and solubilization in soils is a prerequisite to their export by rivers.

The different transport and transformation mechanisms of DBC and PBC are reflected in their apparent radiocarbon ages. In rivers, DBC age is generally modern (contemporary), whereas PBC can be highly variable, up to several thousand years old[30,62] (FIG. 3). This age discrepancy between DBC and PBC is also observed in both bulk organic carbon and other compound-specific fractions[67,68]. 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 ageing in intermediate reservoirs. Freshly produced charcoal and ash can leach considerable amounts of DBC[36,50,64] (BOX 1). From 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 wildfire). This observation runs counter to what has been measured for BC in rivers (FIG. 3). This discrepancy may be driven, in part, by the general lack of spatiotemporal radiocarbon data for BC in rivers globally. Submicrometre-scale BC soot aerosols deposited within river basins also contribute a minor fraction of riverine DBC[2,29], of the order of 5–20%, with wide variation across regions[30,31,69,70].

Riverine DBC fluxes are usually highest at peak discharge and lowest during baseflow[65,66,70–72]. This coupling between DBC concentration and discharge results from DBC mobilization from upper organic soil horizons during heavy rainfalls[45]. 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[73,74]. However, the DBC content in bulk riverine DOC can vary between 2% and 15% depending upon biome, latitude, climate, soil type and land cover[47,75] (FIG. 3). Moreover, DBC and DOC export are largely decoupled in some locations, such as the Amazon River and other channels in Brazil[31,47,69,] 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 probably replenished more quickly than pore water DBC following prior rainfall events owing to the greater recalcitrance of soil BC)[47,76]. Freshly burned watersheds can have higher in-stream concentrations of DBC that can persist for years after the fire event[77,78]. 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[65,79,80]. With changes in watershed properties, mainly due to agricultural activities, shifts in molecular composition and reactivity of DBC can be expected[81,82] 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[62], because 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[83]. In addition, PBC deposited within the stream corridor can be resuspended during periods of high discharge[65,74]. This successive hydrological redistribution of river-transported material within stream channels and alluvial plains[48,84] causes an observed lag between fire occurrence and sedimentary charcoal deposition in coastal basins[85]. 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[62], including locations where environmental conditions favour both preservation or mineralization. In several high-latitude rivers[62], the apparent age of PBC was as high as 17,000 ^{14}C years (FIG. 3). The ratio

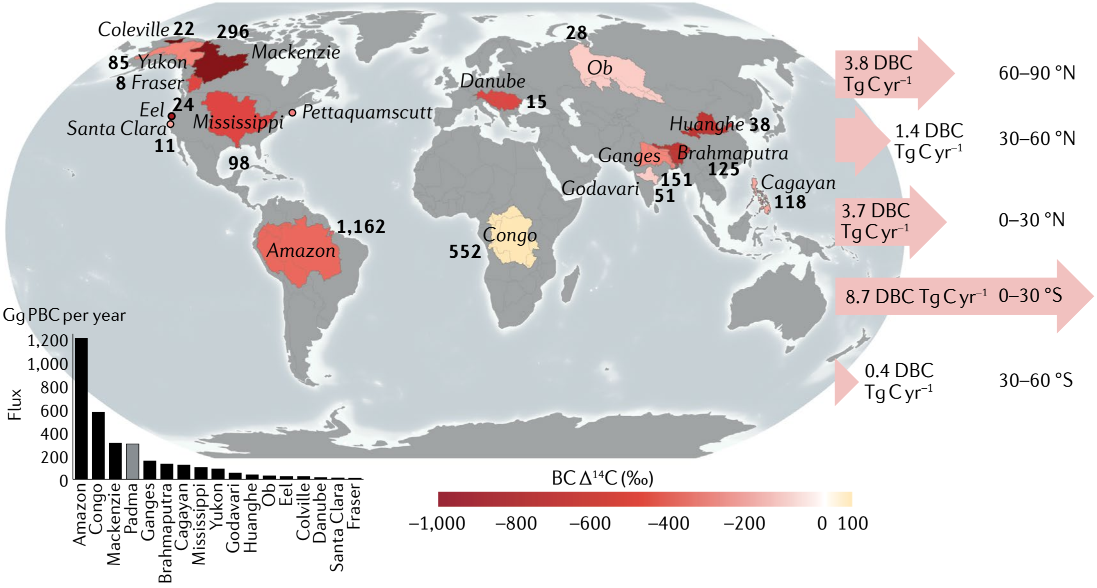


Fig. 3 | **BC in terrestrial systems.** Riverine particulate black carbon (PBC) Δ^{14}C values, shown by basin on the map. Fluxes of PBC are shown in the bar graph[62]. Horizontal arrows indicate the global flux of dissolved black carbon (DBC) from each 30° latitude range (Tg C per year), based on values in REF.[2]. In terrestrial systems, DBC Δ^{14}C signatures are generally modern, whereas PBC is older. Marine DBC Δ^{14}C signatures are not shown here. BC, black carbon. Figure adapted from REF.[62], Springer Nature Limited.

Box 1 | **Measuring BC**

The use of consistent scientific language and methods to describe black carbon (BC) (and fire-derived pyrogenic 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 artefacts that should be considered in the comparison and interpretation of results[136]. The main approaches used by various disciplines are described here.

Atmospheric sciences

Aerosol BC (soot) is quantified using optical approaches that detect particles with highly absorptive properties that are characteristic of BC[172,173]. Optical methods fundamentally differ from other BC observation approaches, and methodological intercomparisons have been small in scale[173], but optical methods are generally thought to identify only the most persistent forms of pyrogenic carbon[137,172,174].

Soil science

BC is usually measured using benzenepolycarboxylic 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[175–177]. ^{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[178], isolating samples for stable and radiocarbon analysis[179]. The weak nitric acid method isolates and quantifies the BC fraction in mineral soil samples[180].

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[164,181,182]. 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 dissolved black carbon (DBC)[183]. A correction factor accounts for the conversion efficiency of DBC into benzenepolycarboxylic acids during the analytic digestion method[183,184]. For consistency, BC data should be published before and after these corrections[113,136].

Radiocarbon (Δ^{14}C) and stable carbon (δ^{13}C) isotopic analysis of chemothermal BC residues[69] and BC-derived benzenepolycarboxylic acids[185–187] have enabled unprecedented insight into potential sources and environmental residence times of BC in the Earth system.

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[65] (FIG. 3). However, the PBC to POC ratio in global rivers is roughly constant (15.8 ± 0.9%) (FIG. 4a), regardless of environmental conditions or watershed characteristics[62], which permits scaling of PBC fluxes.

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 owing to biogeochemical processes, such as photodegradation and biodegradation[86–88], specifically in two loops carrying carbon from land to inland waters, and then from tidal wetlands to the ocean ocean[89]. In situ rates for BC degradation and remineralization along the river-to-ocean continuum have not been measured 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[87]. 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[90]. The addition of bio-labile substrates (for example, algal biomass and exudates) might enhance the decomposition of environmentally persistent organic matter such as BC[91]. This priming effect, which has been well studied in soils[56], is an emerging research topic in aquatic environments[88,92], 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[46]. The photolability of DBC is mainly controlled by the abundance of polycyclic aromatic structures, with larger condensed structures being more susceptible to photo-oxidation than less condensed structural features[46]. In laboratory experiments, the photochemical half-life of polycyclic aromatic structures is one to two days and therefore is much shorter than the typical riverine transit time to the ocean[95]. However, the DBC content is relatively high in most river mouths (12 ± 5% of DOC)[2]. 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, DBC of lower molecular weight is mineralized by microbes first[53], whereas DBC of high molecular weight is comparably resistant[46]. Microbial remineralization and photodegradation are probably coupled by a process in which photo-exposure breaks down the condensed aromatic structures, thereby potentially increasing the bioavailability of DBC[46,53,99]. The overall balance between the two processes in the environment is, however, unknown. The photo-mineralization rates of organic matter in the Amazon River are seven times greater than for microbial remineralization. However, when intergraded over the entire water column, microbial remineralization is likely to be the dominant organic matter removal process because it is not restricted to surface waters, as is photo-mineralization[97]. There is currently no global estimate for losses of DBC via microbial degradation at aquatic interfaces.

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].

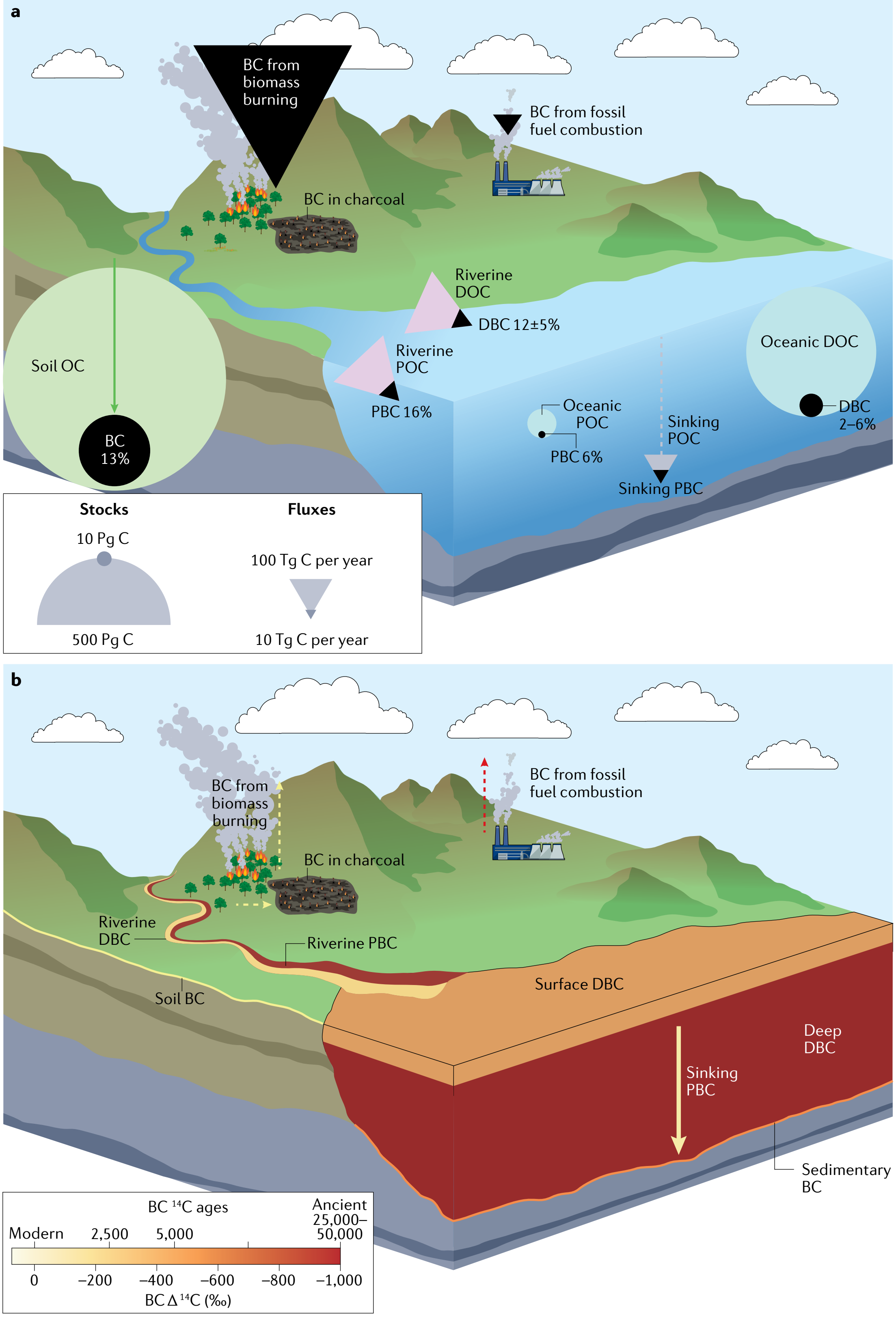
The fraction of DBC that escapes mineralization at the river–ocean interface becomes part of the 662 Pg C marine DOC pool[45,107] (FIG. 4a). DBC accounts for about 2–6% of oceanic DOC, which corresponds to a 12–14 Pg C standing stock of DBC in the global oceans[13,108] (TABLE 1). DBC in the Atlantic, Pacific and Arctic Oceans ranges from 1.4 to 2.6 μM in the surface and is 1.2 ± 0.1 μM in the deep Atlantic. The average ^{14}C age of surface DBC is 4,800 ± 620 ^{14}C years and much older in the deep ocean (23,000–25,000 ^{14}C years)[13,109]. The range of DBC structures and ^{14}C ages indicates that DBC is not homogeneous in the ocean and consists of two distinct pools of marine DBC, a younger pool that cycles on centennial timescales and an ancient pool that cycles on >10^5 year timescales[13]. This suggests that despite its polyaromatic structure, most BC delivered via rivers is not accumulating in the ocean, given the low concentrations observed despite larger inputs by rivers. Therefore, loss processes such as photodegradation and microbial degradation along this long pathway could be important for altering and removing DBC[46,53,110].

At the basin scale, DBC behaves largely conservatively on a timescale of decades to centuries in the absence of photodegradation[45,108,110]. 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[70]. The global removal flux of DBC to abyssal sediments via sorption to sinking particles has been estimated as 40–85 Tg C per year[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 as-yet-unidentified sources of DBC in the ocean 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 per year via the 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 per year) are sufficient to sustain the turnover of the entire oceanic DBC pool in just 500 years (simply dividing the marine stock by the riverine discharge)[13]. This value suggests that the apparent ^{14}C ages of oceanic DBC should be young. However, apparent ^{14}C ages of oceanic DBC are on average 4,800 ± 620 ^{14}C years in the surface ocean (though with a large range, probably due to variable inputs of modern DBC through rivers and aerosols)[13,36,109]. In the deep ocean, apparent ages are >20,000 ^{14}C years[13] (FIG. 4b and TABLE 1). 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[112], although still longer than the timescale of meridional circulation in the deep ocean. These long residence times and smaller removal fluxes in the deep ocean suggests that the size of the deep-ocean DBC pool can increase or decrease depending on the strength of the source[112]. Thus, despite its expected recalcitrance, most BC delivered by rivers is not accumulating in the ocean DBC as would be expected, suggesting losses are important in balancing the BC budget.

This conundrum highlights the gaps in our understanding of DBC losses in the ocean, which include photo-oxidation in the surface ocean, sorption of DBC onto sinking POC, burial of DBC in hadal zones and (potentially, but not yet investigated) losses of DBC by bursting bubble plumes (FIG. 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 ocean[109]. 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. Therefore, a realistic and scalable rate for the photo-oxidation of DBC is still needed.

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[35,113]. 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 19–40% of freshly produced primary marine aerosols contains aged DOC[114]. Because DBC is an aged component of DOC, and assuming DBC is 6% of DOC[13], this



un-measured loss could represent 0.02–0.48 Tg BC per year. However, the actual amount of BC lost by primary marine aerosol formation is unknown[114].

Although 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

◀ Fig. 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 ratios of BC to organic carbon shown as percentages. **b** | Estimates of BC $\Delta^{14}C$ values (darker reds indicate older ^{14}C ages). Values of stocks, fluxes and BC ages in TABLE 1. The largest stocks and fluxes of BC are observed on land because 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 particulate 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 owing to its conservative behaviour during transport to the oceans. Eventually, some BC is deposited to the deep ocean sediments, where it enters the geological stores. DBC, dissolved black carbon; OC, organic carbon; PBC, particulate black carbon. Panel **a** adapted from REF.[62], Springer Nature Limited, and from REF.[2], CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

in the oceans or to an autochthonous, marine source of oceanic DBC[115] (Supplementary Fig. 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 that there is another major source of DBC in the ocean, but the main source of riverine DBC (biomass fires) 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[108,115]. 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]. Organic-matter-rich hydrothermal systems can release low amounts (0.000003–0.000005 Tg per year) of DBC to the water column[122]. 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[123].

A newly identified, allochthonous source of DBC to oceanic surface waters[124] 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.

Insights into the age of oceanic DBC

The conundrum associated with measured radiocarbon ages[13,115,125], 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[70]. It also suggests that 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[70]. Here, we incorporate current known losses, stocks, ages and fluxes (TABLE 1 and Supplementary Table 1) into an oceanic box model with seven boxes and a simplified overturning circulation[126,127] (Supplementary Information). 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 Fig. 1).

Consistent with previous work[13], 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 homogeneous pool with a single $\Delta^{14}C$ value using a box model (Supplementary Fig. 2a,b). 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‰)[13]. Moreover, DBC might have two distinct molecular constituents — one that is old, abundant and recalcitrant; and another that is young, sparse and labile. Having these constituents would suggest that DBC follows the same mixing processes as bulk oceanic DOC[128] 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 to be minor for several reasons. First, the annual production of biomass-derived (contemporary) BC (128 ± 84 Tg per year)[23] substantially outweighs the input of fossil-fuel derived BC because fossil fuel combustion is a recent phenomenon (since around 1750). Secondly, as soil formation rates span centuries to millennia, the vast majority of DBC eroded from soils predates the beginning of the industrial revolution, and thus must be predominantly biomass-derived, as riverine DOC globally is modern ($\Delta^{14}C$ = +22 to +46‰)[129] compared to 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 to be 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[130], 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. From a conservative, first-order estimate scaled up from an asphalt volcano in the Gulf of Mexico, about 3.3–5.0 × 10^6 g (0.000005 Tg) DBC could be released from petroleum seepages per year[122].

To assess the role of hydrothermal carbon input, a larger estimated input compared to measurements[122] from the sea floor of 0.12–1.2 Tg per year 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 per year)[131] and methane seeps (0.2–20 Tg per year)[132]. Assuming hydrothermal DBC content in DOC is present at the upper limit of the percentage of DBC of marine DOC (assuming that the percentage of DBC in marine DOC is in the range 2–6%)[13,108], then hydrothermal DBC fluxes would cover a range of 0.012–1.2 Tg DBC per year by pre-aged hydrothermal sources. Using the smaller input of 0.012 Tg DBC per year, pre-aged sediment input reconciles the budgets better, but the overall modelled age range between surface (about 7,000 years) and subsurface (about 11,000 years) remains too narrow. A 10× higher sediment source (1.2 Tg per year) would increase the subsurface age to >20,000 years, but overestimates bulk DBC concentrations (Supplementary Fig. 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 modelling 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[100,111,112] that are needed to reconcile the low concentrations in the ocean.

Table 1 | **BC and OC stocks and fluxes**

Pools and processes	Radiocarbon	Percentage BC content of OC	Value of BC fluxes (Tg per year) or stocks (Pg)	Refs.
Fluxes (Tg per year)				
Production of BC in post-fire residues (charcoal, charred plant material)	–	Assumed 50 (±30)	128 ± 84	2,23
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 2–12 Tg per year; to ocean DOC pool 1.8 ± .83 Tg per year	28,32,164–166
River PBC	Variable between rivers; average age 3,700 ± 400 years	15.8 ± 9	17–37 Tg per year	62
River DBC	Modern Yangtze River −60 ± 30‰; Yellow River −140 ± 20‰; Pearl River −91 ± 3‰	12 ± 5	18 ± 4 Tg per year	2,30,69
Leaching DBC from soils to rivers	–	–	203 Tg per year	38
Biodegradation at river–ocean interfaces	–	–	Unknown	–
Marine sinking PBC	1,700 ± 200 years	Upper 100 m 0.5–2.5%; below 100 m depth 6%	40–85 Tg per year; 16 Tg per year (limited data)	100,112,164,167,168
Transport to hadal zones	–	–	1.0–0.5 Tg per year	111
Loss by primary aerosol formation	–	–	Unknown	114
Ultraviolet loss	–	–	2–4 Tg per year	93
Coastal sedimentation	–	–	Unknown	–
Pre-aged hydrothermal fluxes from DBC and DOC	–	–	For DBC: 0.000003–0.000005 Tg per year (3.3×10^6 to 5.0×10^6 g) Pre-aged hydrothermal DOC in range of 1.2–5 Tg per year; methane seep DOC inputs to the deep ocean of 0.2–20 Tg per year	122,131,132
Pools (Pg)				
Terrestrial soils	Variable surface age; modern to millennia	13% on average in the top 2 m of soil	160–200 Pg	14,55,56
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	13,108
Oceanic sediments	Surface 6,000 ± 800 years; deep 24,000 ± 520 years	4–22% of ocean sediment OC pool	Global coastal zones 480–1140 Pg; global open ocean 80–240 Pg	100,133,169

Values in the table were used to construct FIG. 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.

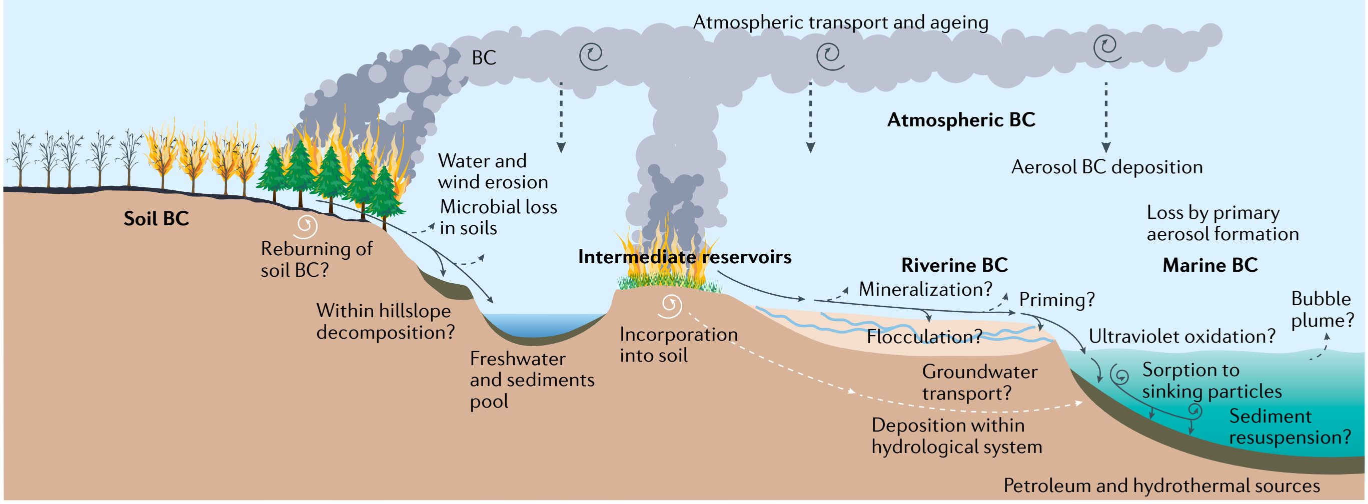


Fig. 5 | **BC processes across the Earth system.** Key black carbon (BC) processes along the land–river–ocean continuum are highlighted, and its processes with major unknowns are noted with question marks. Atmospheric BC is the best understood, followed by marine BC. There is an emerging understanding 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.

A third proposed explanation is that the oceanic stocks of DBC experience pre-ageing on land before transport to the ocean[83,133]. Although DBC in rivers is generally modern, aged PBC from rivers might solubilize to the DBC fraction at river–ocean interfaces[10]. Riverine PBC experiences long periods of ageing in intermediate terrestrial reservoirs (estimating 1,500–3,000 ^{14}C years), such as in alluvial fans[84]. If solubilized to DBC, the PBC could potentially act as an aged DBC source[62,83]. However, taking these values into account does not conclusively reconcile the BC budget (Supplementary Fig. 2g,h). The input of pre-aged material increases the overall age in the box model simulation, especially in the deep ocean (around 24,000 years, closer to the measured values), but the resulting surface ocean BC age is too old (around 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[13] 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.

Summary and future perspectives

In summary, BC is environmentally persistent[8] and represents a mechanism for long-term carbon sequestration over centuries to millennia[134,135]. 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[55,56]. Likewise, the modelled ocean BC concentrations versus observation-based age profiles do not agree, on the basis of 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 to enable 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 (FIG. 5 and TABLE 2). We also highlight judicious observations that are likely to provide critical constraints in understanding the role of BC in the Earth system as a potential negative carbon feedback.

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[136]. A cross-laboratory comparison that incorporates multiple methods measuring a larger range of BC reference materials with isotopic measurements[137,138] 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

Table 2 | **Assessment of the level of BC process understanding required for incorporation into models**

Earth system 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 under-represented soils
	*Microbial loss in soils	Quantify long-term (decades to centuries) mineralization rates
	****Biotic transformation in soils	Field-based studies, incubations, mesocosm experiments and upscaling
	***Abiotic transformation in soils	Description, quantification and modelling, 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 modelling
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 labelling studies using isotopes
	*Biodegradation at river–ocean interfaces	Establish biodegradation 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 photodegradation rates under key conditions; measure flocculation and dissolution along salinity transect
	*Transfer between DBC and PBC pools	Regional studies of pristine versus anthropogenically affected locations
	**Fractionation of DBC $\delta^{13}C$	Measure DBC $\delta^{13}C$ across aquatic continuum
Models	*Modelling 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 scale up
	*Decomposition in intermediate reservoirs	In situ laboratory 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 upwelling and downwelling regions (to address photoactivity and bioactivity, respectively)
	**Photodegradation of DBC	Establish photodegradation 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 multilayer seawater sampling campaign; sample localized sources
	****Decomposition estimates inferred by mass balance	In situ measurements
	****Turnover and ages inferred by ^{14}C	Global marine DBC $\Delta^{14}C$ measurements

Table 2 (cont.) | **Assessment of the level of BC process understanding required for incorporation into models**

Earth system component	Process	Knowledge or research effort needed
Oceans (cont.)		
Oceanic PBC	**Storage in marine POC	Spatiotemporal measurements, global estimates of fluxes and ^{14}C measurements
	*Transfer between POC and DOC pools	Laboratory dissolved organic matter 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 whether it comes from a DBC source
Models	*Global ocean modelling	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

The number of asterisks indicates the level of understanding of these terms related to the proportion of the research effort and number of studies, as used in REF.[170]. *Limited understanding (with low or scarce measurements, laboratory-based testing, unknown processes or methods impeding the process); **emerging understanding (uncertain, not global but with good quality regional studies, in-situ testing, but not able to quantify robustly); ***ready understanding (the processes can quantify on global scales, estimates exist, and there is an understanding of the drivers or processes); ****applied knowledge (where information is used only in individual models, or included in coupled models but parameterization is needed). BC, black carbon; DBC, dissolved black carbon; DOC, dissolved organic carbon; PBC, particulate black carbon; POC, particulate organic carbon.

fraction of DBC, based on its molecular formulas[81,139,140]. Atomic force microscopy can also quantify and characterize DBC structures, based on visualization of polycondensed aromatics[141]. Combining approaches like these could address method biases associated with different analytical measurements[31,81,139] 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 intercomparisons, such as petrogenic and lithogenic lignite, coal and petroleum[137,142]. Recoveries of BC for coal, oil and lignite samples have already been reported[142], and these are present in negligible amounts in the rocks eroded in the global river catchments[62], but potentially important condensed aromatic carbon contributions have not yet been explored. For example, Green River Shale as a reference standard is a good analogue of riverine petrogenic carbon, yet has only had very low BC recoveries[137] (BOX 1). 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[143]. Other potential sources of condensed organic matter derived from composting[144] and degraded lignin products[145] should also be considered. At the moment, there are no quantitative constraints on non-pyrogenic sources of BC in the ocean, but they are likely to have contributions.

DBC and PBC fractions should be analysed synchronously, given that BC cycling occurs along a size continuum[146,147] (FIG. 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 is 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[70,100,148]. In rivers, BC is unequally distributed across operationally defined dissolved, colloidal and particulate size fractions[82] and within the DOC pool[94]. Therefore, BC might also be unequally distributed within the oceanic DBC and PBC pools, requiring the routine quantification of both pools.

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 (such as uplands, slopes and depositional environments). In particular, decomposition rates in lakes, reservoirs and other inland water bodies are 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 us 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 modelled 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[31,45,139]. At present, although well represented in the China Sea[101,105,106,149,150] and the Northwestern Pacific[70,151], 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[89] requires research to target coupled processes occurring in aqueous and solid phases. For example, priming effects[91,152] and BC–mineral interactions[153,154] could affect BC reactivity.

DBC sources in the ocean. The lack of explanation for the aged 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 model and predict future fire–hydrology interactions better.

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 timescales. It will also enable models to address better how future changes to BC production rates may influence the carbon cycle[7]. Box models such as the one trialled here are useful for rough assessments, but a higher-resolution spatial model with localized river and atmospheric sources is required to further constrain the processes and fate of marine DBC[127]. 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[112]. Targeting potential sources of DBC in the ocean will help us to identify whether there are other BC sources to oceanic DBC, explaining the stable isotope differences between oceanic and riverine DBC[115].

At present, the time, effort and expense of sample collection and processing is hindering progress in measuring oceanic 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 the links between DBC molecular markers and chromophoric properties of DOC and at a higher spatiotemporal resolution[125]. 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[46]. As part of ocean-observing systems, gliders equipped with fluorescence sensors targeting polycyclic aromatic hydrocarbons could potentially increase the coverage of deep open ocean environments that are not accessible by satellites[160,161]. Also, biosensors could be engineered to detect the presence of BC in soils and waters; initial research on this topic seems very promising[162,163]. Lastly, establishing regional or global correlations between BC concentrations and high resolution or remote sensing measurements (such as discharge and absorbance data from satellites) could scale land-based assessments through time and space.

Data availability

The fluxes of PBC, radiocarbon ages of PBC and mapped river basins derive from REF.[62]. 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 FIG. 4 derive from the studies cited in TABLE 1. The data set is on the PANGAEA data repository (www.pangaea.de) under the username alyshacoppola (connected to the ORCID ID https://orcid.org/0000-0002-9928-2786).

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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.T.L., A.I.C., M.W.J. and M.S. contributed to the box model conceptualization for oceanic black carbon and S.T.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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