

Review

Black Carbon's Properties and Role in the Environment: A Comprehensive Review

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Abstract: Produced from incomplete combustion of biomass and fossil fuel in the absence of oxygen, black carbon (BC) is the collective term for a range of carbonaceous substances encompassing partly charred plant residues to highly graphitized soot. Depending on its form, condition of origin and storage (from the atmosphere to the geosphere), and surrounding environmental conditions, BC can influence the environment at local, regional and global scales in different ways. In this paper, we review and synthesize recent findings and discussions on the nature of these different forms of BC and their impacts, particularly in relation to pollution and climate change. We start by describing the different types of BCs and their mechanisms of formation. To elucidate their pollutant sorption properties, we present some models involving polycyclic aromatic hydrocarbons and organic carbon. Subsequently, we discuss the stability of BC in the environment, summarizing the results of studies that showed a lack of chemical degradation of BC in soil and those that exposed BC to severe oxidative reactions to degrade it. After a brief overview of BC extraction and measurement methods and BC use for source attribution studies, we reflect upon its significance in the environment, first by going over a theory that it could represent parts of what is called the ‘missing sink’ of carbon in global carbon cycle models. Elaborating upon the relationship of BC with polycyclic hydrocarbons, we show its significance for the sorption and transport of pollutants. A description of pulmonary-respiratory health effects of soot BC inhalation is followed by a discussion on its impact on climate and climate change. We explain how soot BC acts as a global warming agent through light (and heat)

absorption and how it reduces the snow's albedo and promotes its uncharacteristic thawing. On a more positive note, we conclude this review by illustrating recent observations and simulations of how pyrolytic processes can stabilize plant carbon stocks in the form of biochar BC that can sequester carbon and can help mitigate climate change, in addition to improving soil fertility.

Keywords: soil carbon sequestration; carbon budget; atmospheric pollution; polycyclic aromatic hydrocarbons; climate; biochar

1. Introduction

As the atmospheric carbon dioxide (CO₂) levels continue to increase from pre-industrial concentrations of 280 ppm (parts per million volume) to an average value of 385 ppm, as reported in 2008 [1], precise investigation and documentation of different carbon (C) forms, pools and sinks is of utmost significance. Carbon dioxide is the most commonly studied form of carbon emissions. Black carbon (BC) in the form of aerosols has received far less consideration, although it is a primary air pollutant produced by combustion activities and has a high global warming potential of 680 on a 100-year basis [2]. When BC is buried and incorporated in the pedosphere, its long residence time and tendency to enhance other soil chemical and physical properties can increase the soil's potential to sequester carbon. Such burial is preceded by natural, anthropogenic or a mixture of both kinds of events such as wildfires, prescribed burns, biomass-based cooking and fossil fuel combustion. Subsequent *ex-situ* deposition of BC after aeolian or alluvial transport may occurs.

Playing a significant role in the carbon cycle, BC simultaneously influences the quality of air from local to intercontinental distances from its point of origin. Maximizing BC formation (as charcoal and char) during combustion processes can decrease CO₂ emission on one hand, whereas on the other hand, it can increase atmospheric pollution with excess soot BC yield. The global dimming effect is another consequence of aerosol BC emission. The emission and transport of BC in the environment is also associated with the fate of other organic substances, particularly polycyclic aromatic hydrocarbons (PAHs), whose isomers can be utilized to trace the sources of BC in soils and sediments. In this paper, we elaborate upon the above properties of BC, focusing on what they imply for the environment and humans.

2. Properties of Black Carbon

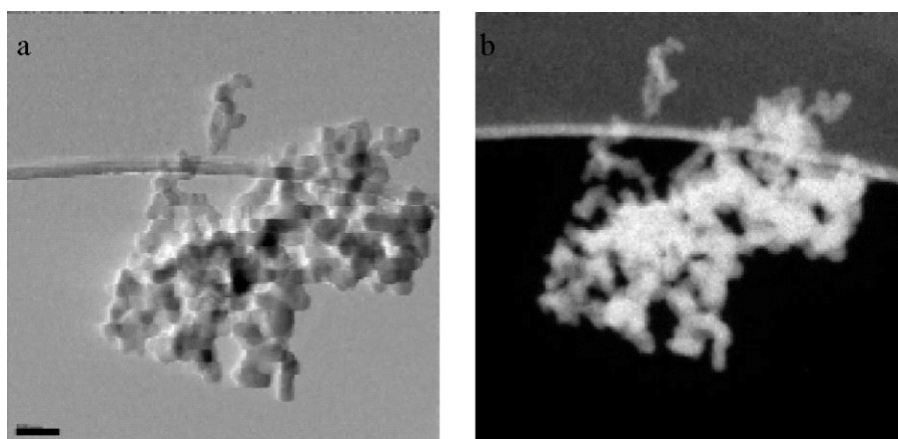
2.1. Origin, Types and Composition

Black carbon originates from biomass and fossil fuels. It comprises a range of carbonaceous materials from char BC, the partially combusted solid residues of plant tissues, to highly graphitized soot BC, the volatile substances formed within flames [3]. At their onset, soot or aerosol BC particles form as hydrophobic primary spherule aggregates with irregular geometry providing active sites for deposition of chemical species [4,5]. With decreasing particle size (particularly with sizes smaller

than 2 mm), the ability of these particles to remain airborne in the atmosphere increases, promoting long distance transport [6]. Immediately after fires, emitted BC particles larger than 1 μm may fail to become airborne or may otherwise quickly drop to the nearest surface [7,8]. Precipitation and runoff events may eventually wash such BC particles remaining on the soil surface to rivers and oceans unless deposition occurs further than 1 km from significant water bodies [7]. Larger BC particles and charred materials may not be transported and may instead remain on the soil at, if not close to, the place of production and deposition. Time and natural processes such as bioturbation can mix and accumulate such BC materials with the soil, promoting C sequestration and enhancing nutrient sorption, as described later in this paper.

The size of BC materials spans from a few nanometers for atmospheric aerosols (soot BC) to a few centimeters for charcoal fragments of combusted plant materials. In spite of their common sources and aromatic hydrogen deficient chemical composition, charcoal BC, soot BC and other components of the combustion continuum exhibit significant physical and chemical variations [8,9]. The bulk composition of BC is dominated by condensed aromatic rings and a few functional groups making it resistant to decay [10]. The extent of polymerization, macromolecular structure (graphitic vs. diamond) and surface functional group composition of BC is influenced by the type of combustion precursor (vegetation type), the duration and temperature of combustion in the absence of oxygen and the extent of post-combustion aging or weathering [11].

Figure 1. Electron energy loss spectroscopy (EELS) of NIST reference soot material (comprising n-hexane rings). (a). Transmission Electron Microscopy (TEM) image of soot black carbon on a holey carbon film support (above dense transverse line) (b). Field emission transmission electron microscopy (FTEM) image of the same, also called the carbon map, with bright portion representing elemental carbon portions in Figure (a); black color shows absence of carbon in vacuum background (images collected at the University of California Microscopy Facility).



The C:H:N ratio of BC can vary widely but its carbon concentration is on average, over 60% with accessory elements hydrogen, oxygen, nitrogen and sulfur [11]. Soot BC is more recalcitrant than char BC because of its high formation temperature, low internal microporosity and low O/C ratio [12]. Cope [13] observed soot BC with H: C ratios of 0.25–0.69 and O: C ratios of 0.08–0.33. Diesel soot (Figure

1) from the US National Institute of Standards and Technology (NIST) has a C:H:N ratio of 1:0.1:0.016 with 100% aromaticity. This ratio for BC from Boston Harbor sediments has been observed to be 1:0.1:0.07 [14].

Black carbon *versus* elemental carbon

The term ‘black carbon’ is often used interchangeably with the term ‘elemental carbon’ in the atmospheric sciences. Both are light-absorbing carbon compounds, but whereas BC is formed from incomplete combustion in reduced or anoxic environments, the term ‘elemental carbon’ is used for carbon fractions measured after oxidative combustion in the presence of oxygen above a certain temperature threshold. Another light absorbing carbon is ‘brown carbon’, which is a non-soot organic carbon aerosol originating from humic like substances (HULIS), bioaerosols and tar [15-17].

2.2. Fossil Fuel and Biomass Origins of BC: Attributing Sources of and with BC

Whereas Novakov *et al.* [18] used the ratio of total C to BC in aerosols to apportion BC sources, Brodowski *et al.* [19] were able to distinguish source-based differences in shapes, sizes, surface properties and partial oxidation of the surface of soil BC particles for vegetation fire and coal combustion sources. Here, we discuss how BC in aerosols, soils and sediments have been utilized for fossil fuel and biomass source apportionment and how PAHs have been employed for specific BC source attribution.

2.2.1. Radiocarbons

Soot BC from biomass and fossil fuel combustion are different in properties and adsorbed species [20]. Their physical, chemical and radiocarbon properties can be exploited to examine past and current combustion activities, land fire histories and source apportionment of particulate matters (PMs). For instance, BC derived from fossil fuel is fully depleted in radiocarbons (^{14}C), whereas BC from combusted biomass reflects approximate atmospheric ^{14}C abundance of the time when the biomass of origin was created, minus loss through radioactive decay. This property makes BC a good tool to assess emissions from fossil fuel combustion, which may not be identified or quantified adequately through other means. For this reason, sediments, soil and aerosol BC has been used for particulate pollution analysis and emission source apportionment studies with the use of radiocarbons [21-23].

2.2.2. PAH isomers

The PAH isomer ratios of benzo[a] pyrene to benzo[e]pyrene {b[a]p/b[e]p}, benzo[b]fluoranthene to benzo[k]fluoranthene {b[b]f/b[k]f} and benzo[a]anthracene to chrysene {b[a]a/chry} can provide an indication of the source of BC [24]. More than 50% of PAHs are associated with atmospheric aerosols and distinct isomer ratios exist for combustion sources [24]. Calculation of these ratios at any

particular point downstream of a watershed can be used to estimate BC emission from different upstream sources, both point and non-point. Mitra *et al.* [25] used these ratios from total suspended sediments in the Mississippi river to estimate the contribution of BC from combustion sources into the ocean. Such data from surface and deep river sediments can be correlated with ^{14}C analysis of BC. These ratios can further be used to develop models of combustion events and practices relating to BC emission, deposition, and climate change through time.

PAH isomers can be photolysed during atmospheric transport. Mitra *et al.* [25] used the following equation (Dickhut *et al.* [24]) for adjustment of PAH in total suspended solids in the Mississippi River:

$$(\text{isomer ratio})_{\text{photoadjusted}} = (\text{isomer ratio})_{\text{TSS}} \times \exp[(\lambda_n - \lambda_d) \times 60 \text{ hours}] \quad (1)$$

where, λ_n and λ_d are the average photodegradation rate constants per hour of the PAHs. Mitra *et al.* [25] then utilized the PAH isomer ratios to estimate the contribution of BC from different combustion sources (Table 1).

Table 1. PAH isomer ratios corresponding with combustion source of emissions (adapted from [24,25]).

Sources	Isomer ratios		
	b[a]a/chry	b[b]f/b[k]f	b[a]p/b[e]p
Automobiles	0.53	1.26	0.88
Smelters	0.6	2.69	0.81
Wood	0.79	0.92	1.52
Coal/coke	1.11	3.7	1.48

2.2.3. Particulate matter pollution

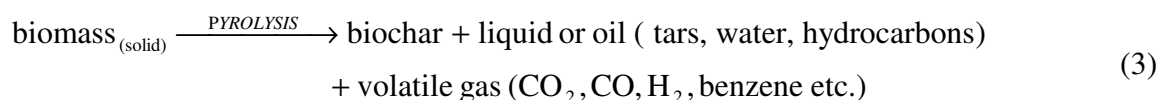
Black carbon has been reported as a better marker of total PM sources than standard mass concentration measurements [26] because of its longer lifetime (40 hours to a month) in aerosol form [27], a dry deposition rate of 0.1 cm s^{-1} for both hydrophobic and hydrophilic forms [28] and the fact that BC is hydrophobic and chemically inert ([9,28,29]). In Europe, BC contributes 5–10% to $\text{PM}_{2.5}$ and less to PM_{10} [30]. Such estimates of BC contribution to PM do not currently exist for the USA. Most studies on particulate pollution in the USA have dealt only with PM_{10} and $\text{PM}_{2.5}$, not clearly differentiating between fossil fuel and biomass produced emissions [31,32].

3. Formation Models for BC

Here, we present some models formulated by prior studies to outline the BC formation processes. One such model was initially discussed by Esser *et al.* [33]. They assumed that BC formation in natural environments is proportional to phytomass, respective to the litter pools affected by fires and that all carbon burned by fires goes to the air (cb_{air}), into BC (cb_{BC}) or into litter (cb_{L}) (Equation 2):

$$\text{cb}_{\text{air}} + \text{cb}_{\text{BC}} + \text{cb}_{\text{L}} = 1 \quad (2)$$

The basic formation model of char BC or biochar (which will be described later) through pyrolysis is shown in Equation 3. The proportions of the final products can be changed by adjusting the set temperature and the rate of heating to reach it. Higher biochar yields occur at low heating rates and temperatures lower than 300 °C due to the dominance of the dehydration step of the cellulose, forming anhydrocellulose, its more stable form. Dehydration is the fourth degradation step in pyrolysis, occurring after depolymerization, hydrolysis and oxidation and preceding decarboxylation. At temperatures >300 °C, depolymerization of cellulose occurs, yielding levoglucosan. When the heating rate is faster, shorter time is allowed for the dehydration step, yielding a higher percentage of unstable products that form primary volatiles [34-37]:



Kuhlbusch [38] discussed the BC formation coefficient (K_{bc}) as that part of the charcoal which is produced by vegetation fires and which is biologically not decomposable. This coefficient increases linearly with lower burning efficiency, which depends on factors such as flame or heat temperature, rate of heating or burning and inherent moisture in the biomass. Kuhlbusch and Crutzen [39] plotted BC as the percentage of total C in the burn residue of experimental forest fires against the CO/CO₂ emission ratio, showing that smoldering combustion produced significantly higher BC than the flaming phase. Pyrolyzing biomass at different temperatures, Dermirbas [40] formulated the following equation for the amount of ‘total carbon’ or BC of biochar as a linear function of pyrolysis temperature (T):

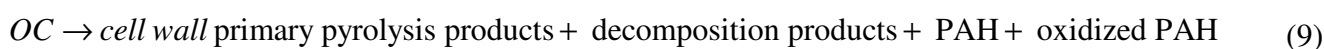
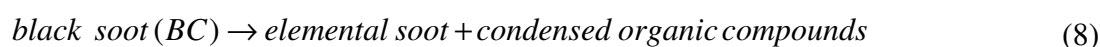
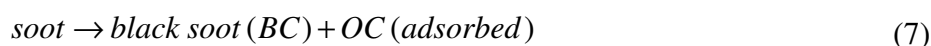
$$\text{total carbon} = 0.041T + 55.21 \quad (4)$$

A very high correlation coefficient (R^2) between T and biochar BC was observed. Dermirbas [40] further proposed this equation for the biochar formation relation with T:

$$\text{biochar} = 0.00005T^2 - 0.105T + 85.08 \quad (5)$$

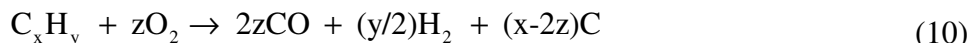
As shown above and as will be discussed later in this paper, all pyrolysis conditions need to be optimized to maximize the yield of BC residue or biochar with respect to initial biomass and for the BC production process to function as part of an energy efficient carbon sequestration mechanism, as discussed in the later section on carbon sequestration.

In atmospheric sciences, the soot BC formation process from biomass is described as comprising elemental and condensed organic carbon production steps [20,41-43] (Equations 6–9):

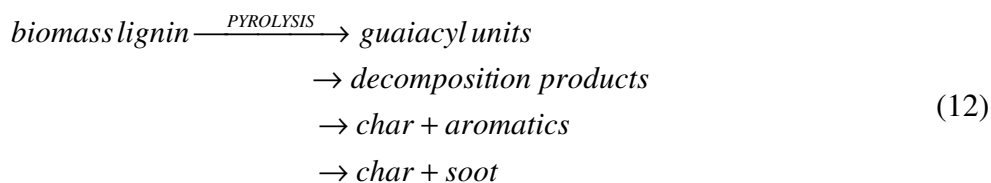
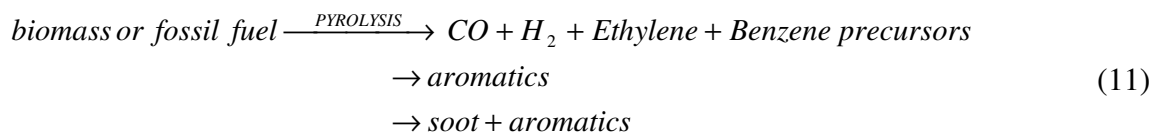


Soot BC formation from high temperature incomplete combustion of carbonaceous fuels such as hydrocarbons (C_xH_y) or fossil fuels can be explained by Equation 10 [44], where the C on the product

side denotes the carbon stock of the yielded soot BC. It is evident from the reaction that higher amounts of oxygen in the process produce higher CO and less soot BC:



Fitzpatrick [20] proposed the following soot formation models for both biomass and fossil fuel sources:



The inherent biomass property affecting the soot yield is the cellulose/lignin ratio (Equations 11 and 12). The soot formation and oxidation of any produced soot is the same for both fossil fuel and biomass in the first reaction steps, with the last step involving soot nucleation forming aggregates which can be as long as 30 nm in diameter [20]. Both types of soot contain oxygen, from oxygen functionality incorporated during soot growth as well as by surface oxidation on reactive sites. The soot precursors themselves comprise small quantities of oxygen, with $C_{25}H_{30}$ as the smallest unit in a seven-ring structure linked to similar structures forming a soot particle [20,45-48].

4. Sorption Properties

Black carbon surfaces are porous with apolar and aromatic surfaces and can contribute 1–10% of the total fraction of organic matter (f_{oc}) in soils and sediments [49]. They have a high surface to volume ratio and a strong affinity to non-polar substances such as polycyclic aromatic hydrocarbons (PAHs), dioxins, furans (PCDD/Fs), PCBs, and PBDEs [50,51]. They show high affinity for pollutants, particularly planar aromatic compounds [14]. After their release, PAHs are sorbed by both soil and sedimentary organic matter and BC in the environment. High molecular weight PAHs have high affinity to BC [52].

Black carbon sorbs organic solutes during mass transport in surface aquatic systems and constitutes approximately 3–38% of total organic carbon mass. Jones *et al.* [53] proposed that biomass soot BC contains oxygen as part of the particle structure and that surface oxygenates make it hydrophilic, aiding in the adsorption of many species.

Oen *et al.* [54] observed a greater correlation of PAHs with BC ($r^2 = 0.85$) than with OC ($r^2 = 0.15$) in four Norwegian Harbor sediments, regardless of their origin, PAH concentration and size fraction of sediments. The sorption of PAHs by BC was more dominant than by OC partitioning. In three U.S. harbors located in California, Wisconsin and New York, Ghosh and co-workers [55] found that PAHs sorbed on semisolid coal tar pitch were more bioavailable than those on carbonaceous particles such as coal, coke, charcoal BC.

Gustafsson *et al.* [56] suggested a model describing the observed distribution coefficient of pyrene, a PAH, as a sum of two isotherms involving the OC fraction and the BC fraction [57]:

$$K_d = f_{oc} K_{oc} + f_{BC} K_{BC} \quad (13)$$

where, K_d is the solid-water distribution coefficient in $L\ kg^{-1}$ solid, f_{oc} is the weight fraction of OC in the solid phase representing the organic matter content, K_{oc} is the normalized distribution coefficient in $L\ kg_{oc}^{-1}$ for the compound of interest, in this case, pyrene.

Accardy-Dey and Gschwend [57] proposed the mixed models below (involving both linear and Freundlich isotherms) for sorption of PAHs as pyrene on BC in Boston Harbor sediments:

$$C_{is} = f_{oc} K_{oc} C_{iw} + f_{BC} K_{BC} C_{iw} \quad (14)$$

where C_{is} is the concentration of sorbed PAH, f_{oc} is the OC content, K_{oc} for pyrene is $10^{4.7}$, f_{BC} is the BC content, K_{BC} for pyrene (coefficient of BC sorption) and C_{iw} is the concentration of PAH in solution. The Freundlich term ($K_{if} C_{iw}$) dominates the above sorption model at low concentrations PAH. The absorption term ($K_{ip} C_{iw}$) dominates when the concentration of PAH is very high ($K_{if} C_{iw} \gg 1$) [14]. The expected sorbed PAH concentrations in the above case, in the absence of BC, is given by:

$$C_{is} = f_{oc} \times K_{oc} \times C_{iw} \quad (15)$$

As shown above, the sorption and hence transport process of PAH is enhanced by BC.

5. Stability of Black Carbon in the Environment

The aromatic structure of BC makes it chemically recalcitrant, while its surface functionality and sorption of other minerals and organic compounds facilitate physical protection. These properties increase its lifetime in the environment by rendering it chemically and thermodynamically stable [19,58]. Masiello and Druffel [21] observed the radiocarbon ages of BC from northeastern Pacific and Southern ocean sediments at 50 cm depth to be 2,400 to 13,900 years before present (BP), respectively. Glaser *et al.* [59] estimated the radiocarbon based mean residence times of biogenic BC to be 1,000–1,500 years. Below, we summarize different findings on the stability and residence time of different forms of BC in soils and sediments.

While conducting isotopic analyses of graphitic BC samples isolated from pre-industrial marine and terrestrial sediments, Dickens *et al.* [60] observed that the BC in oceans was terrestrially derived and almost entirely depleted of radiocarbon, suggesting that it was graphite weathered from rocks, rather than a combustion product. They concluded that the presence of fossil graphitic BC in sediments had led to overestimation of combustion-derived BC in marine sediments and, depending on its susceptibility to oxidation, this recycled carbon may be locked away from the biologically mediated C cycle for many geologic cycles.

Based on proposed BC recalcitrance and production rates [39,61,62] since the Last Glacial Minimum, BC would be expected to comprise 25–125% of the soil and sediment organic carbon pool [21,58,63]. Published values of the proportion of soil C occupied by BC range from 3–7% in South East Asia, less than 35% in Australia and the U.S. to less than 45% in Germany [64,65]. Assuming that the rate of intercontinental BC transport is lower than the rate of production, a

significant amount of BC appears to be undergoing degradation [58]. Soluble products of such degradation have been found to include hydrogen-deficient molecules in dissolved organic matter (DOM) from oceans and rivers [66,67].

Black Carbon Oxidation and Degradation: Review of Past Experiments

The exact nature of BC surfaces may be a critical feature in the determination of their fate and impact in terrestrial systems. The mechanisms of BC degradation are not yet well known. Both biotic and abiotic transformations could strongly influence the surface properties of BC particles [68]. We present past findings related to such surface reactions, or lack of it, in this section.

During origination, soot BC shows a hydrophobic and aromatic nature [8]. Some studies have indicated that BC can be degraded and mineralized by severe oxidative reactions in soils and sediments [63,69]. Earlier, Donnet [70] used kinetics to demonstrate BC oxidation into carbon dioxide and degradation products such as carboxylic aliphatics and phenols, both based on separate oxidation time dependent rate factors.

Exposure to high concentration of natural substances has shown a potential to influence BC's resistance to degradation. Chughtai *et al.* [71] reported that soot could be solubilized in a water solution of 50 ppb of ozone, which creates hydrophilic carboxylic groups on the soot exterior, despite soot's hydrophobic and aromatic nature during formation [8]. Hamer *et al.* [69] observed enhanced mineralization of BC after the addition of exogenous C to laboratory microcosms. Mineralization rates increased by 30% and 100% for wheat and wood char, respectively, demonstrating the linkage between BC and the broader C cycle.

Microbial networks are likely primary drivers in the mineralization of BC [67,72], though their effectiveness may vary widely between ecosystems. Small losses of charcoal were observed from microbial inoculation at 35 °C after 12 days, proving BC refractory nature but indicating that some degree of degradation is possible [73].

Brodowski *et al.* [19] with the use of SEM/EDX, observed that soil BC particles varied in shapes and surface properties due to differences in origin (vegetation fires or coal combustion) and due to partial oxidation of rough surface elements. They observed that oxidized elements at edges of BC structures made them prone to interaction with minerals.

Through spatially resolved C-NEXAFS measurements, Lehmann *et al.* [68] showed clear differences in the extent of oxidation of bulk, and surface regions of BC particles isolated from Brazilian soils of different ages. Carbon K-edge x-ray spectra indicated that though the interiors of BC particles were highly aromatic, these same particles had high concentrations of phenolic and carboxylic functional groups on their surfaces. More recently, Cheng *et al.* [74] observed that compared to newly formed BC incubated for a year, 130 years old BC were significantly oxidized on their surfaces (rather than the entire particle) with increased elemental oxygen, increased carboxylic and phenolic functional groups, disappearance of surface positive charges and evolution of surface negative charges after 12 months of incubation.

Rumpel *et al.* [64] did not observe any BC association with the soil mineral phase in slash and burn agriculture exposed tropical soils of northern Laos. However, they observed that BC influenced the

$\delta^{13}\text{C}$ and the $\delta^{15}\text{N}$ stable isotope ratios in the soils and that it was susceptible to erosion downslopes. Hilscher *et al.* [75] found that two years was enough for the incorporation of charred BC residues into the Ah horizons while also observing that erosion could remove BC from surface soils in steeper lands.

Clearly more information on what controls the persistence *vs.* degradation of different BC forms is needed before its role in the global C-cycle can be fully understood. Chemical and microbial reactions in the environment may accelerate the conversion of solid BC to gaseous carbon dioxide while physical dislocation by wind, air and water can affect its *in situ* quantification. Black carbon recalcitrance and C budgeting studies need to consider these factors by investigating the chemical and microbial properties of the BC substrates and the watershed scale physical processes of the study sites.

6. Black Carbon Extraction, Detection, Analysis

Studies of BC can be associated with diverse environmental aspects ranging from global C flux to fire histories. Different detection and analysis methods are needed to answer questions related to these different environmental events and BC from different combustion continuums. These methods are based on the definition and type of BC that has to be extracted. Here, we summarize some existing BC extraction and analyses methods, followed by cautionary findings related to their use.

The currently most popular chemical-thermal method of soot BC extraction from soils and sediments [56,76] is abbreviated as CTO-375. It involves the thermal oxidation and volatilization of OCs at 375 °C, followed by *in situ* acidification of samples to remove inorganic carbonates, leaving soot BC residues to be analyzed for radiocarbons and other information or to be quantified with carbon elemental analysis. Dichromate oxidation has been employed to separate BC from humin and kerogen in soil and sediments [76-80]. Simpson and Hatcher [81] employed sodium chlorite in a chemical oxidation method to remove lignin and non-BC aromatic compounds from organic matter. Cross-polarization magic angle spinning (CP-MAS) ^{13}C -Nuclear Magnetic Resonance (NMR) spectroscopy is used for BC measurement in the residue. This method isolates charcoal, soot and other inert non-oxidizable forms of carbon. The residue for BC analysis in this method should comprise only graphitic black carbon or highly condensed BC (soot) and graphite with no charcoal and kerogen [60]. The graphitic BC method developed by Dickens *et al.* [60] distinguishes soot in soil and sediments. It involves the selective isolation of only the most condensed BC, generally soot, along with graphite. It destroys charcoal, kerogen (non-BC highly refractory geopolymers), and other non-graphitic BC organic compounds. They used the method of Arnarson and Keil [82] for density fractionation of sediments with sodium polytungstate solutions of 1.6, 2.0 and 2.5 g cm⁻³. Microscopic measurements and assessments of BC particles may also be conducted using transmission and scanning electron microscopy (TEM and SEM) [19] as well as other microscopes. Anderson and Smith [83] impregnated Sierra meadows sediment samples with epoxy resin to study sediment records of past fires. Charcoal particles at each 1 mm depth increments were measured at 100x with a Reichert microscope.

Masiello [8] showed that discrepancies in BC measurements were revealed with different analysis methods in the past. For instance, Simpson and Hatcher [81] observed that relatively BC-free soil samples could create and show BC from thermal oxidative methods, leading to overestimates of refractory carbon and carbon flux studies in the environment. Krull *et al.* [84] showed that different

oxidation and hydrolysis techniques used to isolate soil BC may in fact isolate different BC pools within a given soil. These pools had differing ^{13}C -NMR spectra and ^{14}C abundances. The NMR showed that residues isolated from some soils were actually dominated by aliphatics, not aryl C. Lignin and other aromatic structures exhibit ^{13}C signals overlapping BC signals in the NMR spectra. Wet and thermal oxidation methods of BC extraction assume that during soil BC isolation, natural organics are totally removed with no effects on BC, to avoid challenges posed by the presence such interfering compounds [81].

Soil and sediment BC studies have developed a clear understanding of the fraction of incomplete combustion products they extract and refer to as BC. However, studies on aerosol BC have mostly employed thermo-optical methods that often describe BC ambiguously [85]. This allows for both positive and negative artefacts from sampling and quantification [18,86]. The term BC is often used to describe elemental carbon in atmospheric sciences. Owing to differences in definitions, sampling, extraction and analysis methods, this BC is often dissimilar to forms of BC described and studied in soil science and oceanography.

7. The Significance of BC in the Environment

7.1. The ‘Missing’ Sink of Carbon

Estimates of the global C cycle, including stocks and fluxes, often report a ‘missing carbon sink’. It has been calculated to be more than 1 Gt C year^{-1} with minor variations depending on different studies throughout the years (Tables 2 and 3). This missing sink that has been associated with black carbon. Approximately 20% of this missing carbon is hypothesized to remain as charcoal BC after forest fires. The soot BC yielded during such fires eventually falls back down to earth during precipitation [87].

Table 2. Global carbon stocks and fluxes, incorporating wetland stocks, as reported in the 1990s (based on [93] [$1 \text{ Gt} = 10^{15} \text{ g}$; (–) Inputs; (+) Outputs]).

Carbon Stocks	Gt Carbon
Atmosphere	750
Oceans	38,000
Soils	1,600 (455 in wetlands)
Land Plants	560 (8 in wetlands)
Carbon Fluxes	Gt C yr⁻¹
Inputs	
Fossil Fuels	+5.4
Deforestation and Land Use	+0.9 to +1.6
Plant Respiration	+60
Microbial Respiration	+60
River DOC and DIC Transport	+/-0.8
Outputs	
Photosynthesis	-120
Peatland Accumulation	-0.07
Ocean Sediment Burial	-0.1

Oceanic Equilibrium Processes	Carbonate	−2
Accumulation in Atmosphere		−3.4
Missing Sink		−1.4 to −1.6

Table 3. Global carbon budget and total missing carbon sinks estimated for different periods [adapted from [94,95]. Fossil fuel emissions include those from cement production. Emission of 1 Gt C equals 3.67 Gt CO₂. IPCC [96] uncertainties for land use change emissions exclude interannual variability and are given at 65% interval of confidence.

Carbon fluxes		Gt C yr ⁻¹	
Period	1980s	1990s	2000–2005
Known major sources			
Fossil fuel combustion	+5.4	+6.3	+7.6
Land use change	+1.7	+1.6	+1.5
Total sources of carbon	+7.1	+7.9	+9.1
Known major sinks			
Atmospheric increase	−3.1	−3.2	−4.1
Ocean uptake	−1.9	−2.1	−2.2
Terrestrial uptake	−0.2	−1.4	−1.4
Total sinks of carbon	−5.2	−6.7	−7.7
Residual or missing sink of carbon	−1.9	−1.2	−1.4
Terrestrial carbon stock		Gt C	
Period	1800–1994	1850–2000	
Residual or missing sink of carbon	−135	−116	

Glaser *et al.* [88], through their study of Terra Preta soils, described at the end of this paper, concluded that BC can act as a significant C sink. Black carbon formation and deposition in soils and sediments enhances the accumulation of biomass-produced carbon into a slow cycling carbon pool, permitting its storage and transfer from the faster cycling atmosphere-biosphere system [10,21,25,39,89]. It is thus involved in channelization of carbon away from biomass formation and cycling into a refractory pool, which is poorly mineralizable by microbial communities [90].

Approximately 12 to 24 Tg C is annually produced as BC from fossil fuel [91]. Biomass burning produces 50 to 260 Tg of C year^{−1} as BC (1 Tg = 10¹² g) of which approximately 80% is fire residue [39,62]. Based on experimental burns in the laboratory, Kuhlbusch and Crutzen [39,62] calculated that 1.4% to 1.7% of carbon exposed to fires is converted to BC. Considering this yield, its recalcitrant properties and its long residence time of 2,400 to 13,900 years in soil and sediments [21], BC may reduce net CO₂ emission from permanent deforestation by 2–18% and represent part of the missing carbon [62,92].

The estimated pool of carbon in soils and plants of wetlands is 463 Gigatonnes (Gt) (Table 2). Currently, there is no clear and precise data on BC carbon transfer from wetlands to rivers, oceans, and the atmosphere. The carbon accumulation in peatlands is estimated to be 0.07 Gt per year. Considering the ‘missing carbon sink’ of 1.4 to 1.6 Gt per year, it is reasonable to say that similar to forest ecosystems, some of it may remain stored in wetlands as BC after natural or prescribed fires and after

wet or dry deposition of soot particulates from fossil fuel combustion. Masiello and Druffel [21] observed that BC comprised 12–31% of the sedimentary organic carbon in two deep oceans sites. This BC radiocarbon (^{14}C) age was thousands of years older than concurrently deposited non-BC SOC.

Differences in environmental turnover times of different BC types are significant, and highlight our lack of knowledge concerning BC decomposition including biotic and abiotic process [8]. Despite its refractory nature, BC may have a more dynamic role in the global carbon cycle than previously thought [8]. Masiello *et al.* [22] observed that BC in shelf sediments was affected by oxygen exposure, based on differences between BC and SOC ^{14}C ages with oxidation conditions. They observed that $11 \pm 4\%$ of the sedimentary organic carbon in oxic deposits was BC. In the anoxic sediments, BC comprised $5.2 \pm 1.4\%$ of the total organic carbon. In spite of clear evidence that BC can be a substantial part of the soil carbon pool, and that it may cycle very differently than much less recalcitrant C, there is still a great deal of uncertainty about its measurement and persistence in terrestrial and aquatic environments.

7.2. Sorption of Pollutants

As described earlier, the role of BC in the sorption of pollutants is significant. Two complementary processes bind persistent organic pollutants (POPs) to BC: occlusion inside BC pores during soot formation as well as during surface adsorption during and after soot formation are the [51,97]. Soot BC emitted to the atmosphere is dry and wet deposited to surface waters and land. The char BC deposited and remaining on the land surface in an unincorporated form is carried to surface waters through precipitation runoff and sedimentation. During origination as well such transports, BC particles sorb xenobiotic and naturally occurring organic pollutants in soils and sediments, controlling their fate and bioavailability [49]. Use of a nonsteady state spatially resolved mass balance model of chemical transport modified to include BC showed that BC has a higher influence than aquatic biota on the cycling, distribution, total amount, bioavailability, and recovery times of polybrominated diphenyl ethers (PBDEs) in the Baltic sea [51].

7.3. Health Effects

Health effects of particles depend on their sizes and the substances sorbed on their surfaces. Smaller particles such as soot BC, which can vary in size from ultrafine (less than $0.1\ \mu\text{m}$) to fine (less than $2.5\ \mu\text{m}$) (Figure 2), can be more detrimental to health than larger ones. Following inhalation, particles larger than $4\ \mu\text{m}$ and below $0.002\ \mu\text{m}$ have a higher tendency to deposit in the mouth and throat, while particles between $0.002 \pm 0.2\ \mu\text{m}$ deposit in the alveolar region of the lungs [98,99], (Figure 3).

The size of particles, including soot, from combustion processes vary depending on the temperature and phase of the wood combustion process. Forsberg *et al.* [100] observed an average size of $0.065\ \mu\text{m}$ at the beginning of combustion while the smoldering phase showed average particles sizes of both 0.025 and $0.15\ \mu\text{m}$. Primary C particles or BC from vehicular exhaust were observed to be $0.024 \pm 0.006\ \mu\text{m}$ while those from residential wood smoke were observed to be $0.031 \pm 0.007\ \mu\text{m}$

in diameter [101]. Schauer *et al.* [102] observed that the average fine particle emission rate of fireplace combustion of pine, oak and Eucalyptus wood was respectively 10, 5 and 9 g kg⁻¹ of wood while the elemental carbon contribution to this emission was 3 weight percentage of the fine particulate mass (FPM) for both oak and Eucalyptus and 1.4% FPM for pine wood. The BC contribution can assumed to be close to that of the elemental carbon. Organic carbon contribution was respectively 56%, 59% and 44% of FPM for pine, oak and Eucalyptus wood.

Figure 2. Size distribution of particles emitted from different sources (adapted from Danish Environmental Protection Agency data [105]).

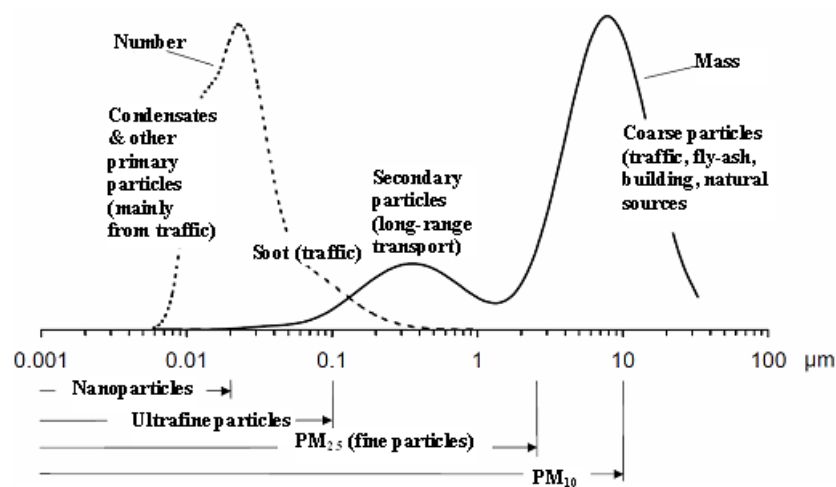
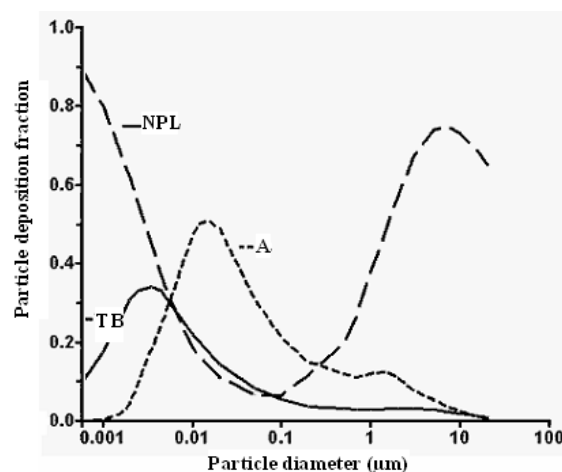


Figure 3. Size based distribution of inhaled particles in the human respiratory tract (A: Alveolar, TB: Tracheobroncheal, NPL: Nasal, Pharyngeal, Laryngeal) (adapted from Forsberg [99]).



Soot BC carries PAHs sorbed to its surface into the lungs. This process is followed by absorption of the PAHs into the bloodstream through the alveolar epithelium. The soot particles themselves can also cause health effects. It may take weeks to years for insoluble particles such as soot to be cleared from the alveolar regions. Mechanisms such as transepithelial passage and phagocytosis by macrophages followed by mucociliary escalation enable such removal. Particles < 0.1 μm can enter the

circulatory system through the alveolar-capillary endothelium. Such ultrafine particles can enter extrapulmonary organs such as the liver. As particle loading increases, their transepithelial transport increases [103,104].

7.4. Climate Impacts

There is an increasing awareness that BC is having a measurable effect on atmospheric and land surface warming, primarily through radiative scattering and absorption in the atmosphere and through changes to system albedo at the land surface. Both of these effects make BC a potent driver of climate change from local to global scales. After CO₂ which exerts a positive radiative forcing of 1.6, BC is the second largest contributor to global warming, causing a net positive radiative forcing (surface warming) of 1 to 1.2 Wm⁻² (± 0.4 Wm⁻²) through the following processes [106-108]: absorption and interception of direct sunlight (negative forcing) contributing to surface dimming and reducing evaporation and rainfall globally; absorption of the solar radiation reflected by the earth and clouds (positive radiative forcing); deposition on sea ice and snow; increasing the absorption of sunlight (positive radiative forcing); and evaporation of low clouds aided by BC caused warming (positive forcing) [109].

The 100-year global warming potential (GWP) of atmospheric BC has been estimated to be 680 [2] and 510 [110] globally while it is estimate to be 374 for BC of European origin and 677 for African BC [111]. It has been called the second greatest greenhouse pollutant as the magnitude of its direct radiative forcing exceeds that due to methane. This, in combination with its short lifetime of a few hours to a few days, could make the control of its emissions from fossil fuel, one of the quickest and the most effective ways of slowing global warming [112].

Aerosol BC particles can scatter short wave radiations from the sun before reaching the earth surface (dimming and cooling effect) and can also absorb long wave radiations emitted from the earth back to the atmosphere (warming effect). The surface dimming due to aerosol BC cannot be directly compared with that of greenhouse gas forcings because it does not necessarily cause a cooling effect and it mostly results from increase in atmospheric solar absorption, which can be factor of 3 or larger than the dimming due to reflection of sunlight (cooling effect) by GHGs [109]. The strength of these effects is related to other atmospheric components as well as the location and concentration of the aerosols within the atmosphere. The amount of absorption is measured by the ratio of scattering to extinction (sum of scattering and absorption), the single scattering albedo[(SSA) = (SSA)], which below a certain critical value, causes the earth-aerosol system to reflect less radiation than the earth alone, leading to net warming [113]. In regions of highly absorbing aerosols, the radiative impact of aerosols at the top of the atmosphere can change from cooling to warming, particularly over highly reflective surfaces such as snow and clouds [114]. Absorption of radiation in the atmosphere occurs mainly by non-organic particulate carbon with optical and physical properties associated with soot BC, at wavelengths less than 4 μ m [114]. Black carbon exhibits a strong spectral dependence inversely proportional to the incident wavelength across the entire wavelength range, compared to other absorbing aerosols such as OC and soil dust, which show major absorption only at 600 nm [115]. The extent to which BC is mixed with primarily scattering aerosol components such as sulfates and reactive organic gases (ROGs) determines the radiative properties of individual aerosol particles [116]. Another factor that should be considered with respect to BC climate forcings is the source of BC. Fossil fuel BC (as primary emissions) has low OC to elemental carbon ratio, producing an overall warming effect

whereas biomass BC has high OC to elemental carbon ratio with the potential of neutralizing the warming effect of the elemental carbon [20,41–43].

Prior observational and simulation studies [117–119] over the Indian Ocean have helped to explain how aerosol BC may be responsible for monsoon rainfall reduction in this region. Interception of sunlight by excess aerosol BCs causes reduction in absorption of solar radiation by the land and sea surface which in turn experience reduced evaporation. Increase in atmospheric stability due to BC caused warming and deceleration of summer monsoonal circulation have also been found to cause Asian summer monsoon rainfall reduction in model simulations.

Solar light and heat absorption by snow and ice is significantly enhanced by soot BC deposited on snow and sea ice [120,121]. This effect, along with that of atmospheric BC, has contributed to the retreat of Arctic Sea ice and increased melting of Himalayan snow and glaciers [122,123]. The retreat of the Himalayan-Hindu Kush (HHK) glaciers has accelerated since the 1970s, corresponding with a large warming trend of about 0.25 °C per decade observed over the HHK regions [124]. Atmospheric warming by aerosol BC and deposition of dark soot over bright snow surfaces may be important contributing factors [109]. Employing satellite and ground base observations for over 5 years, and a climate model, Ramanathan *et al.* [108] showed that the contribution of aerosol BC (from the entire Asian continent) to the warming trend of the atmosphere between 1 to 5 km (corresponding to HHK glaciers location) was as much as that of greenhouse gases. These BC particles raised atmospheric solar heating up to 50% between 1 and 3 km. Aerosol BCs cooled the surface over most of the Asian plains at lower elevations above sea level while warming the overlying atmosphere. The model was simulated with the emission history of soot for the last 70 years and Asian climate data from 1930 to 2005 with and without aerosol BCs [109].

7.5. Sequestration of Carbon and Nutrients in the Pedosphere

Black carbon has a high carbon sequestration potential due to its chemical recalcitrance and long mean decomposition rate, as elaborated upon earlier. Recent examination of this potential has shown that considering soil BC in climate models for high frequency fire affected regions of Australia reduces predicted carbon dioxide emissions estimation by up to 24.4% [125]. The reason is that fires helped in biochar BC production, curtailing emissions that would be expected from degradation of the source biomass. In this section, we discuss biochar as a form of BC that can be employed to sequester carbon at a large scale in regions with high abundance of dead or decaying biomass.

Biochar is the charcoal form of BC, produced through pyrolysis or the low temperature combustion of biomass at less than 600 °C in the absence of oxygen. Biochar is different from charcoal due to its intended use and fate through deliberate incorporation in soils to store plant nutrients and improve soil fertility. In addition to natural production through fires and practices such as slash and char, biochar can be anthropogenically produced from waste biomass in large-scale plants or at a smaller scale such as with the use of cookstoves designed for optimum biochar yield with minimum to no smoke. Terra Preta soils (Portuguese for dark earth), which were created between 450 BC and AD 950 [126] are an example of ancient biochar's strong effects on soil carbon and fertility. These rich soils were formed in the Amazon Basin by an indigenous land management practice of slash and char agriculture that

involved low temperature and reduced oxygen smoldering of slashed biomass to generate more charcoal than ash on soil in pre-Columbian times. After addition and mixing in soil, over time, after oxidation and charging, these charcoal masses were able to sequester large amounts of soil nutrients on their highly porous surface and generated high microbial activity, allowing for continued high soil fertility for centuries. As much as 70% higher BC, nutrients and organic matter than surrounding unamended soils have been observed in them [88,127].

The incorporation of biochar in soil can lead to sustainable carbon sequestration. The biochar formation process takes carbon sequestration from afforestation a step further by concentrating and locking, on average, approximately 50% of the original carbon content of standing and rapidly decomposing dead biomass into a more stable form [128,129]. The rest of the biomass is released during pyrolysis as gas and oil that can be captured for use as an energy source [130], further reducing emissions [128]. Carbon sequestration with biochar points to the possibility of sequestering carbon by biasing biomass pyrolysis practices to yield high proportions of refractory BC char residues from the majority of the initial carbon burnt [131]. Essentially, a small decrease in combustion efficiency may increase the yield of biochar, providing greenhouse gas offsets and carbon sequestration. Another significant benefit is the reduction in emissions of particulates and other emissions which harm human respiratory health. The mechanism by which biochar formation could be enhanced during pyrolysis was explained earlier in this paper (section on formation models of BC).

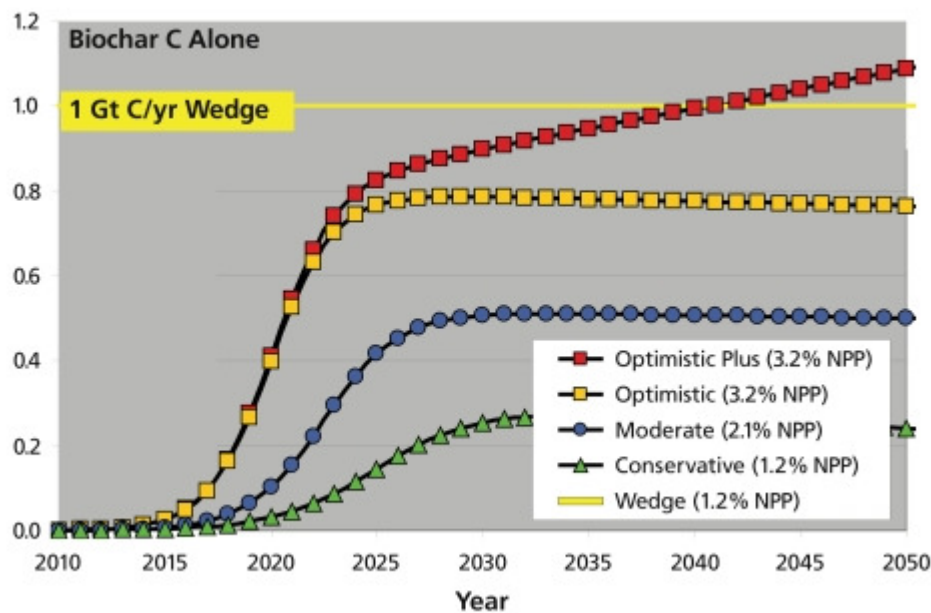
Due to its high surface area, charge density and negative surface charge, biochar BC has very high exchangeable cation sorption and retention capacity [132]. Over time, carboxylic groups formed on the edges of the aromatic part of BC increases biochar's nutrient holding capacity [88]. These properties enable its use for topsoil productivity improvement as well for reducing leaching of pollutants such as dissolved phosphates and nitrates into the groundwater and other water bodies. The pyrolysis temperature has to be above 400 °C for these biochar benefits to be manifested via high pH, cation exchange capacity and surface area [133].

In the US, Lehman [128] calculated biochar BC yield from pyrolysis of forest residues (200 million hectares of timber production forests), fast-growing vegetation (30 million hectares of idle cropland) and crop residues (120 million hectares of harvested cropland). They observed that in each case, 1.6 billion tonnes of carbon could be sequestered in the soil (10% of annual fossil fuel emissions for year 2005), if the biochar is returned to the soil and not burned. Globally, estimates have shown that biochar could be used to potentially reduce atmospheric carbon dioxide concentration by 37 ppm through the sequestration of 400 billion tones of carbon over this century [134]. Assuming that 2.1% of the annual carbon photosynthesized and incorporated into plants would be globally available for production of biochar with 40% carbonization efficiency, the International Biochar Initiative [135] estimated that 0.5 billion metric tons of atmospheric carbon could be sequestered annually (Figure 4).

Using the energy from the pyrolysis process to replace fossil fuel combustion, this rate would increase to 1.2 billion metric tons per year, offsetting 29% of 2009 annual increase rates of carbon dioxide emissions [135,136]. Due to its carbon sequestration properties, the process of biochar production and integration in soils could be a low-risk and efficient climate change mitigation approach [137]. Carbon offsets and carbon emission reduction schemes such as the clean development mechanism could prove valuable for the successful implementation of biochar production projects

around the world. On December 2009, the United Nations Convention of Climate Change and Desertification (UNCCD) determined that biochar would be considered for negotiations as a mitigation strategy for the second Kyoto Protocol commitment period starting in 2013. As interest in this cheap strategy grows, such international consideration is helping to generate more research, testing and evaluation to determine its environmental and commercial value.

Figure 4. Four Scenarios for potential carbon offsets from biochar between years 2010 and 2050 [135].



8. Conclusions

Although combustion of biomass and fossil fuel are the only forms of BC production, its effects vary distinctively depending on its different forms. It can store carbon for the long terms in soils and sediments but it can also cause severe health problems and contribute to global warming. It is an atmospheric pollutant with high global warming potentials. However, it is also an integral part of the global carbon budget and, if properly utilized, can play a crucial role in mitigating climate change impacts. Any mechanism targeted toward reducing soot BC should aim at all combustion activities within humankind's control and at large geographic scales since its climate and pollution effects are far reaching. In this context, it would be appropriate to say that the realization of its global influence on climate is very timely, allowing for increased allocation of scientific and monetary resources for research and programs geared towards the alleviation of problems associated with it. For instance, improved cookstove programs in developing countries are now gaining more attention due to their role in reducing soot BC for climate change mitigation, in addition to their prior function of reducing pulmonary-respiratory diseases and improving biomass burning efficiency. Recent developments in biochar cookstoves research and promotion in developing countries is a good sign too. In addition to significant emissions reduction, they also yield biochar for sequestering carbon and improving soil fertility. Both large and small-scale biochar plants are now being established globally. The availability of dead biomass or feedstock, their environmental impacts and the commercial viability of the plants

will determine their success. Regardless of the scale of such facilities and projects involving biochar production and application in soils, the direct and indirect reduction in C emissions as estimated and targeted, along with stable net carbon gain in the pedosphere should be verified and ensured. If current findings and projections of biochar's carbon sequestration potential are validated, biochar production could prove to be one of the least costly but most convenient climate change mitigation strategies that could be adopted at any location where there is access to waste biomass. Through linkages with carbon offset based financial mechanisms such as the clean development mechanism, many agricultural communities, particularly in developing countries, would also benefit immensely from this.

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