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Black Carbon (Biochar) In Water/Soil Environments: Molecular Structure, Sorption, Stability, and Potential Risk

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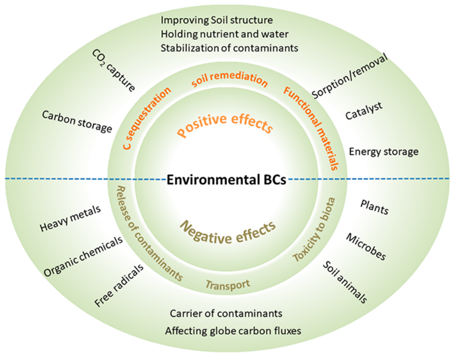
Supporting Information

ABSTRACT: Black carbon (BC) is ubiquitous in the environments and participates in various biogeochemical processes. Both positive and negative effects of BC (especially biochar) on the ecosystem have been identified, which are mainly derived from its diverse physicochemical properties. Nevertheless, few studies systematically examined the linkage between the evolution of BC molecular structure with the resulted BC properties, environmental functions as well as potential risk, which is critical for understanding the BC environmental behavior and utilization as a multifunctional product. Thus, this review highlights the molecular structure evolution of BC during pyrolysis and the impact of BC physicochemical properties on its sorption behavior, stability, and potential risk in terrestrial and aqueous ecosystems. Given the wide application of BC and its important role in biogeochemical processes, future research should focus on the following: (1) establishing methodology to more precisely predict and design BC properties on the basis of pyrolysis and phase transformation of biomass; (2) developing an assessment system to evaluate the long-term effect of BC on stabilization and bioavailability of contaminants, agrochemicals, and nutrient elements in soils; and (3) elucidating the interaction mechanisms of BC with plant roots, microorganisms, and soil components.



1. INTRODUCTION

Environmental black carbon (BC), including carbonaceous residue of combustion (i.e., charcoal and soot, or char) and intentionally made BC (biochar), frequently makes up 1−20% of the total organic carbon in soils and sediments,[1,2] and play an important role in various biogeochemical processes (e.g., nutrient availability, microbial activity, transport and fate of chemicals).[3−6] BC is not a well-defined chemical substance and commonly referred as a combustion continuum from partially charred biomass to highly refractory char, soot, and graphite with striking heterogeneity in physicochemical properties.[7,8] However, several general characteristics of BC can be summarized from a great deal of existing literature:[8−15] (1) the aromatic C content (in the range of ca. 10−90%) in BC is greatly elevated relative to non-BC organic matter in soils; (2) BC is a heterogeneous mixture having both amorphous less-carbonized fraction and microcrystalline graphitic structure, mainly determined by pyrolysis condition; (3) a three-dimensional porous structure with high specific surface area is developed. Because of the specific properties, BC, especially biochar, has attracted widespread attention on its potential benefits in carbon sequestration,[16−18] immobilization of hazardous chemicals,[14,19,20] and soil productivity.[21−23] However, several critical issues before extensive utilization of BC have to be clarified including molecular structure evolution and micropore development with heat treatment temperature (HTT), the relationship between BC physicochemical properties and its function as a soil modifier and/or sorbent, its stability in the terrestrial and aqueous ecosystems, as well as its related environmental risk. These uncertainties directly challenge the development of appropriate BC products for various environmental and agricultural purposes. As a result, commercial exploitation of BC as a soil amendment is not yet fully established.[24]

The occurrence, quantification, characterization of naturally occurred environmental BC have been comprehensively studied in the last decades.[25−27] However, with increasing interest in the application of biochar, there is a growing need to more accurately characterize and classify the material with an aim of optimizing production conditions and better understanding its environmental behavior.[28] While much effort has been paid on the fractionation and characterization of a range of BC continuum,[10,13,29] the existing literature on the development of BC structure and its forming mechanism remains limited. Furthermore, once released into the environment, some critical properties of BC (such as porosity, hydrophobicity, and redox capacity) are likely to be altered by a range of chemical and/or biological processes including oxidization,[30] decomposition,[31] and binding with natural components such as natural organic matter (NOM)[32] and minerals. The variation of BC properties would affect its

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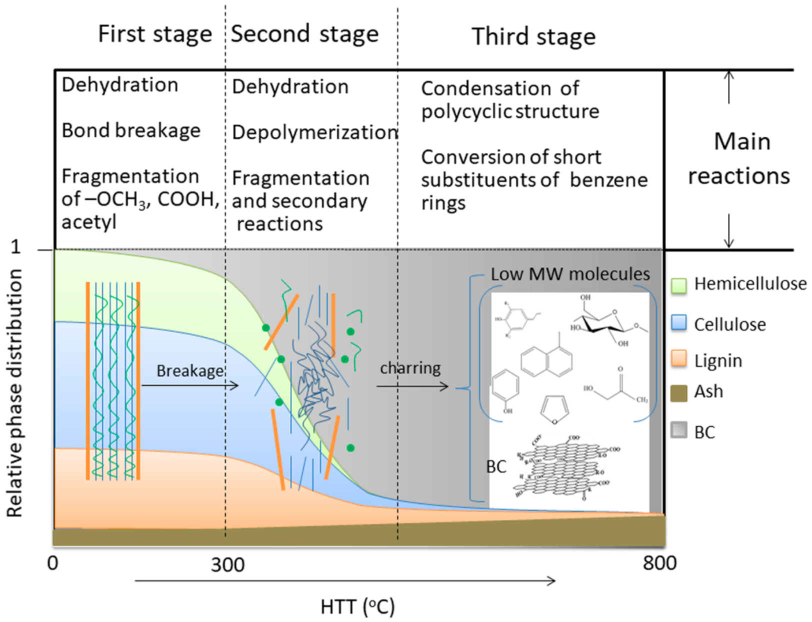

Figure 1. Illustration of biomass pyrolysis process, reactions and evolution of various phases with increasing thermal treatment temperature (HTT). During the process, main components of biomass (hemicellulose, cellulose and lignin) were gradually decomposed and converted into BC phase. Generally, for pure organic materials, the hemicellulose breaks down with a temperature from 220 to 315 °C and that for cellulose and lignin is in the range of 315–400 °C and 160–900 °C, respectively.[72]

stability in the environment, interaction with environmental sorbates, and the fate of nutrient elements and hazardous chemicals. Also, the related environmental risks of BC including release of contaminants,[33] toxicity to biota,[34] as well as affecting global carbon fluxes and transport of contaminants[35] can be important concerns before its large-scale application in environmental and agricultural practices.

Currently, a number of reviews have systematically discussed the physicochemical properties of BC and its agronomic and environmental benefits, specifically including pyrolysis techniques and structure development,[24,36–38] soil fertility,[4,39–42] contaminant removal or stabilization,[6,20,43,44] and carbon sequestration.[45–48] Although some studies noticed the possible environmental risk related to BC applications,[49,50] the evolution of BC molecular structure and its implications on sorption properties, stability, and risk are seldom addressed. This knowledge is of importance for BC utilization in an effective and safe manner, as well as for predicting its environmental behavior. Therefore, the objectives of the present review are to (1) critically analyze the latest progress related to the structural development and characterization of BC, its sorption behavior, stability, and environmental risk; and (2) highlight the important knowledge gaps in the aforementioned aspects and provide suggestions for future research. BC discussed in this review specifically refers to pyrochars. The production, properties and applications of hydrochars were summarized elsewhere.[51]

2. MORPHOLOGY, FRACTIONS, AND MOLECULAR STRUCTURE OF BC

2.1. Biomass Pyrolysis and Thermal Structural Transition of BC. Biomass pyrolysis can be broadly classified into two major categories according to the operating conditions, that is, fast pyrolysis and slow pyrolysis.[52] Fast pyrolysis is characterized by fast heating rate (>200 K/min) and short vapor residence time (∼2 s) at medium temperatures (400–600 °C).[24] This process is more suitable for the production of liquid and/or gaseous products.[53] Slow pyrolysis is characterized by a slow heating rate (5–10 °C/min) with a longer vapor residence time (mins to hours) and a wider temperature range (300–800 °C).[37] This condition is similar to the naturally occurred burning process and more favorable for the production of BC. Different types of reactions vary with increasing HTT (see details in the Supporting Information (SI) Section 1). The overall decomposition of biomass in the slow pyrolysis (or carbonization) is depicted in Figure 1. The formation of BC is a complicated physicochemical process, which is dependent on (1) the pyrolysis mechanisms of the main biomass components, that is, cellulose, hemicellulose, and lignin; (2) the interactions of these biomass components;[54] and (3) the effects of inherent inorganic species such as alkali and alkaline earth metallic elements.[55] It is generally agreed that thermal conversion of biomass and resulting BC characteristics are mainly regulated by the nature of feedstock and heating temperature.[37,56] Although it is difficult to effectively control and tune the properties of resulted BC, some general trends can be obtained from the literature. For the heating temperature, the morphology of BC largely maintains the macrostructure of feedstock during relatively low temperature pyrolysis since low HTT (usually < ∼300 °C) is not sufficient to break down the cross-linkage between carbon atoms in raw materials. With increasing HTT (from 300 to 800 °C), removal of simple molecules such as ethylene and esters from outer surfaces of feedstock could gradually enhance the development of pore structure and surface area of BC. However, a high HTT may also induce deformation and collapse of some fine-pore structure.[57] Besides surface area, the alkalinity and pH of BC can be elevated with increasing HTT, probably due to the decrease of surface oxyl groups and increased crystallization of inherent minerals.[58,59] Cao et al.[60] observed that the minimum aromatic fused ring cluster size increased from 20 to 76 carbons with HTT from 300 to 700 °C determined by NMR. On the other hand, for the nature of feedstock, different compositions of biomass constituents could significantly affect the degradation mechanism and BC properties. In general, the higher the content of lignin in biomass, the higher yields and fixed carbon content of BC.[61,62] Similarly, the high yield of BC is closely related to the high ash content in feedstock (e.g., animal litter and solid sludge), which is little volatilized but enriched during the pyrolysis. However, it is still a big challenge to precisely predict or simulate the pyrolysis mechanism and products of naturally occurring lignocellulosic biomass when compared with "pure" mixtures of lignin and cellulose.[52,63] One of the main reasons is the presence of inherent mineral constituents. Numerous studies found that the mineral elements could substantially influence the carbonization processes and BC properties.[55,64−66] For instance, several key characteristics of BC were observed to have positive correlation with mineral contents, including cation and anion exchange capacity,[67] pH, and alkalinity.[58] Oppositely, the high content of minerals could reduce the carbon content[68] and porosity of BC.[69] Relative to the pyrolysis of cellulose and lignin, the catalytic activity of mineral contents in biomass is less understood. An urgent need is to examine how and to what extent the minerals would affect the formation of BC, such as the transformation of aliphatic carbon into aromatic carbon, the size of aromatic clusters and degree of graphitization, and the species and distribution of mineral elements in BC. Additionally, it is found that free radicals can be generated and stabilized during the pyrolysis of biomass, which could have profound effects on the ecological functions of BC in the environment such as plant growth[70] and organic contaminant degradation.[71] Thus, special attention should be given to the effect of biomass composition and charring conditions on the formation, reactivity, and characteristics of BC's free radicals.

Based on the pyrolysis reactions of biomass, the charred materials can be considered as polycondensed aromatic systems wherein the degree of condensation may differ according to the pyrolytic conditions.[73] Keiluweit et al.[10] suggested that biomass-derived BC can be divided into four distinct categories (i.e., transition, amorphous, composite, and turbostratic chars) based on their chemical phases and physical states as HTT increased from 100 to 700 °C (see section 2 in the SI). It can be concluded from this thermal transition process that the highly amorphous carbon materials in biopolymers is gradually converted into increasingly condensed forms of carbon. Considering the importance of structural changes of BC, a number of parameters have been used to quantitatively characterize the phase transitions in BC (see Section 3 in the SI). In this review, the variations of aromaticity/aliphaticity and BET-surface area (N_2-S_{BET}) of BC as a function of HTT in a large data set is presented in Figure 2(a). Aromaticity increases greatly with HTT from 200 °C to ~700 °C and then reaches a plateau and stays constant with higher HTT. Conversely, aliphaticity decreases sharply with increasing HTT and cannot be detected when HTT is higher than 700 °C. Thus, the majority of variation in molecular structure of BC is completed under 700 °C. Then, more condensed aromatic forms of carbon can be further created with higher HTT because the highest value of aromatic condensation was found to occur at 1000 °C.[28] Notably, both aromaticity and N_2-S_{BET} share a similar increasing trend as a function of HTT, demonstrating that the development of porosity is mainly contributed by the aromatic moieties of BC. Particularly, we find that the N_2-S_{BET} increased sharply as the aromaticity of BC is higher than ~80%.

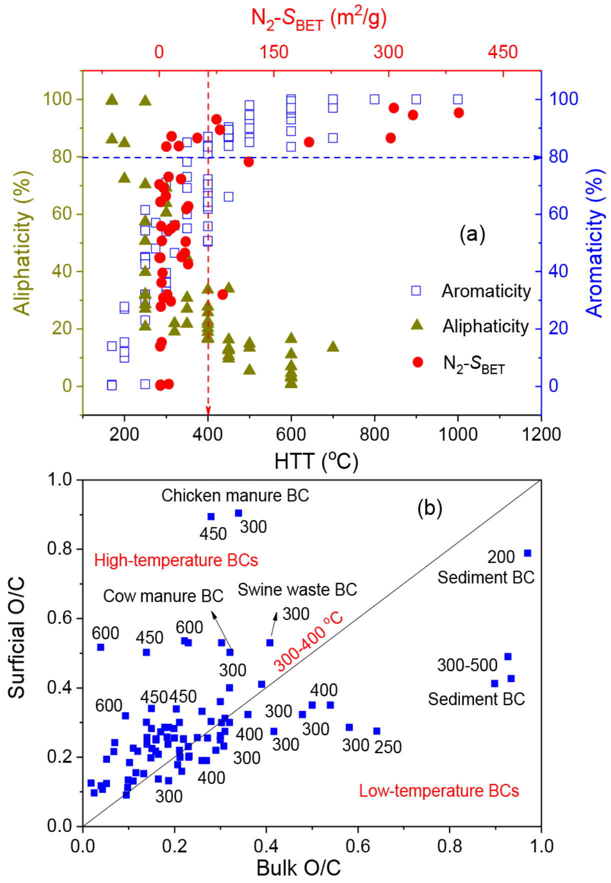

Figure 2. Evolution of structure and composition of BC with heat treatment temperature (HTT). (a) Relationship of aromaticity, aliphaticity, or BET-surface area (N_2-S_{BET}) with HTT. Aromaticity (%) or aliphaticity (%) was calculated from ^{13}C NMR data by expressing aromatic C (100−165 ppm) or aliphatic C (0−109 ppm) as a percentage of both aliphatic C and aromatic C (0−165 ppm). Data were collected from refs 28,82−87. (b) Van Krevelen plot of bulk vs surficial O/C atomic ratios for BC derived from various feedstock types. The numbers close to the data points in the figure are the charring temperatures of BC. Data were either from our own unpublished data or cited from refs 57,68,85,88−90.

Meanwhile, the 80% aromaticity for most BC can be obtained when the HTT increases beyond 400 °C. Thus, the temperature of ~400 °C might be viewed as a boundary between low-temperature BC and high-temperature BC derived from plant-biomass. For the low-temperature BC (HTT < 400 °C), the development of porosity remains at a very low level, which is mainly attributed to the release and/or decomposition of volatile organic fractions from carbon skeleton.[37,74] At this stage, the porous structure is largely dominated by meso- and macro-pores.[59,75,76]

For the high-temperature BC (HTT > 400 °C), however, its surface area and pore volume increase dramatically with increasing HTT, which is mainly derived from the phase conversion of amorphous C (both aromatic and aliphatic forms) to graphitic crystallites. The graphene sheets are denser than the original amorphous C forms, thus the phase conversion leads to the formation of fine pore structures, especially micropores (d < 2 nm).[10] However, the enhancement of porosity and surface area of BC is not always positively related to the increase of HTT. Zhang et al.[75] found that the N_2-S_{BET} of rice straw BC significantly increased from 15.4 to

195.3 m^2/g with the HTT from 500 to 700 °C, but then decreased to 106.2 m^2/g when the HTT further increased to 900 °C. Similar results were obtained by others.[77,78] Several suggestions were used to explain the reduction of N_2-S_{BET} at higher HTT, including structural ordering, pore widening and/or the coalescence of neighboring nanopores,[78] thermal deactivation,[79] and pore blocking due to carbon melting. Additionally, the presence of minerals could also affect the development of porosity. However, considering the close relationship between aromaticity and N_2-S_{BET} of BC (Figure 2a), it is reasonable to believe that the biomass components (mainly lignin) of feedstock play a more important role in the evolution of porosity than mineral elements especially for plant biomass. This is probably due to the weak autocatalytic efficiency of the inherent minerals[37] or the low mineral content in the plant feedstock. By contrast, for the raw materials with high mineral contents such as animal waste (ca. 24−79%) and sewage sludge (ca. 37−90%),[80] the effect of inorganic constituents (especially alkali and alkaline earth metals) on the pore structure of BC cannot be overlooked. A number of studies examined the structural properties of BC derived from a wide range of plant-, animal (or municipal) waste-sources, however, their results are not always consistent. For example, although the BC was prepared in similar manners including feedstock and HTT (200−650 °C), Sun et al.[68] found that the N_2-S_{BET} (0.8−285 m^2/g) of BC negatively correlated with the ash contents; while Zhao et al.[76] observed that the municipal waste BC had higher N_2-S_{BET} (13.3−113 m^2/g) and pore volume than plant based BC (2.78−203 m^2/g) due to the higher content of minerals in municipal waste. Thus, the effect of inorganic constituents seems complicated and sensitive to charring condition and other biomass constituents. Moreover, it has been demonstrated that BC is redox-active because of its quinone and aromatic structures.[81] In principle, the pool of redox-active moieties in BC could be composed of both organic and inorganic components. However, the impact of inorganic constituents (e.g., metal oxides) on BC redox properties is less understood relative to organic constituents. The growing evidence for the importance of inorganic constituents in BC formation and characteristics makes it necessary to systematically examine the unique role of minerals in the structural evolution and electron-chemical properties of BC (e.g., redox properties and electron transferring/storage capacities).

2.2. Elemental Composition and Surface Chemical Properties of BC. Elemental composition of BC is mainly composed of C, H, O, N, and mineral elements.[62] Relative elemental contents of BC during the pyrolysis often witness a progressive decrease in molar ratios of both H/C and O/C with increasing HTT due to dehydration reactions.[28] Relative to bulk elemental content, the variation of surficial elemental composition of BC exhibits a more direct effect on its properties and interaction with surrounding environments. However, the spatial distribution of elements including C and O has not been extensively summarized in the literature. Thus, a Van Krevelen diagram (Figure 2b) was used to compare the difference in O/C atomic ratios between bulk and surficial elemental compositions of various BC. For plant-derived BC, low-temperature samples generally have higher bulk O/C atomic ratios relative to surficial O/C ratios; however, the opposite trend is found for high-temperature BC. This indicates that more O atoms tend to redistribute from interior to BC surface at higher temperature, which has important implications for BC's reactivity. From the collected data (Figure 2b), we suggest that the range of 300−400 °C can be considered as the temperature boundary above which the surficial O/C ratios generally increase beyond the bulk ratios for the plant-derived BC. Note that the surficial O content of BC produced above 700 °C would be greatly reduced owing to thermolysis of oxyl groups.[91] For BC derived from sediment or manure, by contrast, they exhibit higher O/C atomic ratios both in the surface and bulk than that derived from plants, which is closely related to its higher content of minerals. The interaction of organic matter with minerals during BC formation is discussed elsewhere.[77] Compared with sediment BC, manure BC has much higher surficial O/C ratio than that of the bulk even at relatively low temperatures (i.e., 300 °C), likely indicating their distinct environmental applications. The high bulk O/C ratio in the sediment BC can be partly ascribed to the lower organic carbon content (e.g., 22%) in the sediment.[77] Also, particle size of BC could also play a crucial role in the distribution of oxyl groups. Qiu et al.[90] reported that the surficial O/C ratio of dissolved rice-straw BC was up to 4.38, which is 10 times higher than that of bulk BC. Consistently, we recently fractionated BC particles (produced at 300−600 °C) with different sizes i.e., 0−0.1, 1−5, 5−50, and 50−250 μm and found that the nanoparticles had significantly higher surficial O/C ratio than that of the larger-sized particles.

Although surface functional groups play a crucial role in the properties and environmental applications of BC, the quantification of oxyl groups on BC surface is still not well understood.[92] Most of studies measured the O-containing groups of BC by a typical method, that is, Boehm titration.[93,94] Different from activated carbon, however, BC contains inorganic basic components including carbonates, oxides, and hydroxides, inorganic acidic species (such as silica and alumina) and organic acids.[58] These components can interfere with the validity of the titration.[95] Some efforts have been made to improve the accuracy of Boehm titration, such as pretreatments[95] or using various reactants and titration procedures.[96] However, little is still known on the respective contribution of ash and dissolved organic carbon to the functional content of BC surfaces. The characterization of functional groups on entire BC surfaces would be more valid by combining chemical (like acid−base titration) and spectroscopic techniques. For example, Chen et al.[92] identified four major acid/base groups with a wide range of pK_a values on manure-derived BC surface using an integrated method. Relative to O-containing groups, the nitrogen composition and species in BC are much less examined under differing pyrolysis conditions. Generally, the nitrogen in the forms of protein, amine, pyrrolic, and pyridine is less heat resistant and likely to convert into heterocyclic-N with increasing HTT (e.g., 300−550 °C).[97] The N-doped BCs could be important functional materials and have improved performances in sorption, catalysis, and capacitors relative to original BCs. We recently examined the nature of C−N bonds on the surface of N-doped BC.[98] It was found that pyridine- and pyrrolic-like N was the main components (>50 atom %) as pyrolysis temperature was below 600 °C. When the temperature further increased, graphitic-N was formed and increased at the expense of pyridine- and pyrrolic-like N. Besides N, the speciation and transformation of other heteroelements (e.g., S, P, Si) in BC with increasing HTT as well as their effects on BC properties and functions also need to be further understood in the future.[99,100]

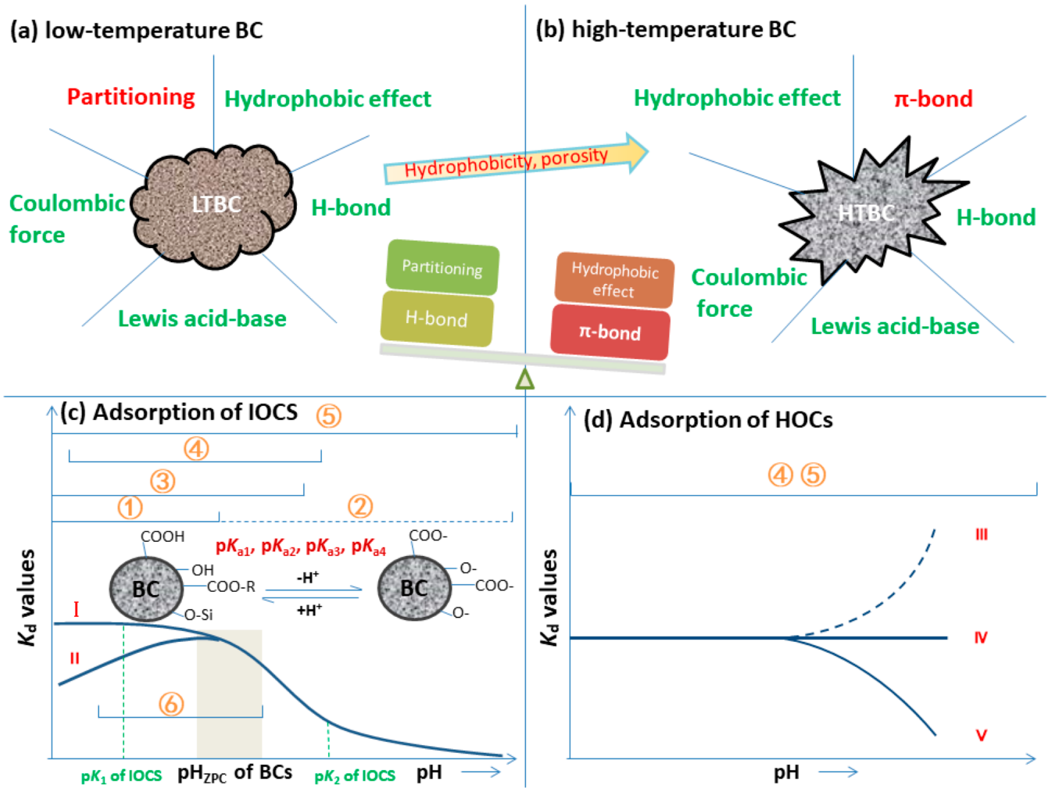

Figure 3. Proposed interactions of (a) low-temperature BC (LTBC) and (b) high-temperature BC (HTBC) with organic compounds. (c) pH-dependent sorption trends (I and II) of ionizable organic compounds (IOCs) on BC, where ①-⑥ represent positive charge repulsion, negative charge repulsion, H-bond, hydrophobic effect, π-bond, and Lewis acid−base interactions, respectively. The contributions of these interactions are highly pH-dependent. The gray area on X-axis indicates the ranges of pH_{ZPC} of various BC reported in the literature. The green dot lines represent $pK_{1,\,2}$ values of a model IOC (e.g., sulfamethoxazole). (d) Sorption trends (III, IV and V) of nonionic HOCs on BC, where only ④ and ⑤ (i.e., hydrophobic effect and π-bond) play a major role.

3. INTERACTIONS OF BC WITH ORGANIC COMPOUNDS AND HEAVY METALS

3.1. Interactions of BC with Organic Compounds.

Sorption is a critical process for environmental and agricultural applications of BC as an amendment. Different from activated carbon, BC is generally obtained at low temperatures and without activation process and thus is not fully carbonized.[74,101] The relative carbonized (for adsorption) and noncarbonized (for partition) fractions determine its sorption behavior for organics.[74,102] Adsorption is characterized by nonlinear isotherms and competition between coexisting adsorbates; whereas partition is a linear and noncompetitive process. Figure 3 and SI Table S1 summarize the current knowledge regarding the molecular interactions of organic compounds with low- and high-temperature BC (a,b) and pH-dependent sorption trends of both ionizable organic compounds (IOCs) and hydrophobic organic compounds (HOCs) on BC (c,d). It is accepted that the sorption of HOCs on BC can be viewed as a transition from a partition dominant to an adsorption dominant process with increasing HTT as a result of increased hydrophobicity and porosity of BC.[57,74] During the process, the contributions of partitioning and H-bond to overall sorption gradually decrease; whereas those of hydrophobic effect and π-bond increase correspondingly owing to the thermal structural transition of BC as mentioned above. Also, Coulombic force and Lewis acid−base interactions can contribute to the organic sorption of BC, which are dependent on charge density and nature of functional groups on BC.[98]

For sorption of IOCs, two pH-dependent sorption trends were reported in previous studies. For trend (I), the sorption changes slightly in the range of $pH < pH_{ZPC}$ (zero point of charge) of BC, and then decreases greatly when the aqueous pH increases above the pH_{ZPC} of BC; and for trend (II), the sorption of IOCs increases with increasing pH and then decreases similar to trend (I) in the range of $pH > pH_{ZPC}$ of BC. The discrepancy between the two sorption trends is mainly derived from the different contributions of electrostatic repulsion and sorption contributors (such as H-bond, hydrophobic effect, π-bond, and Lewis acid−base interactions). The pH_{ZPC} of BC is generally higher than 4.0,[88,103,104] and its dissociation constants (pK_a) cover a wide range of pH values (2−11) due to the various acid/base groups.[92] BC is positively charged at $pH < pH_{ZPC}$ and negatively charged at $pH > pH_{ZPC}$.[88] The sorption would probably follow the trend (II) if electrostatic repulsion between positively charged BC and protonated species of IOCs plays a major role. Otherwise, if the sorption contributors (H-bond, hydrophobic effect, π-bond, and Lewis acid−base interactions) can offset the positive charge repulsion, the sorption would follow the trend (I). For example, the cationic species of sulfamethoxazole has similar sorption to BC relative to the neutral species even though it is much less hydrophobic than the latter.[104] That is because the protonated species is a stronger π-electron-acceptor than the neutral species due to the electron-withdrawing ability of positively charged amino group (referred to as π^+-π bonding). Additionally, for IOCs with amine groups (e.g., tylosin), Lewis acid−base interactions between IOCs (as Lewis base) and oxyl groups (as Lewis acid) on BC may also contribute to their sorption within the range of $pH < pH_{ZPC}$.[105] In alkaline conditions, a special H-bond, i.e., negative charge-assisted H-bond, was recently identified to greatly contribute to the sorption of anionic IOCs on BC, particularly when the values between pK_a of IOCs and pH_{ZPC} of BC are similar.[88,103]

For sorption of HOCs, different sorption trends (III, IV, and V) with pH were observed in the literature. For nonpolar HOCs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated benzenes, their sorption to BC is independent of solution pH (i.e., trend IV) because the changes in charge density of sorbate/sorbent with pH have little effect on their interactions. However, for nitroaromatic compounds, several studies found that their sorption on carbon surfaces greatly increased when pH changed from 2 to 11 (trend III).[57,106] We also noted that 1,3-dinitrobenzene had stronger competition for the sorption of 1,3-dichlorbenzene on BC at pH 12 relative to pH 2.[57] This probably can be explained by the fact that deprotonation of acidic groups (−COOH, −OH) of BC was facilitated by increased pH and thus enhanced $\pi-\pi$ interactions between nitroaromatics (π-electron acceptors) and BC because −COO− is a stronger electron donor than − COOH. We can conclude that, for these nonionic HOCs, only hydrophobic and/or $\pi-\pi$ interactions play the major role in their sorption to BC. By contrast, some HOCs such as aniline and phenolic chemicals can also be ionizable to an extent and thus involve specific interactions with BC. Due to hydrophobic nature of ionizable HOCs (judged by their K_{ow}), however, hydrophobic effect generally plays a more dominant role in their sorption relative to the hydrophilic IOCs with multiple pK_a values (e.g., antibiotics). The lower sorption of dissociated species of ionizable HOCs (trend V) is mainly due to decreased hydrophobic effect, electronic repulsion, and/or the disappearing of H-bonding donor ability.[107] A potential increased sorption (trend III) with pH has not been reported for ionizable HOCs but may be possible on BC according to the electron donor−acceptor (EDA) theory. The electron-donating ability of π/n-electron donors such as carboxyl and amino groups would increase with increasing pH because their dissociated species are even stronger electron-donors. Hence, the strength of both $\pi-\pi$ and n-π EDA interactions with electron-depleted sites on BC (electron acceptor) could be enhanced when these groups are ionized at higher pH as the increased sorption has been observed for chemicals such as 2-naphthol and 1-naphthylamine with carbon nanotubes.[108] Overall, the organic sorption on BC is greatly dependent on the balance between sorption contributors and resisters. More accurate quantification of their respective contributions to the overall sorption would be greatly benefited from a comprehensive characterization of both BC and organic sorbates at various environmental conditions, and the development of modeling techniques such as molecular dynamics simulations.[109,110] This information is important for designing functional BC sorbent and evaluating the effect of BC on the environmental behavior of contaminants.

3.2. Interactions of BC with Heavy Metals. Different from organics, the sorption of heavy metals on BC is mainly driven by electrostatic interactions and sorption-precipitation between functional groups of BC and heavy metals.[111] Thus, the sorption affinity and capacity of heavy metals are more dependent on surface chemistry of BC than the surface area and pore volume. Generally, heavy metals can be sorbed on the oppositely charged sites on BC through electrostatic attraction. The retained heavy metals are considered to be fully hydrated and present in the diffuse double layer as electrostatic outer-sphere complexes.[112] Therefore, the sorbed heavy metals are easily replaced and have relatively high leachability. In addition, four molecular interactions can also be involved based on the current references (SI Table S2): (1) ion-exchange, (2) metal−ligand complexation, (3) cation-π bonding, and (4) surface (co)precipitation.[113−117] Ion-exchange is one of the most observed mechanisms for heavy metal sorption on BC. The negatively charged sites occupied by cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) are probably the main locations for ion-exchange of heavy metals on BC. For metal−ligand complexation, the sorbed heavy metals could be partially dehydrated and coordinately complexed with oxyl groups on BC to form inner-sphere and/or outer-sphere complexes, which is unfavorable for the exchange with other metal ions in solutions.[118] Cation-π bonding likely occurs between metal cations (electron acceptors) and delocalized π-electrons (C═C, C═O) (electron donors) in the surface of BC.[114] For example, the sorption of Cd^{2+} on low-carbonized BC was mainly derived from Cd^{2+}-π bonding with soft ligands such as C═O; while that on high-carbonized BC most probably involved Cd^{2+} bonding with electron rich domains on graphene-like structures.[114] Conversely, the graphite surface of BC could also act as an electron acceptor for anions (e.g., F^-, Cl^-, and Br^-).[119] However, anion-π bonding has not been reported for the sorption of anionic metals on BC in the literature. Additionally, sorption of heavy metals can also be attributed to their precipitation mainly as phosphate, carbonate or hydroxide on the surface of BC,[62,113,120,121] which could greatly enhance sorption capacity of heavy metals on BC.

Although sorption efficiency and mechanisms of heavy metals on various BC are extensively examined,[93,94] the intrinsic relationship between BC structure and sorption is still not well understood due to the diversity of BC surface.[114] For example, it was found that ion-exchange was the predominant mechanism for the sorption of Cd and Pb on BC (produced at 600 °C) derived from five waste agro-materials (nut shells, plum stones, wheat straws, grape stalk, and grape husks).[122] Conversely, Zhang et al.[123] attributed Cd sorption on water hyacinth BC (produced at 450 °C) mainly to ion-exchange and surface complexation. Wang et al.[124] found that complexation, Pb^{2+}-π interaction and precipitation jointly contributed to Pb sorption on BC prepared from ten materials at 300−600 °C. For relatively high temperature BC (>500 °C), Pb sorption via complexation was reduced, but the contribution of Pb^{2+}-π interaction was enhanced. Despite significant differences in physicochemical properties of BC, some useful information can be obtained from these previous studies: (1) ion-exchange with exchangeable metal ions on BC is one of the most important sorption mechanisms of heavy metals on low-temperature BC. However, with increasing HTT, the sorption by ion-exchange becomes increasingly overwhelmed by other controlling factors such as coordination by π electrons (C═C) of carbon and precipitation[125] due to the reduction of surface functional groups and formation of graphitic structures; (2) the mineral composition and structure of BC also play a crucial role in the sorption of heavy metals by providing additional active sites. Meanwhile, the alkalinity of BC induced by minerals could promote removal of heavy metals through precipitation; and (3) the interaction between heavy metals and BC is dependent on thermally induced characteristics of BC including pyrolysis of volatile matter, changes of fused carbon rings (e.g., degree of functionalization, sheet stacking, and size), and the reaction between carbon and heteroelements because it could alter the quadrupole moments and polarizability of carbon surfaces.[126] Furthermore, the sorption mechanisms could be distinct at different reaction conditions (primarily pH and coexisting ions). Therefore, for the complex reaction system, statistical methods such as multivariate chemometric technique[122] and meta-analysis may be useful to screening the main mechanism(s) and their respective contributions, and/or establishing the ideal conditions for heavy metal removal.

4. STABILITY OF BC IN THE ENVIRONMENT

4.1. Physical Degradation of BC. Once introduced into soils, BC is likely to experience physical disintegration into smaller fragments including colloids, nanoparticles,[127] and dissolved BC[90] due to weathering and aging, which could have significant implications for environmental behavior of BC. The possible mechanisms for BC physical degradation suggested by Spokas et al.[128] include: (1) rapid dissolution of high O/C ratio BC upon being exposed to desiccation and rewetting/saturation cycles; and (2) expansion of BC physical structure from sorption of water molecules due to exothermic graphitic sheet swelling. The respective fraction of colloidal and dissolved BC varies greatly for different BC, which may depend on starting raw materials,[90] HTT,[129] climate and soil conditions.[130] It was revealed that the colloidal and/or dissolved BC had unique properties such as higher phototransformation/degradation rate,[131] more oxygen functional groups and mineral matters but lower aromaticity,[90,129] and producing more reactive oxygen species.[132] The mobility in dissolved and colloidal phases was suggested to be an important pathway of BC for downward migration in soils and aquifers.[130] Thus, it is conceivable that these smaller size fractions of BC would have distinct environmental behavior and recalcitrance relative to bulk BC. However, compared with chemical and microbial degradation of BC, its physical friability in soils has not aroused sufficient research interests at present despite its importance for BC's stability.[128] The kinetics and intrinsic mechanisms for physical disintegration of BC in soils are largely unknown; meanwhile, the effect of interaction between soil components (e.g., NOM and minerals) with BC particles on this physical process also requires further scrutiny.

4.2. Chemical Decomposition of BC. It has been suggested that abiotic processes including carbonate dissolution[133] and chemical oxidation[30] significantly contribute to the decomposition of BC. Carbonate dissolution is one of the primary patterns for inorganic carbon release from BC. Comparatively, chemical oxidation may be a more important mechanism directly regulating BC decomposition. Oxidative process can increase the contents of oxygen and hydrogen on BC surface, promote the formation of O-containing groups (e.g., −OH, −COOH, and C=O), and alter the amphoteric properties,[45,134] all of which could facilitate the decomposition of BC. Furthermore, oxidation can also benefit for microbial metabolization of highly aromatic BC, such as by decreasing hydrophobicity of BC and promoting BC to split into smaller pieces which is favorable for microbial accessibility.[135] The chemical stability of BC is mainly determined by the molecular structure of BC and environmental conditions.[45] It is believed that the biochemical recalcitrance of BC is closely related with its aromaticity and condensation degree of aromatic carbon,[28,31,136] as indicated by the atomic ratios of O/C and H/C. Nguyen et al.,[31] reported that carbon loss and potential cation exchange capacity significantly ($p < 0.05$) correlated with O/C ratio of BC. It is suggested that a molar ratio of O/C lower than 0.2 could probably provide at minimum a 1000 year BC half-life in the environment.[47] However, besides atomic ratios, the influences of other BC molecular properties such as the size, configuration, and heteroatoms of polyaromatic rings on its resistance to oxidation are seldom examined. For example, both the configuration of polyaromatic rings and presence of heteroatoms could affect the generation and activity of free radicals on carbon surface,[137−139] which would have a great implication to the decomposition of BC.

It should be noted that the stability of BC is also affected by soil and environmental conditions such as moisture, temperature, pH, and the influence of NOM and minerals.[45,140,141] For moisture, unsaturated and alternating saturated-unsaturated conditions are feasible for BC degradation due to the increased carboxylic and − OH functional groups under these conditions.[142] Similarly, higher incubation temperature (40 or 60 °C) substantially decreased the mean residence time of BC in different soils[140] partly because of the accelerated oxidizing reactions. Comparatively, few study systematically examined the effect of pH on BC stability in soils. A previous study found that the changes of soil pH and electrical conductivity had little effect on BC mineralization in a 60 days experiment;[143] while a recent work suggested that the surface roughness and hydrophilicity of BC increased after incubated in an acidic Planosol for two years.[144] It is reasonable to believe that soil pH could play an important role in BC decomposition for a long period because pH has major control on microbial community, enzyme activity, and biochemical processes. Moreover, the effect of NOM and minerals on BC stability is more complicated because diverse mechanisms are involved in this ternary system. The porous structure of BC makes it a good sorbent for NOM especially the aliphatic molecules with smaller size.[145] The lower sorption for larger aromatic organics is mainly caused by the size exclusion effect.[145] However, the current understanding of the interaction between BC and NOM is still limited. Besides the hydrophobic sorption and size exclusion, some newly reported mechanisms (e.g., negative charge-assisted H-bond and EDA interactions) probably also contribute to the binding of NOM to BC. Thus, more work is required to investigate the details of nanoscale interactions. After sorbed, NOM might enhance the stability of BC by blocking enzymes from accessing the BC surface as well as oxidation and dissolution of BC components.[45] On the other hand, soil minerals can also incorporate with BC surfaces within a short-term (e.g., a few months), and the formed complexes are suggested to increase BC stability.[141,146] Nevertheless, the involved organo-mineral reactions are highly dependent on the types of minerals, surficial functional groups, and inorganic elements of BC, and environmental conditions. For instance, soil minerals can directly attach to the surfaces of chicken manure BC due to its plenty of O-containing groups; while the paper sludge BC prefers to sorb NOM first and then interact with minerals via NOM bridging because of the higher content of Ca and Al on the BC surfaces.[146] Hence, more specific mechanistic investigations are needed to better understand the interactions of BC with mineral phases and predict the BC stability over time.

4.3. Microbial Decomposition of BC. Relative to abiotic decomposition, biologically mediated degradation is likely the dominant pathway for BC decomposition in soils and sediments.[147,148] Increasing studies indicate that BC-derived carbon can be utilized by soil microorganisms evidenced by different methods such as measuring CO_2 efflux,[149] fumigation extraction, and ^{13}C- or ^{14}C-isotopic analysis.[147,150] In many cases, microbial decomposition of BC in soils is roughly composed of two stages, that is, fast-degrading stage and slow-degrading stage. The labile or volatile fractions of BC are rapidly degraded in a short-term, followed by slow degradation of the condensed aromatic ring structures.[148] The labile fractions in BC would represent an energy source for microbial community[136] and enhance the activity of soil microorganisms in the first stage.[151] Consistently, it was observed that addition of BC into soils generally induces a positive priming effect, that is, increasing the mineralization rates of soil organic carbon, in short-term incubations;[152,153] however, BC may induce a negative priming effect on a long-term owing to the sorption of organic matter on BC surfaces and/or into BC-soil microaggregates; that is, physical protection mechanism.[154] Thus, it should be noted that extrapolation from any results of short-term incubation (<2 years)[47] may considerably underestimate the mean residence time of BC in soil because these studies mainly monitor mineralization of labile C components of BC.[136]

The diverse properties and high reactivity of BC could potentially and sometimes differentially affect the microbial biomass growth, community structure, and activity.[155−157] Meanwhile, the responses of microorganisms would in turn influence the decomposition mechanism and kinetics of BC in soils. Both positive and negative effects of BC on soil microbial communities have been reported in the literature. It was found that the ratio of bacteria/fungi increased but that of Gram-negative/Gram-positive bacteria decreased after BC amendment in a forest soil, indicating a shift of microbial communities.[158] Similar results were obtained by Chen et al.[156] and Liao et al.[159] Nevertheless, Quilliam et al.[160] observed that BC in the soil did not provide a significant habitat for soil microbes in a three year incubation experiment. Another 6-year field experiment also suggested that addition of BC just increased the microbial metabolic activity but could not change its community structure.[157] These uncertainties are caused to a great extent by the diversity of BC physicochemical properties including the availability of labile carbon[150] and nutrients,[161] pore volume and surface area,[155] particle size,[162] degree of oxidation,[163] and the generation of free radicals.[70] Furthermore, some recent studies suggest that BC could take part in the electron transfer as an electron shuttle between microorganisms and NOM, minerals, as well as pollutant molecules.[81,164−166] For instance, Xu et al.[165] showed that both BC particles and leachate can facilitate the microbial reduction of hematite through electron shuttling. More efforts are warranted to further explore the bioavailability of electrons in different types of BC, quantification of the reactive components, and the effect of electron shuttling on the microbial transformation and biogeochemical cycles of carbon and other soil elements.

5. ENVIRONMENTAL RISK OF BC

5.1. Release of Contaminants from BC.

Carbonization process of biomass makes it possible to form a wide variety of organic chemicals including volatile organic compounds (VOCs), PAHs, dioxins, and furans (PCDD/DF).[167−169] The concentration and composition of compounds that sorb to BC during pyrolysis are highly dependent on biomass feedstock, HTT, and BC production method (SI Table S3). A number of studies suggested that dioxin-like chemicals are mostly formed on BC surfaces at low HTT (200−400 °C) and short residence time;[169] higher concentrations of solvent-extractable PAHs are largely found in BC produced at medium HTT (400−500 °C);[167] and then the concentrations of dioxins and PAHs in BC decreased at higher HTT (>600 °C) and longer charring duration.[168] However, these studies mainly focus on total concentrations of organic chemicals in BC, and the bioavailable fractions of these compounds originated from BC have received less attention. Recently, Mayer et al.[170] found that most of the BC bound PAHs were desorption-resistant (90−100%) and probably had little bioavailability due to high sorption affinity. They suggested that although high PAH content in the BC, it would act as a sink rather than a source of PAHs. Likewise, it was reported that the strong sorption of BC for agrochemicals like herbicides could reduce their bioavailability and efficiency in soil.[14] On the other hand, most of these sorption−desorption experiments were carried out on freshly prepared BC and took little consideration of aging effect. The variation in properties of BC upon environmental exposure (e.g., oxidation and pore fouling by organic matter) would greatly affect (strengthen or weaken) the interactions between BC and organic chemicals.[171] Thus, more precise characterization of BC structure (e.g., porosity, surface charge, and oxyl groups) and phase transformation is needed to fully understand and predict the relationship of BC properties with the release of its inherent organic chemicals, which is critically important for sustainable application of BC.

Besides organic compounds, BC may also contain some metal contaminants (e.g., Cu, Cd, and Pb), which are mainly originated from heavy metal-containing feedstocks such as sewage sludge[172] and residue of biogas production[173] (SI Table S4). It is suggested that pyrolysis is a promising method to utilize sewage sludge and the obtained BC could significantly reduce the bioavailability and leaching of heavy metals.[113,172] However, a previous study found that the conversion of sewage sludge to BC reduced the content of PAHs but increased that of heavy metals (Pb, Cd, Zn, Cu, Ni, and Cr).[174] Moreover, Stefaniuk et al.[173] observed that the contents of PAHs and certain heavy metals in BC derived from residue of biogas production increased with increasing HTT. We can infer from these results that the release of heavy metals from BC not only depends on heavy metal content in the raw materials but also the transformation, morphology, mineral types, and dissolution of heavy metals in BC under different HTTs, all of which deserve further investigation in the future, especially under different environmentally relevant conditions.

5.2. Negative Impact to Organisms.

Despite the acceptable content of contaminants (e.g., PAHs and heavy metals) for the majority of BC, it may have a negative effect on soil/water biota.[173,174] For example, a significant correlation between the content of PAHs in BC and toxicity was reported for a sensitive organism (*Daphnia magna*).[175] Toxic effects of BC were also observed for other tested organisms including wheat,[176] collembolan,[177] and arthropod.[173] However, it should be noted that not all the negative effects are originated from the inherent contaminants but probably from other characteristics of BC such as the generation of free radicals,[70] high pH and soluble K^+, Na^+.[177,178] On the other hand, although several BC quality guidelines have been proposed including the IBI Biochar Standard, the European Biochar Certificate, and the UK Biochar Quality Mandate (SI Table S5), they only put a limit on the total concentrations of PAHs and heavy metals in

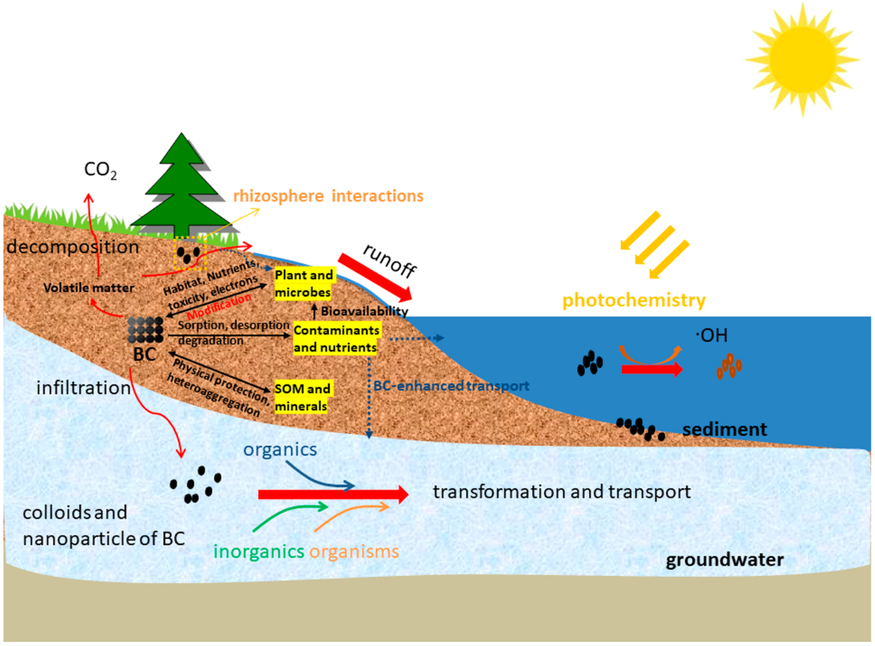

Figure 4. Schematic diagram for transport and fate of BC in soil/water systems. After released into soil, BC generally transports in environmental matrixes via decomposition, runoff, and infiltration. In the interfaces between BC and solid (soil and sediment) as well as aqueous phase, the dominant biogeochemical processes mainly include sorption/desorption, transformation by environmental components and/or UV, and interactions with plant root, microorganism, and SOM/mineral.

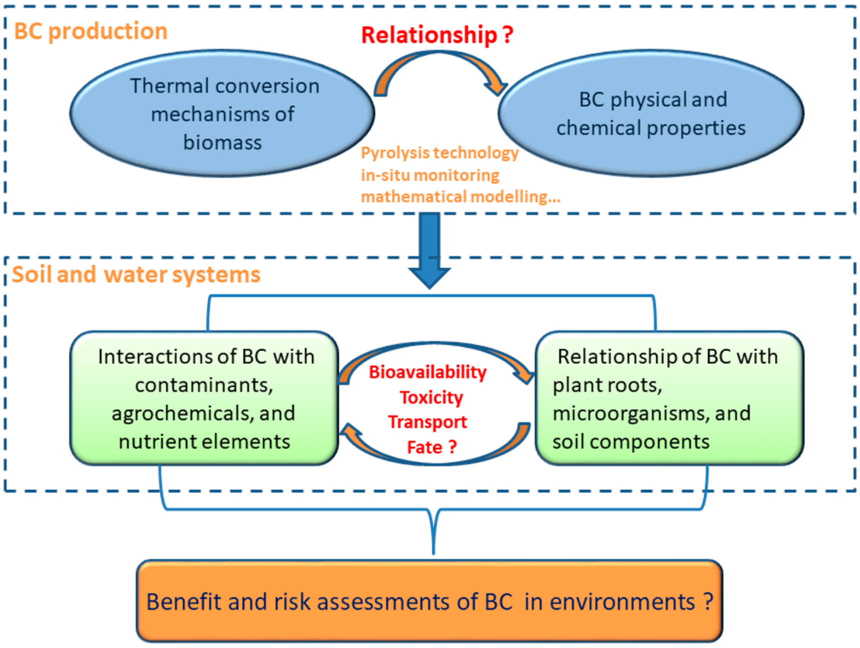

Figure 5. Suggestions for future research priorities of BC.

BC which could not fully reflect the real ecotoxicity of the contaminants. Thus, more efforts are needed to examine the bioavailability of contaminants in BC and closely related issues such as combined toxicity of coexisting contaminants, effect of environmental conditions on exposure of BC contaminants, and precise approach for toxicity assessment.

5.3. Facilitated Transport and Transformation of Contaminants. As mentioned in part 4.1., BC contains a fraction of colloidal and dissolved carbon with distinct environmental behavior relative to that of bulk BC. Figure 4 summarized the transport and fate of BC in the environment. Due to the high mobility in environments, they not only affect the stability of BC but also could be a potential carrier for sorbed contaminants.[127] The colloidal BC exhibits much higher sorption affinity for PAHs and heavy metals than bulk BC because of high S_{BET} and surface activity.[129] However, to our best knowledge, there are few studies on the facilitated transport of contaminants by colloidal BC in the soil/water system. Furthermore, it is expected that the colloidal BC would interact or heteroaggregate with other natural fine particles (e.g., minerals) and NOM during the transport process, which is likely to alter the suspension, chemical composition and/or surface charge properties of colloidal BC and thus the sorption and desorption for contaminants. This knowledge is of importance for better understanding the transport and bioavailability of contaminants in the environment.

Additionally, recent studies revealed that BC is not a merely passive sorbent but a catalytically active material that can promote the degradation and redox reactions of organic compounds and metals.[164,179] It is found that catalytic ability of BC is mainly derived from (1) the graphitic and (semi-) quinone structures which can accept and donate electrons[81,165] and (2) free radicals generated in BC production process which generally have long lifetimes varying from days to months.[70] These properties of BC have significant consequences for biogeochemical transformation and environmental behavior of contaminants in soils. For example, free radical-promoted degradation of *p*-nitrophenol,[179] 2-chlorobipenyl,[71] and diethyl phthalate[180] was observed for various types of BC. These studies highlight that apart from sorption, transformation (degradation and redox) is also an important process regulating the fate of contaminants after BC application. It is expected that both the sorbed NOM and BC-colloid heteroaggregate would affect the composition and redox capacity of BC, and thus alter its binding mechanism with contaminants. However, compared to engineered nanoparticles (e.g., graphene oxide,[181] carbon nanotubes,[182] gold nanoparticles[183]), the heteroaggregation of BC nanoparticles with minerals has not received much attention although they have high stability against self-aggregation and surface activity in aqueous solution. Additional work needs to be done to clarify the mechanism of heteroaggregation and how the attached NOM/minerals affect (shielding or enhancing) the (electro)chemistry of BC surfaces.

6. SUMMARY AND PERSPECTIVES

In this review, the molecular structure, sorption, stability, and environmental risk of BC in soil/water systems are discussed. A majority of studies have demonstrated the great potential of BC in various ecological and agricultural applications. However, negative effects and environmental risk related to soil amendment of BC should not be overlooked. Thus, more effort should be given to a thorough understanding of BC properties and their interactions with environmental matrixes so that we can better predict the effect of BC on soil ecology and biogeochemical processes. Specifically, several critical research needs are generalized in Figure 5.

First, a critical question confronting researchers is how to more precisely relate the characteristics of BC with its starting materials and charring conditions. Thus, the link between thermal conversion of biomass and resulted BC properties needs to be more elucidated. The pyrolysis of biomass is a complicated process which could be distinct among feedstocks due to varying compositions and contents of constituents. It is necessary to combine multiple methods such as in situ monitoring and analysis, advanced pyrolysis technology, and mathematical modeling to more precisely understand the pyrolysis mechanism of biomass and formation of BC, and predict the properties of resulted BC.[184] This would be useful to design BC with preferable physicochemical properties for specific purpose and effectively control the release of inherent contaminants. Meanwhile, it is also very beneficial for the synthesis of BC-based functional materials.

Second, the assessment of BC effect on the stabilization and bioavailability of contaminants, agrochemicals, and nutrient elements in soils should be further conducted. While sorption of BC for a wide range of organic compounds and metal ions is well-studied, the irreversibility and desorption kinetics of sorbed chemicals with different soil conditions and increasing aging time are still poorly understood. It is well accepted that BC has a pronounced effect on reducing the leachability and bioavailability of HOCs in soils due to high sorption affinity. Comparatively, the interactions between BC and ionizable compounds as well as metal ions are variable with BC surface chemistry and solution conditions. Thus, further effort should be focused on examining the aging effect on BC efficacy in stabilization of these chemicals under different soil conditions. On the other hand, the colloidal and dissolved forms of BC can be readily released from bulk BC by infiltration and surface runoff,[185] however, how and to what extent can they affect the transport and fate of contaminants in the environments is still largely unknown.

Third, in order to maximize the potential benefits of BC in soil environments, the interaction mechanisms of BC with plant roots, microorganisms, and soil components (NOM and minerals) warrant further research. It has been observed that chemical and physical properties of soil can be influenced by BC addition, such as pH, water content, and cation exchange capacity.[186] However, soils have strong buffering ability so whether the effects of BC are greatly assimilated in a short-term after addition or it can make a significant change to soil properties is still not clear at present. Similarly, the characteristics of BC can also be altered by surrounding NOM, minerals, and living organisms. For example, pore fouling of BC by humic substances could result in pore blockage and impeded desorption of HOCs.[187,188] Accordingly, can we believe that the actual release of inherent contaminants from BC may be less than expected? Conversely, we recently found that the presence of low molecular weight organic acids is favorable to the release of dissolved organic fractions and probably inherent contaminants from BC by disrupting their linkages with BC surface.[189] This result at least indicates that the effect of BC in rhizosphere may be different from that in bulk soil. Comparatively, the influence of BC on biogeochemical processes in rhizosphere is still poorly known. Overall, the net effect of BC in soils cannot be generalized at present due to lack of sufficient data on the relationships of BC properties with surrounding environments, soil components, and living organisms.

Apart from the above-mentioned aspects, more concrete BC classification based on distinct purposes of use need to be established as soon as possible, which is of very importance for comparison between BC products and more extensive applications of BC. Moreover, the easily modified surface functionality and porosity make BC a promising substrate for the synthesis of various functional materials,[37] which is still in the infant stage and needs more research focus in the future. The last but not the least, long-term benefit and risk assessments of BC application in soils are required for the development and application of environmental friendly and sustainable BC materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b02528.

Types of reactions as a function of HTT; distinct categories of biomass BC; important parameters characterize the phase transitions in BC; possible sorption mechanisms of organic molecules and heavy metals on BC; the concentrations of PAHs, Dioxins/Furans, and heavy metals in BC; the maximum allowed thresholds for BC materials according to different criteria (PDF)

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Notes

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■ REFERENCES

(1) Lehmann, J.; Skjemstad, J.; Sohi, S.; Carter, J.; Barson, M.; Falloon, P.; Coleman, K.; Woodbury, P.; Krull, E. Australian climate-carbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* **2008**, *1* (12), 832−835.

(2) Wu, F.; Xing, B. *Natural Organic Matter and Its Significance in the Environment*; Science Press: Beijing, 2009.

(3) Lehmann, J. A handful of carbon. *Nature* **2007**, *447* (7141), 143−144.

(4) Atkinson, C. J.; Fitzgerald, J. D.; Hipps, N. A. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant Soil* **2010**, *337* (1−2), 1−18.

(5) Sohi, S. P.; Krull, E.; Lopez-Capel, E.; Bol, R. A review of biochar and its use and function in soil. In *Adv. Agron.*, Sparks, D. L., Ed. **2010**; Vol. *105*, pp 47−82; 10.1016/S0065-2113(10)05002-9

(6) Beesley, L.; Moreno-Jiménez, E.; Gomez-Eyles, J. L.; Harris, E.; Robinson, B.; Sizmur, T. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environ. Pollut.* **2011**, *159* (12), 3269−3282.

(7) Seiler, W.; Crutzen, P. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Clim. Change* **1980**, *2* (3), 207−247.

(8) Preston, C. M.; Schmidt, M. W. I. Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* **2006**, *3* (4), 397−420.

(9) Koelmans, A. A.; Jonker, M. T. O.; Cornelissen, G.; Bucheli, T. D.; Van Noort, P. C. M.; Gustafsson, O. Black carbon: The reverse of its dark side. *Chemosphere* **2006**, *63* (3), 365−377.

(10) Keiluweit, M.; Nico, P. S.; Johnson, M. G.; Kleber, M. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* **2010**, *44* (4), 1247−1253.

(11) Fernandes, M. B.; Skjemstad, J. O.; Johnson, B. B.; Wells, J. D.; Brooks, P. Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features. *Chemosphere* **2003**, *51* (8), 785−795.

(12) McBeath, A. V.; Smernik, R. J. Variation in the degree of aromatic condensation of chars. *Org. Geochem.* **2009**, *40* (12), 1161−1168.

(13) Bourke, J.; Manley-Harris, M.; Fushimi, C.; Dowaki, K.; Nunoura, T.; Antal, M. J. Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal. *Ind. Eng. Chem. Res.* **2007**, *46* (18), 5954−5967.

(14) Kookana, R. S. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: A review. *Aust. J. Soil Res.* **2010**, *48* (6−7), 627−637.

(15) Knicker, H.; Hilscher, A.; Gonzalez-Vila, F. J.; Almendros, G. A new conceptual model for the structural properties of char produced during vegetation fires. *Org. Geochem.* **2008**, *39* (8), 935−939.

(16) Tenenbaum, D. J. Biochar: Carbon mitigation from the ground up. *Environ. Health Persp.* **2009**, *117* (2), A70−A73.

(17) Lal, R. Soil carbon sequestration impacts on global climate change and food security. *Science* **2004**, *304* (5677), 1623−1627.

(18) Woolf, D.; Amonette, J. E.; Street-Perrott, F. A.; Lehmann, J.; Joseph, S. Sustainable biochar to mitigate global climate change. *Nat. Commun.* **2010**, *1*. 1DOI: 10.1038/ncomms10533.

(19) Nguyen, T. H.; Cho, H.-H.; Poster, D. L.; Ball, W. P. Evidence for a pore-filling mechanism in the adsorption of aromatic hydrocarbons to a natural wood char. *Environ. Sci. Technol.* **2007**, *41* (4), 1212−1217.

(20) Mohan, D.; Sarswat, A.; Ok, Y. S.; Pittman, C. U., Jr. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent - A critical review. *Bioresour. Technol.* **2014**, *160*, 191−202.

(21) Liang, B.; Lehmann, J.; Solomon, D.; Kinyangi, J.; Grossman, J.; O'Neill, B.; Skjemstad, J. O.; Thies, J.; Luizao, F. J.; Petersen, J.; Neves, E. G. Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.* **2006**, *70* (5), 1719−1730.

(22) Chan, K. Y.; Van, Z. L.; Meszaros, I.; Downie, A.; Joseph, S. Agronomic values of greenwaste biochar as a soil amendment. *Aust. J. Soil Res.* **2007**, *45*, 629−634.

(23) Silber, A.; Levkovitch, I.; Graber, E. R. pH-dependent mineral release and surface properties of cornstraw biochar: Agronomic implications. *Environ. Sci. Technol.* **2010**, *44* (24), 9318−9323.

(24) Manyà, J. J. Pyrolysis for Biochar Purposes: A review to establish current knowledge gaps and research needs. *Environ. Sci. Technol.* **2012**, *46* (15), 7939−7954.

(25) Forbes, M. S.; Raison, R. J.; Skjemstad, J. O. Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Sci. Total Environ.* **2006**, *370* (1), 190−206.

(26) Schmidt, M. W. I.; Noack, A. G. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochem. Cy* **2000**, *14* (3), 777−793.

(27) Cornelissen, G.; Gustafsson, O.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; Van Noort, P. C. M. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **2005**, *39* (18), 6881−6895.

(28) Wiedemeier, D. B.; Abiven, S.; Hockaday, W. C.; Keiluweit, M.; Kleber, M.; Masiello, C. A.; McBeath, A. V.; Nico, P. S.; Pyle, L. A.; Schneider, M. P. W.; Smernik, R. J.; Wiesenberg, G. L. B.; Schmidt, M. W. I. Aromaticity and degree of aromatic condensation of char. *Org. Geochem.* **2015**, *78*, 135−143.

(29) Podgorski, D. C.; Hamdan, R.; McKenna, A. M.; Nyadong, L.; Rodgers, R. P.; Marshall, A. G.; Cooper, W. T. Characterization of pyrogenic black carbon by desorption atmospheric pressure photoionization fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2012**, *84* (3), 1281−1287.

(30) Zimmerman, A. R. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environ. Sci. Technol.* **2010**, *44* (4), 1295−1301.

(31) Nguyen, B. T.; Lehmann, J.; Hockaday, W. C.; Joseph, S.; Masiello, C. A. Temperature sensitivity of black carbon decomposition and oxidation. *Environ. Sci. Technol.* **2010**, *44* (9), 3324−3331.

(32) Pignatello, J. J.; Kwon, S.; Lu, Y. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): Attenuation of surface activity by humic and fulvic Acids. *Environ. Sci. Technol.* **2006**, *40* (24), 7757−7763.

DOI: 10.1021/acs.est.7b02528

(33) Ghidotti, M.; Fabbri, D.; Hornung, A. Profiles of volatile organic compounds in biochar: Insights into process conditions and quality assessment. *ACS Sustainable Chem. Eng.* **2017**, *5* (1), 510−517.

(34) Wang, Y. Y.; Jing, X. R.; Li, L. L.; Liu, W. J.; Tong, Z. H.; Jiang, H. Biotoxicity evaluations of three typical biochars using a simulated system of fast pyrolytic biochar extracts on organisms of three kingdoms. *ACS Sustainable Chem. Eng.* **2017**, *5* (1), 481−488.

(35) Jaffe, R.; Ding, Y.; Niggemann, J.; Vahatalo, A. V.; Stubbins, A.; Spencer, R. G. M.; Campbell, J.; Dittmar, T. Global charcoal mobilization from soils via dissolution and riverine transport to the oceans. *Science* **2013**, *340* (6130), 345−347.

(36) Xie, T.; Reddy, K. R.; Wang, C.; Yargicoglu, E.; Spokas, K. Characteristics and applications of biochar for environmental remediation: A review. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45* (9), 939−969.

(37) Liu, W. J.; Jiang, H.; Yu, H. Q. Development of biochar-based functional materials: Toward a sustainable platform carbon material. *Chem. Rev.* **2015**, *115* (22), 12251−12285.

(38) Laird, D. A.; Brown, R. C.; Amonette, J. E.; Lehmann, J. Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuels, Bioprod. Biorefin.* **2009**, *3* (5), 547−562.

(39) Ding, Y.; Liu, Y. G.; Liu, S. B.; Li, Z. W.; Tan, X. F.; Huang, X. X.; Zeng, G. M.; Zhou, L.; Zheng, B. H. Biochar to improve soil fertility. A review. *Agron. Sustainable Dev.* **2016**, *36* (2), 36.

(40) Ali, S.; Rizwan, M.; Qayyum, M. F.; Ok, Y. S.; Ibrahim, M.; Riaz, M.; Arif, M. S.; Hafeez, F.; Al-Wabel, M. I.; Shahzad, A. N. Biochar soil amendment on alleviation of drought and salt stress in plants: A critical review. *Environ. Sci. Pollut. Res.* **2017**, *24* (14), 12700−12712.

(41) Biederman, L. A.; Harpole, W. S. Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy* **2013**, *5* (2), 202−214.

(42) Jeffery, S.; Verheijen, F. G. A.; van der Velde, M.; Bastos, A. C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agric., Ecosyst. Environ.* **2011**, *144* (1), 175−187.

(43) Ahmad, M.; Rajapaksha, A. U.; Lim, J.; Zhang, M.; Bolan, N.; Mohan, D.; Vithanage, M.; Lee, S.; Ok, Y. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere* **2014**, *99*, 19−33.

(44) Inyang, M. I.; Gao, B.; Yao, Y.; Xue, Y. W.; Zimmerman, A.; Mosa, A.; Pullammanappallil, P.; Ok, Y. S.; Cao, X. D. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46* (4), 406−433.

(45) Wang, J. Y.; Xiong, Z. Q.; Kuzyakov, Y. Biochar stability in soil: Meta-analysis of decomposition and priming effects. *GCB Bioenergy* **2016**, *8* (3), 512−523.

(46) Gupta, S.; Kua, H. W. Factors determining the potential of biochar as a carbon capturing and sequestering construction material: Critical review. *J. Mater. Civ. Eng.* **2017**, *29* (9), 04017086.

(47) Spokas, K. A. Review of the stability of biochar in soils: Predictability of O:C molar ratios. *Carbon Manage.* **2010**, *1* (2), 289−303.

(48) Gurwick, N. P.; Moore, L. A.; Kelly, C.; Elias, P. A systematic review of biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. *PLoS One* **2013**, *8* (9), e75932.

(49) Kookana, R. S.; Sarmah, A. K.; Van Zwieten, L.; Krull, E.; Singh, B. Biochar application to soil: agronomic and environmental benefits and unintended consequences. In *Adv. Agron.*, Sparks, D. L., Ed.; **2011**; Vol. *112*, pp 103−143.10.1016/B978-0-12-385538-1.00003-2

(50) Kuppusamy, S.; Thavamani, P.; Megharaj, M.; Venkateswarlu, K.; Naidu, R. Agronomic and remedial benefits and risks of applying biochar to soil: Current knowledge and future research directions. *Environ. Int.* **2016**, *87*, 1−12.

(51) Kambo, H. S.; Dutta, A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renewable Sustainable Energy Rev.* **2015**, *45*, 359−378.

(52) Sharma, A.; Pareek, V.; Zhang, D. Biomass pyrolysis-A review of modelling, process parameters and catalytic studies. *Renewable Sustainable Energy Rev.* **2015**, *50*, 1081−1096.

(53) Demirbas, A.; Arin, G. An overview of biomass pyrolysis. *Energy Sources* **2002**, *24* (5), 471−482.

(54) Zhou, H.; Wu, C.; Meng, A.; Zhang, Y.; Williams, P. T. Effect of interactions of biomass constituents on polycyclic aromatic hydrocarbons (PAH) formation during fast pyrolysis. *J. Anal. Appl. Pyrolysis* **2014**, *110*, 264−269.

(55) Hu, S.; Jiang, L.; Wang, Y.; Su, S.; Sun, L.; Xu, B.; He, L.; Xiang, J. Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures. *Bioresour. Technol.* **2015**, *192*, 23−30.

(56) Tripathi, M.; Sahu, J. N.; Ganesan, P. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renewable Sustainable Energy Rev.* **2016**, *55*, 467−481.

(57) Lian, F.; Huang, F.; Chen, W.; Xing, B. S.; Zhu, L. Y. Sorption of apolar and polar organic contaminants by waste tire rubber and its chars in single- and bi-solute systems. *Environ. Pollut.* **2011**, *159* (4), 850−857.

(58) Yuan, J. H.; Xu, R. K.; Zhang, H. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol.* **2011**, *102* (3), 3488−3497.

(59) Xiao, F.; Pignatello, J. J. Interactions of triazine herbicides with biochar: Steric and electronic effects. *Water Res.* **2015**, *80*, 179−188.

(60) Cao, X.; Pignatello, J. J.; Li, Y.; Lattao, C.; Chappell, M. A.; Chen, N.; Miller, L. F.; Mao, J. Characterization of wood chars produced at different temperatures using advanced solid-state ^{13}C nmr spectroscopic techniques. *Energy Fuels* **2012**, *26* (9), 5983−5991.

(61) Qu, T.; Guo, W.; Shen, L.; Xiao, J.; Zhao, K. Experimental study of biomass pyrolysis based on three major components: Hemicellulose, cellulose, and lignin. *Ind. Eng. Chem. Res.* **2011**, *50* (18), 10424−10433.

(62) Sun, J.; Lian, F.; Liu, Z.; Zhu, L.; Song, Z. Biochars derived from various crop straws: Characterization and Cd(II) removal potential. *Ecotoxicol. Environ. Saf.* **2014**, *106* (0), 226−231.

(63) George, A.; Morgan, T. J.; Kandiyoti, R. Pyrolytic reactions of lignin within naturally occurring plant matrices: Challenges in biomass pyrolysis modeling due to synergistic effects. *Energy Fuels* **2014**, *28* (11), 6918−6927.

(64) Xiao, X.; Chen, B.; Zhu, L. Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. *Environ. Sci. Technol.* **2014**, *48* (6), 3411−3419.

(65) Collard, F. X.; Blin, J.; Bensakhria, A.; Valette, J. Influence of impregnated metal on the pyrolysis conversion of biomass constituents. *J. Anal. Appl. Pyrolysis* **2012**, *95*, 213−226.

(66) Di Blasi, C.; Galgano, A.; Branca, C. Influences of the chemical state of alkaline compounds and the nature of alkali metal on wood pyrolysis. *Ind. Eng. Chem. Res.* **2009**, *48* (7), 3359−3369.

(67) Zhao, L.; Cao, X.; Zheng, W.; Wang, Q.; Yang, F. Endogenous minerals have influences on surface electrochemistry and ion exchange properties of biochar. *Chemosphere* **2015**, *136*, 133−139.

(68) Sun, K.; Kang, M.; Ro, K. S.; Libra, J. A.; Zhao, Y.; Xing, B. Variation in sorption of propiconazole with biochars: The effect of temperature, mineral, molecular structure, and nano-porosity. *Chemosphere* **2016**, *142*, 56−63.

(69) Jin, J.; Sun, K.; Wu, F.; Gao, B.; Wang, Z.; Kang, M.; Bai, Y.; Zhao, Y.; Liu, X.; Xing, B. Single-solute and bi-solute sorption of phenanthrene and dibutyl phthalate by plant- and manure-derived biochars. *Sci. Total Environ.* **2014**, *473−474* (0), 308−316.

(70) Liao, S.; Pan, B.; Li, H.; Zhang, D.; Xing, B. Detecting free radicals in biochars and determining their ability to inhibit the germination and growth of corn, wheat and rice seedlings. *Environ. Sci. Technol.* **2014**, *48* (15), 8581−8587.

(71) Fang, G.; Gao, J.; Liu, C.; Dionysiou, D. D.; Wang, Y.; Zhou, D. Key Role of persistent free radicals in hydrogen peroxide activation by

biochar: implications to organic contaminant degradation. *Environ. Sci. Technol.* **2014**, *48* (3), 1902−1910.

(72) Yang, H.; Yan, R.; Chen, H.; Lee, D. H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86* (12−13), 1781−1788.

(73) McBeath, A. V.; Smernik, R. J.; Krull, E. S.; Lehmann, J. The influence of feedstock and production temperature on biochar carbon chemistry: A solid-state C-13 NMR study. *Biomass Bioenergy* **2014**, *60*, 121−129.

(74) Chen, B.; Zhou, D.; Zhu, L. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environ. Sci. Technol.* **2008**, *42* (14), 5137−5143.

(75) Zhang, Y. L.; Wu, W. G.; Zhao, S. H.; Long, Y. F.; Luo, Y. H. Experimental study on pyrolysis tar removal over rice straw char and inner pore structure evolution of char. *Fuel Process. Technol.* **2015**, *134*, 333−344.

(76) Zhao, L.; Zheng, W.; Cao, X. D. Distribution and evolution of organic matter phases during biochar formation and their importance in carbon loss and pore structure. *Chem. Eng. J.* **2014**, *250*, 240−247.

(77) Pan, B.; Huang, P.; Wu, M.; Wang, Z.; Wang, P.; Jiao, X.; Xing, B. Physicochemical and sorption properties of thermally-treated sediments with high organic matter content. *Bioresour. Technol.* **2012**, *103* (1), 367−373.

(78) Fu, P.; Hu, S.; Xiang, J.; Sun, L. S.; Su, S.; Wang, J. Evaluation of the porous structure development of chars from pyrolysis of rice straw: Effects of pyrolysis temperature and heating rate. *J. Anal. Appl. Pyrolysis* **2012**, *98*, 177−183.

(79) Lu, L. M.; Kong, C. H.; Sahajwalla, V.; Harris, D. Char structural ordering during pyrolysis and combustion and its influence on char reactivity. *Fuel* **2002**, *81* (9), 1215−1225.

(80) Xu, X. Y.; Zhao, Y. H.; Sima, J. K.; Zhao, L.; Masek, O.; Cao, X. D. Indispensable role of biochar-inherent mineral constituents in its environmental applications: A review. *Bioresour. Technol.* **2017**, *241*, 887−899.

(81) Kappler, A.; Wuestner, M. L.; Ruecker, A.; Harter, J.; Halama, M.; Behrens, S. Biochar as an electron shuttle between bacteria and Fe(III) minerals. *Environ. Sci. Technol. Lett.* **2014**, *1* (8), 339−344.

(82) Sun, K.; Keiluweit, M.; Kleber, M.; Pan, Z.; Xing, B. Sorption of fluorinated herbicides to plant biomass-derived biochars as a function of molecular structure. *Bioresour. Technol.* **2011**, *102* (21), 9897−9903.

(83) Wang, X. L.; Xing, B. S. Sorption of organic contaminants by biopolymer-derived chars. *Environ. Sci. Technol.* **2007**, *41* (24), 8342−8348.

(84) Guo, X.; Wang, X.; Zhou, X.; Ding, X.; Fu, B.; Tao, S.; Xing, B. Impact of the simulated diagenesis on sorption of naphthalene and 1-naphthol by soil organic matter and its precursors. *Environ. Sci. Technol.* **2013**, *47* (21), 12148−12155.

(85) Sun, K.; Kang, M.; Zhang, Z.; Jin, J.; Wang, Z.; Pan, Z.; Xu, D.; Wu, F.; Xing, B. Impact of deashing treatment on biochar structural properties and potential sorption mechanisms of phenanthrene. *Environ. Sci. Technol.* **2013**, *47* (20), 11473−11481.

(86) Lattao, C.; Cao, X.; Mao, J.; Schmidt-Rohr, K.; Pignatello, J. J. Influence of molecular structure and adsorbent properties on sorption of organic compounds to a temperature series of wood chars. *Environ. Sci. Technol.* **2014**, *48* (9), 4790−4798.

(87) Zhang, M.; Shu, L.; Shen, X.; Guo, X.; Tao, S.; Xing, B.; Wang, X. Characterization of nitrogen-rich biomaterial-derived biochars and their sorption for aromatic compounds. *Environ. Pollut.* **2014**, *195* (0), 84−90.

(88) Lian, F.; Sun, B.; Song, Z.; Zhu, L.; Qi, X.; Xing, B. Physicochemical properties of herb-residue biochar and its sorption to ionizable antibiotic sulfamethoxazole. *Chem. Eng. J.* **2014**, *248*, 128−134.

(89) Qiu, M.; Sun, K.; Jin, J.; Gao, B.; Yan, Y.; Han, L.; Wu, F.; Xing, B. Properties of the plant- and manure-derived biochars and their sorption of dibutyl phthalate and phenanthrene. *Sci. Rep.* **2015**, *4*; DOI: 10.1038/srep05295.

(90) Qu, X.; Fu, H.; Mao, J.; Ran, Y.; Zhang, D.; Zhu, D. Chemical and structural properties of dissolved black carbon released from biochars. *Carbon* **2016**, *96*, 759−767.

(91) Zhang, J.; Lu, F.; Zhang, H.; Shao, L.; Chen, D.; He, P. Multiscale visualization of the structural and characteristic changes of sewage sludge biochar oriented towards potential agronomic and environmental implication. *Sci. Rep.* **2015**, *5*; DOI: 10.1038/srep09406.

(92) Chen, Z.; Xiao, X.; Chen, B.; Zhu, L. Quantification of chemical states, dissociation constants and contents of oxygen-containing groups on the surface of biochars produced at different temperatures. *Environ. Sci. Technol.* **2015**, *49* (1), 309−317.

(93) Dong, X.; Ma, L. Q.; Zhu, Y.; Li, Y.; Gu, B. Mechanistic investigation of mercury sorption by brazilian pepper biochars of different pyrolytic temperatures based on X-ray photoelectron spectroscopy and flow calorimetry. *Environ. Sci. Technol.* **2013**, *47* (21), 12156−12164.

(94) Uchimiya, M.; Chang, S.; Klasson, K. T. Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. *J. Hazard. Mater.* **2011**, *190* (1−3), 432−441.

(95) Tsechansky, L.; Graber, E. R. Methodological limitations to determining acidic groups at biochar surfaces via the Boehm titration. *Carbon* **2014**, *66*, 730−733.

(96) Fidel, R. B.; Laird, D. A.; Thompson, M. L. Evaluation of modified Boehm titration methods for use with biochars. *J. Environ. Qual.* **2013**, *42* (6), 1771−1778.

(97) Tian, K.; Liu, W. J.; Qian, T. T.; Jiang, H.; Yu, H. Q. Investigation on the evolution of N-containing organic compounds during pyrolysis of sewage sludge. *Environ. Sci. Technol.* **2014**, *48* (18), 10888−10896.

(98) Lian, F.; Cui, G.; Liu, Z.; Duo, L.; Zhang, G.; Xing, B. One-step synthesis of a novel N-doped microporous biochar derived from crop straws with high dye adsorption capacity. *J. Environ. Manage.* **2016**, *176*, 61−68.

(99) Cheah, S.; Malone, S. C.; Feik, C. J. Speciation of sulfur in biochar produced from pyrolysis and gasification of oak and corn stover. *Environ. Sci. Technol.* **2014**, *48* (15), 8474−8480.

(100) Cao, X. D.; Ma, L. N.; Liang, Y.; Gao, B.; Harris, W. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environ. Sci. Technol.* **2011**, *45* (11), 4884−4889.

(101) Cao, X. D.; Ma, L. N.; Gao, B.; Harris, W. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* **2009**, *43* (9), 3285−3291.

(102) Zhou, Z. L.; Shi, D. J.; Qiu, Y. P.; Sheng, G. D. Sorptive domains of pine chars as probed by benzene and nitrobenzene. *Environ. Pollut.* **2010**, *158* (1), 201−206.

(103) Teixidó, M.; Pignatello, J. J.; Beltrán, J. L.; Granados, M.; Peccia, J. Speciation of the ionizable antibiotic sulfamethazine on black carbon (biochar). *Environ. Sci. Technol.* **2011**, *45* (23), 10020−10027.

(104) Xie, M.; Chen, W.; Xu, Z.; Zheng, S.; Zhu, D. Adsorption of sulfonamides to demineralized pine wood biochars prepared under different thermochemical conditions. *Environ. Pollut.* **2014**, *186*, 187−194.

(105) Ji, L.; Chen, W.; Xu, Z.; Zheng, S.; Zhu, D. Graphene nanosheets and graphite oxide as promising adsorbents for removal of organic contaminants from aqueous solution. *J. Environ. Qual.* **2013**, *42* (1), 191−198.

(106) Chen, J. Y.; Chen, W.; Zhu, D. Adsorption of nonionic aromatic compounds to single-walled carbon nanotubes: Effects of aqueous solution chemistry. *Environ. Sci. Technol.* **2008**, *42* (19), 7225−7230.

(107) Yang, K.; Xing, B. Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. *Chem. Rev.* **2010**, *110* (10), 5989−6008.

(108) Chen, W.; Duan, L.; Wang, L. L.; Zhu, D. Q. Adsorption of hydroxyl- and amino-substituted aromatics to carbon manotubes. *Environ. Sci. Technol.* **2008**, *42* (18), 6862−6868.

(109) Geitner, N. K.; Zhao, W.; Ding, F.; Chen, W.; Wiesner, M. R. Mechanistic insights from discrete molecular dynamics simulations of pesticide−nanoparticle interactions. *Environ. Sci. Technol.* **2017**, *51* (15), 8396−8404.

(110) Tang, H.; Zhao, Y.; Yang, X.; Liu, D.; Shao, P.; Zhu, Z.; Shan, S.; Cui, F.; Xing, B. New insight into the aggregation of graphene oxide using molecular dynamics simulations and extended Derjaguin−Landau−Verwey−Overbeek theory. *Environ. Sci. Technol.* **2017**, *51* (17), 9674−9682.

(111) Tan, X. F.; Liu, Y. G.; Zeng, G. M.; Wang, X.; Hu, X. J.; Gu, Y. L.; Yang, Z. Z. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* **2015**, *125*, 70−85.

(112) Loganathan, P.; Vigneswaran, S.; Kandasamy, J.; Naidu, R. Cadmium sorption and desorption in soils: A review. *Crit. Rev. Environ. Sci. Technol.* **2012**, *42* (5), 489−533.

(113) Lu, H.; Zhang, W.; Yang, Y.; Huang, X.; Wang, S.; Qiu, R. Relative distribution of Pb(2+) sorption mechanisms by sludge-derived biochar. *Water Res.* **2012**, *46* (3), 854−62.

(114) Harvey, O. R.; Herbert, B. E.; Rhue, R. D.; Kuo, L. J. Metal interactions at the biochar-water interface: Energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. *Environ. Sci. Technol.* **2011**, *45* (13), 5550−5556.

(115) Dong, X.; Ma, L. Q.; Li, Y. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *J. Hazard. Mater.* **2011**, *190* (1−3), 909−915.

(116) del Rio, J. A. G.; Morando, P. J.; Cicerone, D. S. Natural materials for treatment of industrial effluents: Comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite. Part 1: Batch experiments. *J. Environ. Manage.* **2004**, *71* (2), 169−177.

(117) Du, Y.; Lian, F.; Zhu, L. Y. Biosorption of divalent Pb, Cd and Zn on aragonite and calcite mollusk shells. *Environ. Pollut.* **2011**, *159* (7), 1763−1768.

(118) Lin, D.; Tian, X.; Li, T.; Zhang, Z.; He, X.; Xing, B. Surface-bound humic acid increased Pb^{2+} sorption on carbon nanotubes. *Environ. Pollut.* **2012**, *167*, 138−147.

(119) Shi, G.; Ding, Y.; Fang, H. Unexpectedly strong anion-π interactions on the graphene flakes. *J. Comput. Chem.* **2012**, *33* (14), 1328−1337.

(120) Betts, A. R.; Chen, N.; Hamilton, J. G.; Peak, D. Rates and mechanisms of Zn^{2+} adsorption on a meat and bonemeal biochar. *Environ. Sci. Technol.* **2013**, *47* (24), 14350−14357.

(121) Ippolito, J. A.; Strawn, D. G.; Scheckel, K. G.; Novak, J. M.; Ahmedna, M.; Niandou, M. A. S. Macroscopic and molecular investigations of copper sorption by a steam-activated biochar. *J. Environ. Qual.* **2012**, *41* (4), 1150−1156.

(122) Trakal, L.; Bingöl, D.; Pohořelý, M.; Hruška, M.; Komárek, M. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications. *Bioresour. Technol.* **2014**, *171* (0), 442−451.

(123) Zhang, F.; Wang, X.; Yin, D. X.; Peng, B.; Tan, C. Y.; Liu, Y. G.; Tan, X. F.; Wu, S. X. Efficiency and mechanisms of Cd removal from aqueous solution by biochar derived from water hyacinth (Eichornia crassipes). *J. Environ. Manage.* **2015**, *153*, 68−73.

(124) Wang, Z.; Liu, G.; Zheng, H.; Li, F.; Ngo, H. H.; Guo, W.; Liu, C.; Chen, L.; Xing, B. Investigating the mechanisms of biochar's removal of lead from solution. *Bioresour. Technol.* **2015**, *177* (0), 308−317.

(125) Uchimiya, M.; Lima, I. M.; Klasson, K. T.; Chang, S. C.; Wartelle, L. H.; Rodgers, J. E. Immobilization of heavy metal ions (Cu(II), Cd(II), Ni(II), and Pb(II)) by broiler litter-derived biochars in water and soil. *J. Agric. Food Chem.* **2010**, *58* (9), 5538−5544.

(126) Xiao, F.; Pignatello, J. J. $\pi^{+}-\pi$ Interactions between (hetero)aromatic amine cations and the graphitic surfaces of pyrogenic carbonaceous materials. *Environ. Sci. Technol.* **2015**, *49* (2), 906−914.

(127) Wang, D.; Zhang, W.; Hao, X.; Zhou, D. Transport of biochar particles in saturated granular media: effects of pyrolysis temperature and particle size. *Environ. Sci. Technol.* **2013**, *47* (2), 821−828.

(128) Spokas, K. A.; Novak, J. M.; Masiello, C. A.; Johnson, M. G.; Colosky, E. C.; Ippolito, J. A.; Trigo, C. Physical disintegration of biochar: an overlooked process. *Environ. Sci. Technol. Lett.* **2014**, *1* (8), 326−332.

(129) Qian, L. B.; Zhang, W. Y.; Yan, J. C.; Han, L.; Gao, W. G.; Liu, R. Q.; Chen, M. F. Effective removal of heavy metal by biochar colloids under different pyrolysis temperatures. *Bioresour. Technol.* **2016**, *206*, 217−224.

(130) Guggenberger, G.; Rodionov, A.; Shibistova, O.; Grabe, M.; Kasansky, O. A.; Fuchs, H.; Mikheyeva, N.; Zrazhevskaya, G.; Flessa, H. Storage and mobility of black carbon in permafrost soils of the forest tundra ecotone in Northern Siberia. *Global. Change. Biol.* **2008**, *14* (6), 1367−1381.

(131) Wagner, S.; Jaffe, R. Effect of photodegradation on molecular size distribution and quality of dissolved black carbon. *Org. Geochem.* **2015**, *86*, 1−4.

(132) Fu, H.; Liu, H.; Mao, J.; Chu, W.; Li, Q.; Alvarez, P. J. J.; Qu, X.; Zhu, D. Photochemistry of dissolved black carbon released from biochar: reactive oxygen species generation and phototransformation. *Environ. Sci. Technol.* **2016**, *50* (3), 1218−1226.

(133) Jones, D. L.; Murphy, D. V.; Khalid, M.; Ahmad, W.; Edwards-Jones, G.; DeLuca, T. H. Short-term biochar-induced increase in soil CO_2 release is both biotically and abiotically mediated. *Soil Biol. Biochem.* **2011**, *43* (8), 1723−1731.

(134) Cheng, C. H.; Lehmann, J.; Thies, J. E.; Burton, S. D.; Engelhard, M. H. Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.* **2006**, *37* (11), 1477−1488.

(135) Sand, W. Microbial mechanisms of deterioration of inorganic substrates - A general mechanistic overview. *Int. Biodeterior. Biodegrad.* **1997**, *40* (2−4), 183−190.

(136) Singh, B. P.; Cowie, A. L.; Smernik, R. J. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. *Environ. Sci. Technol.* **2012**, *46* (21), 11770−11778.

(137) Pan, M. L.; Zhang, Y. Y.; Shan, C.; Zhang, X. L.; Gao, G. D.; Pan, B. C. Flat graphene-enhanced electron transfer involved in redox reactions. *Environ. Sci. Technol.* **2017**, *51* (15), 8597−8605.

(138) Nia, Z. K.; Chen, J. Y.; Tang, B.; Yuan, B.; Wang, X. G.; Li, J. L. Optimizing the free radical content of graphene oxide by controlling its reduction. *Carbon* **2017**, *116*, 703−712.

(139) Duan, X. G.; Ao, Z. M.; Sun, H. Q.; Indrawirawan, S.; Wang, Y. X.; Kang, J.; Liang, F. L.; Zhu, Z. H.; Wang, S. B. Nitrogen-doped graphene for generation and evolution of reactive radicals by metal-free catalysis. *ACS Appl. Mater. Interfaces* **2015**, *7* (7), 4169−4178.

(140) Fang, Y. Y.; Singh, B.; Singh, B. P. Effect of temperature on biochar priming effects and its stability in soils. *Soil Biol. Biochem.* **2015**, *80*, 136−145.

(141) Yang, F.; Zhao, L.; Gao, B.; Xu, X. Y.; Cao, X. D. The interfacial behavior between biochar and soil minerals and its effect on biochar stability. *Environ. Sci. Technol.* **2016**, *50* (5), 2264−2271.

(142) Nguyen, B. T.; Lehmann, J. Black carbon decomposition under varying water regimes. *Org. Geochem.* **2009**, *40* (8), 846−853.

(143) Purakayastha, T. J.; Das, K. C.; Gaskin, J.; Harris, K.; Smith, J. L.; Kumari, S. Effect of pyrolysis temperatures on stability and priming effects of C3 and C4 biochars applied to two different soils. *Soil Tillage Res.* **2016**, *155*, 107−115.

(144) Rechberger, M. V.; Kloss, S.; Rennhofer, H.; Tintner, J.; Watzinger, A.; Soja, G.; Lichtenegger, H.; Zehetner, F. Changes in biochar physical and chemical properties: Accelerated biochar aging in an acidic soil. *Carbon* **2017**, *115*, 209−219.

(145) Smebye, A.; Ailing, V.; Vogt, R. D.; Gadmar, T. C.; Mulder, J.; Cornelissen, G.; Hale, S. E. Biochar amendment to soil changes dissolved organic matter content and composition. *Chemosphere* **2016**, *142*, 100−105.

(146) Lin, Y.; Munroe, P.; Joseph, S.; Kimber, S.; Van Zwieten, L. Nanoscale organo-mineral reactions of biochars in ferrosol: An investigation using microscopy. *Plant Soil* **2012**, *357* (1−2), 369−380.

(147) Kuzyakov, Y.; Subbotina, I.; Chen, H.; Bogomolova, I.; Xu, X. Black carbon decomposition and incorporation into soil microbial biomass estimated by C-14 labeling. *Soil Biol. Biochem.* **2009**, *41* (2), 210−219.

(148) Ameloot, N.; Graber, E. R.; Verheijen, F. G. A.; De Neve, S. Interactions between biochar stability and soil organisms: Review and research needs. *Eur. J. Soil Sci.* **2013**, *64* (4), 379−390.

(149) Hamer, U.; Marschner, B.; Brodowski, S.; Amelung, W. Interactive priming of black carbon and glucose mineralisation. *Org. Geochem.* **2004**, *35* (7), 823−830.

(150) Farrell, M.; Kuhn, T. K.; Macdonald, L. M.; Maddern, T. M.; Murphy, D. V.; Hall, P. A.; Singh, B. P.; Baumann, K.; Krull, E. S.; Baldock, J. A. Microbial utilisation of biochar-derived carbon. *Sci. Total Environ.* **2013**, *465*, 288−297.

(151) Bhaduri, D.; Saha, A.; Desai, D.; Meena, H. N. Restoration of carbon and microbial activity in salt-induced soil by application of peanut shell biochar during short-term incubation study. *Chemosphere* **2016**, *148*, 86−98.

(152) Luo, Y.; Durenkamp, M.; De Nobili, M.; Lin, Q.; Brookes, P. C. Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH. *Soil Biol. Biochem.* **2011**, *43* (11), 2304−2314.

(153) Cross, A.; Sohi, S. P. The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. *Soil Biol. Biochem.* **2011**, *43* (10), 2127−2134.

(154) Maestrini, B.; Nannipieri, P.; Abiven, S. A meta-analysis on pyrogenic organic matter induced priming effect. *GCB Bioenergy* **2015**, *7* (4), 577−590.

(155) Luo, Y.; Durenkamp, M.; De Nobili, M.; Lin, Q.; Devonshire, B. J.; Brookes, P. C. Microbial biomass growth, following incorporation of biochars produced at 350 degrees C or 700 degrees C, in a silty-clay loam soil of high and low pH. *Soil Biol. Biochem.* **2013**, *57*, 513−523.

(156) Chen, J.; Sun, X.; Li, L.; Liu, X.; Zhang, B.; Zheng, J.; Pan, G. Change in active microbial community structure, abundance and carbon cycling in an acid rice paddy soil with the addition of biochar. *Eur. J. Soil Sci.* **2016**, *67* (6), 857−867.

(157) Tian, J.; Wang, J. Y.; Dippold, M.; Gao, Y.; Blagodatskaya, E.; Kuzyakov, Y. Biochar affects soil organic matter cycling and microbial functions but does not alter microbial community structure in a paddy soil. *Sci. Total Environ.* **2016**, *556*, 89−97.

(158) Mitchell, P. J.; Simpson, A. J.; Soong, R.; Simpson, M. J. Shifts in microbial community and water-extractable organic matter composition with biochar amendment in a temperate forest soil. *Soil Biol. Biochem.* **2015**, *81*, 244−254.

(159) Liao, N.; Li, Q.; Zhang, W.; Zhou, G. W.; Ma, L. J.; Min, W.; Ye, J.; Hou, Z. N. Effects of biochar on soil microbial community composition and activity in drip-irrigated desert soil. *Eur. J. Soil Biol.* **2016**, *72*, 27−34.

(160) Quilliam, R. S.; Glanville, H. C.; Wade, S. C.; Jones, D. L. Life in the 'charosphere' − Does biochar in agricultural soil provide a significant habitat for microorganisms? *Soil Biol. Biochem.* **2013**, *65*, 287−293.

(161) Prendergast-Miller, M. T.; Duvall, M.; Sohi, S. P. Biochar-root interactions are mediated by biochar nutrient content and impacts on soil nutrient availability. *Eur. J. Soil Sci.* **2014**, *65* (1), 173−185.

(162) Chen, J. H.; Li, S. H.; Liang, C. F.; Xu, Q. F.; Li, Y. C.; Qin, H.; Fuhrmann, J. J. Response of microbial community structure and function to short-term biochar amendment in an intensively managed bamboo (Phyllostachys praecox) plantation soil: Effect of particle size and addition rate. *Sci. Total Environ.* **2017**, *574*, 24−33.

(163) Gibson, C.; Berry, T. D.; Wang, R. Z.; Spencer, J. A.; Johnston, C. T.; Jiang, Y.; Bird, J. A.; Filley, T. R. Weathering of pyrogenic organic matter induces fungal oxidative enzyme response in single culture inoculation experiments. *Org. Geochem.* **2016**, *92*, 32−41.

(164) Saquing, J. M.; Yu, Y.-H.; Chiu, P. C. Wood-derived black carbon (biochar) as a microbial electron donor and acceptor. *Environ. Sci. Technol. Lett.* **2016**, *3* (2), 62−66.

(165) Xu, S.; Adhikari, D.; Huang, R.; Zhang, H.; Tang, Y.; Roden, E.; Yang, Y. Biochar-facilitated microbial reduction of hematite. *Environ. Sci. Technol.* **2016**, *50* (5), 2389−2395.

(166) Fang, G.; Liu, C.; Gao, J.; Dionysiou, D. D.; Zhou, D. Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation. *Environ. Sci. Technol.* **2015**, *49* (9), 5645−5653.

(167) Keiluweit, M.; Kleber, M.; Sparrow, M. A.; Simoneit, B. R. T.; Prahl, F. G. Solvent-extractable Polycyclic aromatic hydrocarbons in biochar: Influence of pyrolysis temperature and feedstock. *Environ. Sci. Technol.* **2012**, *46* (17), 9333−9341.

(168) Hale, S. E.; Lehmann, J.; Rutherford, D.; Zimmerman, A. R.; Bachmann, R. T.; Shitumbanuma, V.; O'Toole, A.; Sundqvist, K. L.; Arp, H. P. H.; Cornelissen, G. Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. *Environ. Sci. Technol.* **2012**, *46* (5), 2830−2838.

(169) Lyu, H. H.; He, Y. H.; Tang, J. C.; Hecker, M.; Liu, Q. L.; Jones, P. D.; Codling, G.; Giesy, J. P. Effect of pyrolysis temperature on potential toxicity of biochar if applied to the environment. *Environ. Pollut.* **2016**, *218*, 1−7.

(170) Mayer, P.; Hilber, I.; Gouliarmou, V.; Hale, S. E.; Cornelissen, G.; Bucheli, T. D. How to determine the environmental exposure of pahs originating from biochar. *Environ. Sci. Technol.* **2016**, *50* (4), 1941−1948.

(171) Mia, S.; Dijkstra, F. A.; Singh, B. Aging induced changes in biochar's functionality and adsorption behavior for phosphate and ammonium. *Environ. Sci. Technol.* **2017**, *51* (15), 8359−8367.

(172) Devi, P.; Saroha, A. K. Risk analysis of pyrolyzed biochar made from paper mill effluent treatment plant sludge for bioavailability and eco-toxicity of heavy metals. *Bioresour. Technol.* **2014**, *162*, 308−315.

(173) Stefaniuk, M.; Oleszczuk, P.; Bartminski, P. Chemical and ecotoxicological evaluation of biochar produced from residues of biogas production. *J. Hazard. Mater.* **2016**, *318*, 417−424.

(174) Zielinska, A.; Oleszczuk, P. The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content. *Biomass Bioenergy* **2015**, *75*, 235−244.

(175) Oleszczuk, P.; Josko, I.; Kusmierz, M. Biochar properties regarding to contaminants content and ecotoxicological assessment. *J. Hazard. Mater.* **2013**, *260*, 375−382.

(176) Jones, D. L.; Quilliam, R. S. Metal contaminated biochar and wood ash negatively affect plant growth and soil quality after land application. *J. Hazard. Mater.* **2014**, *276* (0), 362−370.

(177) Domene, X.; Enders, A.; Hanley, K.; Lehmann, J. Ecotoxicological characterization of biochars: Role of feedstock and pyrolysis temperature. *Sci. Total Environ.* **2015**, *512*, 552−561.

(178) Buss, W.; Graham, M. C.; Shepherd, J. G.; Masek, O. Risks and benefits of marginal biomass-derived biochars for plant growth. *Sci. Total Environ.* **2016**, *569*, 496−506.

(179) Yang, J.; Pan, B.; Li, H.; Liao, S.; Zhang, D.; Wu, M.; Xing, B. Degradation of p-nitrophenol on biochars: Role of persistent free radicals. *Environ. Sci. Technol.* **2016**, *50* (2), 694−700.

(180) Fang, G.; Zhu, C.; Dionysiou, D. D.; Gao, J.; Zhou, D. Mechanism of hydroxyl radical generation from biochar suspensions: Implications to diethyl phthalate degradation. *Bioresour. Technol.* **2015**, *176*, 210−217.

(181) Feng, Y.; Liu, X.; Huynh, K. A.; McCaffery, J. M.; Mao, L.; Gao, S.; Chen, K. L. Heteroaggregation of graphene oxide with nanometer- and micrometer-sized hematite colloids: Influence on nanohybrid aggregation and microparticle sedimentation. *Environ. Sci. Technol.* **2017**, *51* (12), 6821−6828.

(182) Huynh, K. A.; McCaffery, J. M.; Chen, K. L. Heteroaggregation of multiwalled carbon nanotubes and hematite nanoparticles: Rates and mechanisms. *Environ. Sci. Technol.* **2012**, *46* (11), 5912−5920.

(183) Smith, B. M.; Pike, D. J.; Kelly, M. O.; Nason, J. A. Quantification of heteroaggregation between citrate-stabilized gold nanoparticles and hematite colloids. *Environ. Sci. Technol.* **2015**, *49* (21), 12789−12797.

(184) Petrov, D.; Tunega, D.; Gerzabek, M. H.; Oostenbrink, C. Molecular dynamics simulations of the standard leonardite humic acid: microscopic analysis of the structure and dynamics. *Environ. Sci. Technol.* **2017**, *51* (10), 5414−5424.

(185) Wang, B.; Zhang, W.; Li, H.; Fu, H.; Qu, X.; Zhu, D. Micropore clogging by leachable pyrogenic organic carbon: A new

perspective on sorption irreversibility and kinetics of hydrophobic organic contaminants to black carbon. *Environ. Pollut.* **2017**, *220* (Part B), 1349−1358.

(186) Van Zwieten, L.; Kimber, S.; Morris, S.; Chan, K. Y.; Downie, A.; Rust, J.; Joseph, S.; Cowie, A. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* **2010**, *327* (1−2), 235−246.

(187) Kwon, S.; Pignatello, J. J. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): Pseudo pore blockage by model lipid components and its implications for N_2-probed surface properties of natural sorbents. *Environ. Sci. Technol.* **2005**, *39* (20), 7932−7939.

(188) Zhou, Z.; Sun, H.; Zhang, W. Desorption of polycyclic aromatic hydrocarbons from aged and unaged charcoals with and without modification of humic acids. *Environ. Pollut.* **2010**, *158* (5), 1916−1921.

(189) Sun, B.; Lian, F.; Bao, Q.; Liu, Z.; Song, Z.; Zhu, L. Impact of low molecular weight organic acids (LMWOAs) on biochar micropores and sorption properties for sulfamethoxazole. *Environ. Pollut.* **2016**, *214*, 142−148.