agronomy

Review

Impact of Biochar on Organic Contaminants in Soil: A Tool for Mitigating Risk?

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Abstract: The presence of biochar in soils through natural processes (forest fires, bush burning) or through application to soil (agriculture, carbon storage, remediation, waste management) has received a significant amount of scientific and regulatory attention. Biochar alters soil properties, encourages microbial activity and enhances sorption of inorganic and organic compounds, but this strongly depends on the feedstock and production process of biochar. This review considers biochar sources, the production process and result of pyrolysis, interactions of biochar with soil, and associated biota. Furthermore, the paper focuses on the interactions between biochar and common anthropogenic organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), pesticides, and dioxins, which are often deposited in the soil environment. It then considers the feasibility of applying biochar in remediation technologies in addition to other perspective areas yet to be explored.

Keywords: biochar; bioaccessibility; bioavailability; sorption; desorption

1. Introduction

The soil environment is able to store, transform and remove pollutants through a combination of biological, chemical and physical processes [1]. Furthermore, it supports populations of microorganisms and other biota that are involved in the cycling of essential elements and nutrients; it also encourages the processing and sequestration of organic carbon. However, the persistent

exploration and exploitation of mineral and hydrocarbon resources, inappropriate agrochemical use, uncontrolled combustion, as well as increases in population and urbanisation have led to the introduction or displacement of chemicals into the soil environment [2–4]. The environment can become polluted with organic and inorganic chemicals as a result of intended, accidental or naturally occurring events such as manufacturing processes, mineral extraction, poor environmental management and waste disposal activities, application of fertilizer, illegal dumping of wastes, leaking underground storage tanks, abandonment of mines and other industrial activities [1]. In order to classify soil as contaminated, the presence, concentration, environmental behaviour and exposure mechanism/route or a potential toxicity of a chemical to human health or an ecosystem need to be characterised [5]. Subsequently, a suitable method of mitigation is required to render pollutants less mobile and harmful to receptors; this can potentially be achieved by the addition of geosorbents, such as biochar, to contaminated soils.

Soil contamination is often due to a wide range of organic and inorganic compounds; thus, this review considers the use of biochar in contaminated soils as a potential, inexpensive, and natural tool in mitigating/remediating contaminated soil. More specifically, the aims of this paper are to: (i) consider the fate and behaviour of selected contaminants in soil, illustrating their interaction with soil constituents; (ii) examine biochar production properties and interaction with soil; and (iii) highlight the possible ways of enhancing remediation by reducing mobility and bioavailability/bioaccessibility of compounds, using biochar as a management tool.

## 2. Behaviour of Organic Contaminants in Soil

Frequent and uncontrolled deposition of chemicals in the environment has resulted in the formation of environmental regulations to reduce and control soil contamination. The emergence of regulation and technology has brought about a decrease in primary sources of persistent organic pollutants (POPs) [6]. The loss, persistence and mobility of hydrophobic organic contaminants (HOCs) in soil is controlled by a number of variables, including contaminant physicochemical properties, concentration, soil properties, soil-contaminant contact time, and environmental (climatic) factors [7,8]. Polycyclic aromatic hydrocarbons (PAHs) are an important class of HOCs that are classified as highly degradable, pseudo-persistent or persistent in the environment. Unlike deliberate pesticide application, PAHs are more ubiquitous in the environment as they can be released from PAH-containing materials (soot and coal), pyrogenic or biogenic sources and atmospheric deposition. The partitioning behaviour of PAHs in soils is governed by their water solubility and the amount of organic carbon in soil [9], where the contaminants become physically entrapped within soil organic matter and/or diffuse into nanopore structures [10]. The soil organic matter (SOM) comprises of rubbery and glassy phases, where the latter comprises of black carbon geosorbents [11,12]. Black carbon (BC) is the collective term for thermally altered products ranging from partly charred to highly condensed forms of organic carbon, which includes chars, charcoals, biochars, soots and graphite [13]. BC is recalcitrant and has been shown to influence mobility, extractability and/or bioavailability of HOCs in soil [11,14,15]. Further, biochar has been shown to aid in stabilising and restoring SOM in soils [16].

The persistence of PAHs in soils is additionally attributed to their increasing aromaticity, hydrophobicity and molecular recalcitrance, which may differ due to geographical characteristics and

size of area [17,18]. When HOCs, such as PAHs, are released into the environment from either point or diffuse sources, they are subjected to a number of environmental processes: (i) photodegradation, where a chemical may be degraded in sunlight in presence of singlet oxygen, hydroxyl radicals, and other oxidants [19]; (ii) volatilisation may occur, particularly with compounds with higher vapour pressure and at higher temperatures [20]; (iii) when in contact with soils, organic chemicals experience further loss via biodegradation, biota uptake and physical mass transport (soil erosion and run-off) [10]. The mobility of organic compounds in soil and water is governed by their half-life and aqueous solubility, together with the sorption or retardation factor such as K_d, K_{oc} and K_{ow} [21].

Fractions of HOCs can still be retained in soils despite being subjected to loss processes [22,23]. Variations in soil properties can affect the rates and extents of chemical loss [24], whereby the composition of a soil's mineral and organic matter fractions may enhance or retard the loss of the HOCs [10]. In so doing, removal of the putatively mobile fraction which consists of the easily extractable and/or bioavailable/bioaccessible HOC fractions diminishes with increasing soil contact time [25–27]. Persistence and loss are also governed by the characteristics of the HOC, such as polarity, hydrophobicity, aqueous solubility and molecular structure or size [10,17,27,28]. Increases in contaminant-soil contact time (aging), result in the rate of loss decreasing to produce a hockey stick-shaped decay curve [10,24] (Figure 1). To explain this further, when an HOC comes into contact with soil, a portion is rapidly sorbed to soil components (organic matter and clay minerals) through hydrogen and van der Waal forces, whilst remaining fractions take longer time to undergo sorption [29]. Irrespective of the soil constituents and chemical composition, the loss of the organic chemicals from soils has been explicitly described by Semple *et al.* [29] as being through rapid, slow and very slow desorption. The rapidly desorbable fraction is characterised by weak surface chemical interactions between contaminant and organic matter or clay minerals, whilst the slow desorbable fraction refers to strongly bound (reversible) or diffusionally retarded component, whereas the very slow desorbing fraction (irreversible) refers to a covalently or physically entrapped component [29].

Figure 1. The influence of contact time on the extractability and bioaccessibility of a contaminant. Adapted from [10].
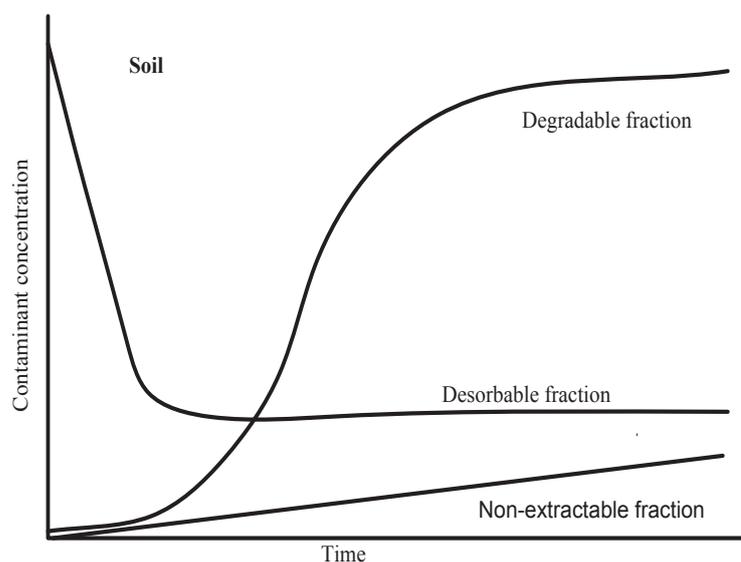
2.1. Impact of Soil Contact Time on Contaminant Mobility and Biota

The soil environment is a three-dimensional structure of water-filled pores, gas-filled pores, and soil particulates (organic matter, sand, silt, clay) [8]. Sorption is referred to as absorption when it penetrates the three-dimensional structure of the matrix, and adsorption when attached to the two-dimensional surface [30]. Linear absorption (partitioning) of HOCs into natural organic matter underestimates the total extent of sorption, but with the addition of non-linear adsorption of HOCs into black carbon nanopore sites, total sorption of HOCs can be deduced [31–33]. These studies [31–33] utilised the non-linear Freundlich model to best illustrate this phenomena, where the interaction between HOCs and black carbon materials depends on dispersive interactions and separation distance [11]. The sorption of HOCs within the soil matrix is thought to be by partitioning or entrapment within the internal matrix of the SOM [34–36]. The SOM is very complex in structure due to varied chemical and microbial processing of biomass, when HOCs containing functional groups similar to those present in SOM gain contact with soil, they undergo similar chemical and microbial processes to become indistinguishable from SOM [36].

2.1.1. Definitions of Bioavailability, Bioaccessibility and Chemical Activity

Although HOCs undergo sorption within the SOM matrix, they are subject to potential release from the reversible sorption sites to become bioavailable, or organisms migrate towards the compounds [37,38]. The total HOC content in soils does not always provide valid information on the potential biodegradable or ecotoxicologically relevant fractions and environmental risk [29,39]. This is because the overestimation of risk may be inferred on basis of the total concentration of the HOC in the soil environment, without taking into account the bioavailability, thermodynamics or transport (pathway) to specific receptors [35,40]. Therefore, in order to assess the risk an organic contaminant may pose to biota, the bioavailable and bioaccessible fractions of the contaminant have to be defined and investigated, as well as the chemical activity of the contaminants in question. Pharmacologists refer to "bioavailability" as the rate and extent of drug absorption or the intact drug molecules bioavailable to the general circulation or site of action [41]. Mammalian toxicologists consider the term to mean availability for crossing cell membrane, and environmental scientists intend the term to represent the accessibility of a chemical for assimilation and potential toxicity [35]. Semple *et al.* [37] went so far as to describe bioavailability as the fraction of a chemical that is freely available to cross an organism's membrane from the medium which the organism inhabits at a given time. Bioaccessibility encompasses both the bioavailable fraction and the potentially bioavailable fractions [37]. In the soil environment, bioavailability and bioaccessibility of organic contaminants relates to the ability and rate in which the contaminant interacts with the biosystem of an organism, as well as potential toxic fraction to biota [29,37]. Further, Semple *et al.* [29] went on to hypothesise that bioavailability describes the rate of uptake or biodegradation, while bioaccessibility describes the extent to which an organic contaminant may be degraded or taken up by soil biota. With respect to remediation, bioaccessibility illustrates the total amount of PAH that can be biodegraded over time. The complex scenario here is that the bioavailability of a compound to one organism may not be same for that of another. Studies have shown that even though bioavailability decreases with an increase in contact

time, the bioaccumulation by earthworms differs from bioavailability to bacteria [42,43]. It is thought that most microorganisms can only degrade contaminants which are present in the aqueous phase or when they adhere to SOM containing substrate [44,45]; this subsequently affects the ability of microbes to attack contaminants sorbed due to aging. However, some microorganisms evolve certain strategies to overcome this constraint by secretion of biosurfactants or adhesion to surface of contaminants [35,44] and by degrading SOM [36]. The amount of bioavailable chemical can be determined by (i) the rate of transfer of the compound from soil to living cells, and/or (ii) the rate of uptake and metabolism [10]. Each of these processes is governed by physicochemical properties of the compound, soil type and the living organisms involved, or biological process [25,35]. The bioaccessible fraction may refer to the rapidly desorbable fraction of an organic compound which may differ in soil type [24]. However, increases in soil-chemical contact time result in decreases in desorbing fractions and also produce a non-bioavailable, highly sequestered (non-extractable) fractions in soils (Figure 1) [24,25]. The concentration of the chemical and properties of soil also determines how much could be sorbed within the soil [46,47]. The chemical activity of a contaminant is closely related to fugacity and freely dissolved concentrations; it quantifies the energetic state of the chemical and determines the potential for diffusion, sorption and partitioning [48]. This illustrates the potential for the bioaccumulation and toxicity of the contaminant [48] through diffusion across membrane and phase boundaries [49]. Reichenberg and Mayer [48] and Reichenberg *et al.* [50] provide illustrative description of chemical activity of organic contaminants. The importance of this phenomenon is based on the fact that the bioconcentration of a particular contaminant in an organism can be determined by the equilibrium partitioning (diffusion or direct contact) between the chemical containing matrix and the organism [51]. Interestingly, the chemical activity is not limited to any environmental medium, regardless of the degree of heterogeneity of the medium [48]; however, the presence of BC, such as biochar, enhances sorption of PAHs, which reduces partitioning and chemical activity of PAHs [52].

In order to manage PAH-contaminated soils, several techniques have been adopted to successfully restrict mobility and toxicity. The exposure and level of contamination can be reduced by either removing the contaminant or rendering it immobile. Bioremediation is the utilisation of microorganisms to biodegrade hazardous organic compounds into harmless substances like CO_2 and water [53]. The increase in SOM of contaminated soil can aid remediation by locking up organic pollutants; however, if the SOM was to be degraded by microorganisms or by photochemical degradation [54–56], it could eventually result in the remobilisation of organic contaminants into the soil environment, thus the soil would become a source rather than a sink [36]. Indeed soil carbon losses have been observed in different regions of the world, with losses of 0.12 kg cm^{-2}y^{-1} and net losses of about 2.9 kg cm^{-2} in the previous 26 years across 2000 sites in England and Wales [57], thus making bound residue of contaminants a postponed problem [36]. Furthermore, the coupling of pollutants to the humic component of SOM may form more toxic compounds, such as dioxins and furans [58]. Therefore, successful management techniques have involved the introduction of recalcitrant SOM into the soil that can enhance the "locking up" of pollutants while providing suitable habitats and substrates for microbial degradation of bioavailable contaminants [59–64]. This can be achieved by the addition of biochar to soils [14,65,66].

2.2. Current Uses of Biochar

Lehmann and Joseph [67] defined biochar as a carbon-rich product obtained when biomass, such as wood, manure, or plant residues are heated in a closed system with little or no air. During exploration in the Amazonia, European explorers in the 19th Century discovered dark soils that have been referred to as the "Terra Preta" soils, which are known to contain large amounts of char-derived carbon and exhibit higher levels of microbial activity and improved nutrient availability and crop yield compared to soils with little or no biochar addition [67–69]. It has been suggested that the indigenous population in the Amazon adopted the process of mulching, burning, charring and application of charcoal and ash to increase soil quality [70]. Biochar has often been produced under controlled temperatures in the absence of oxygen and applied to soils and, in recent times, it has been favoured as a soil management tool due to its long-term stability and recalcitrant nature with soil sequestration capabilities for economic and environmental benefits [67,68,71].

Biochar is produced with the intent of improving soil productivity, carbon storage, mitigation of climate change or filtration of percolating soil water [67]. The increased research and development on strategies to improve and produce bioenergy from renewable energy sources to contribute to the energy needs of developing and developed societies will contribute to the deposition of biochar-like products into the environment [72]. Additionally, it may be produced as a result of uncontrolled bush burning or wild fires and then deposited onto soil [73], and it has been reported that biochar-amended soils have the ability to retain moisture, increase cation exchange capacity (CEC), increase adsorptive capacity and increase pH [74]. The biochar within such soils is thought to be highly stable for thousands of years, being resistant to biochemical decomposition, but the extent of this recalcitrance may well be dependent on the production process [75]. Therefore, there could be growing applications of biochar to soils for agriculture, waste management, carbon capture and contaminated land remediation.

2.3. Biochar Production

Wood is primarily composed of lignin, cellulose, hemicelluloses. However, all wood species vary in chemical compositions, thus the structure of lignin in softwood differs from that of hardwood [76]. The pyrolysis of biomass can be carried out in a reactor via gasification or carbonisation at varying temperatures and times depending on the intended use of the end product. A wide variety of waste biomass materials (wood, manure, rice husk, sewage sludge, municipal waste) can be used to produce biochar [77–79], but this study cannot touch on all of them; however, Verheijen *et al.* [79] critically discussed the potential types of feedstock and the production procedures (pyrolysis).

During heating, there are mass losses, chemical transformations and structural changes, which largely depend on the duration of heating, initial moisture, wood species and temperature of treatment [78,80]. The final thermal conversion of wood yields three basic products; liquid (liquid hydrocarbon and water), solid (biochar) and gas [81]. Wood feedstock, containing higher lignin content, produce the highest biochar yields at 500 °C compared to lower and higher temperatures of pyrolysis [82]; Table 1 highlights the fate of feedstock in a thermal treatment reactor. The physicochemical properties of the biochar largely depend on the heating temperature. For example,

biochar generated at a lower temperature of 350 °C may contain large amounts of favourable nutrients, whilst having lower sorptive capacities than those generated at a higher temperature of 800 °C [83]. This is because the carbon content and aromacity increase with temperature, while oxygen, hydrogen, and polarity decrease with an eventual increase in the volume of micropores [84].

Table 1. Fate of initial feedstock mass in percentage (%) between products of pyrolysis processes [85].

Process	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)
Fast pyrolysis Temperature at 500 °C Short vapour residence time (seconds)	75	12	13
Intermediate pyrolysis Low moderate temperature Moderate vapour residence time (hours)	50	25	25
Slow pyrolysis Low moderate temperature (400–600 °C) Long vapour residence time (days)	30	35	35
Gasification High temperature >800 °C Long vapour residence time	5	10	85

At low temperatures, between 20 °C and 150 °C, wood dries, resulting in a loss of mass, after which hemicelluloses become modified [80] by deacetylation and depolymerisation, whereby released acetic acid acts as a catalyst in the depolymerisation of the polysaccharides [86–88]. There is further dehydration of hemicelluloses resulting in a decrease in the number of hydroxyl groups [89]. At temperatures above 250 °C, lignin carbonisation occurs, thereby resulting in increases in the carbon content forming char, while the concentrations of oxygen and hydrogen decrease [90]. This is accompanied by structural changes and condensation reactions to form lignan [76], with the emission of CO_2 and VOCs [80]. High temperatures can induce the polymerisation of the modified chemical products to form larger molecules that are aromatic and aliphatic in nature [79]; furthermore, there are increases in pore volume and surface area at higher temperatures [91–93]. However, the feedstock material determines the peak temperatures at which the micropores are opened up within the biochar. This was reported by James *et al.* [91], where heating at 820 °C resulted in reduction of micropores and surface area of wood when compared to that at 700 °C. This indicates that there may be a peak temperature to open all pores (micro-, meso-, macro-) for each feedstock material; exceeding such temperatures may further encourage reduction in distribution of micropores. To describe this phenomenon, Table 2 elucidates the impact of heating temperature and residence time on specific surface area and total pore volume of different biochar feedstock materials.

Table 2. Characteristics of biochar from different production processes [91,94–96].

| Feedstock	Temperature (°C)	Residence time	BET N$_2$ Surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Ash content (%)
Orange peel	250	6.0 h	33.3	0.0202	1.05
	500	6.0 h	42.4	0.0191	4.27
	700	6.0 h	201.0	0.0350	2.79
Switch grass	500	1.5 s	21.6	n/a	54.60
Corn stover	500	1.5 s	7.0	n/a	49.70
Switch grass	500	2.0 h	50.2	n/a	52.50
Corn stover	500	2.0 h	20.9	n/a	32.40
P. sylvestris	300	1.0 h	1.0	0.0017	n/a
	500	1.0 h	320.0	0.1860	n/a
B. pendula	300	1.0 h	2.3	0.0035	n/a
	500	1.0 h	6.5	0.0068	n/a
	700	1.0 h	430.0	0.2530	n/a
	820	1.0 h	66.0	0.0600	

3. Interactions between Biochar and Soil

When biochar is incorporated into soil, it exhibits natural oxidation through the formation of functional groups, thereby providing sites that can retain nutrients and other organic compounds [97,98]. The oxidation processes include; (1) increases in O and H and decrease in C contents; (2) the formation of *O*-containing functional groups, and (3) a decrease of surface negative charges [98–100]. This potential can be enhanced by the biochar production temperature [88,98] and the use of chemical oxidants [89,101]. However, when biochar particles are aged in soil, further oxidation leads to the evolution of negative charges there by increasing the CEC [102]. Browdowski *et al.* [103] showed that oxidised biochar particles may be bound to soil minerals through association with clay and silt-sized minerals, small biochar particles bound to minerals and small minerals bound to large biochar particles, thus decreasing the potential of its decomposition. When bound to soil minerals, which often happens rapidly, it can enhance the ability of the soil-biochar complex to sorb organic compounds present in soil. Biochar also interacts directly with organic matter of soil by sorption [102].

3.1. Biochar Adsorption and Stability

The sorptive capacity of biochar to HOCs is controlled by carbonised and non-carbonised fractions and the surface and bulk properties of biochar [104,105]. Sorptive characteristics can equally be affected by hydrophilic groups on biochar [91]. The adsorption of aromatic molecules, such as PAHs to wood chars is rapid and is assisted by π-π electron interactions and pore-filling mechanisms [96], multilayer adsorption, surface coverage, condensation in capillary pores, and adsorption into the polymetric matrix [106]. When a portion of a HOC is sorbed to the exterior surfaces of biochar and other portions are trapped within internal nanopores, it limits the mass transfer of the chemical to microorganisms [107] (Figure 2). Figure 2 shows an illustration of non-bioavailable HOCs entrapped

within biochar sorption sites, whilst some fractions are located on desorbable sites for microbial degradation.

Figure 2. Description of HOC availability to microorganisms. Adapted from [11].
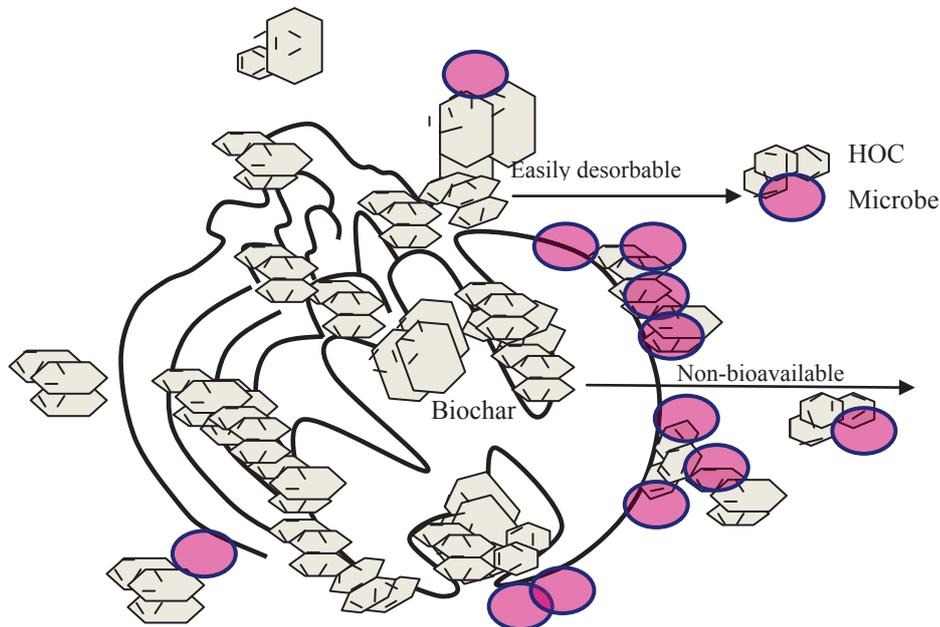
Despite being highly recalcitrant, biochar has the potential to be degraded by microorganisms co-metabolically [108]. This was demonstrated by labelling biochar feedstock with ^{14}C before pyrolysis and exposing the biochar to microorganisms in the presence of glucose. Following the removal of the glucose, biochar decomposition decreased strongly [109]. Hamer *et al.* [108] also showed that the stability of biochar is attributed to the feedstock, as corn stover and rye char were decomposed more rapidly than wood char. Biochar, derived from mango prunings, has been shown to have a mean residence time of 600 years at 26 °C and 3264 years at 10 °C with low mineralisation rates under field conditions; however, the major loss mechanism of biochar has been attributed to erosion fluxes [110]. When biochar-like particles were mixed with soils, biotic degradation was shown not to exceed 2% after 96 days of mineralisation [111]. Mašek *et al.* [112] explained that the stability of biochar is tailored to the carbon yield within the solid product and the carbon yield contains both non-stable and stable fractions. Using accelerated aging techniques, the authors showed that the fraction of stable biochar is slightly independent on pyrolysis temperature, whilst the CO_2 evolution from incubation of biochar in soil refers to non-stable fractions. The non-stable fraction consists of labile and semi-labile types, where the former represents the part of biochar microbiologically released within months of application and the latter is a large portion of biochar composed of more recalcitrant compounds that can remain for years to decades after application and further be stabilised [112]. However, degradation of biochar occurs through biological, chemical and physical processes [110,112,113], Thus, when considering degradation based on half-life, Spokas [113] further explained that when O:C ratio of biochar is <0.2 then the half-life of biochar will be over 1000 years; whereas, when the O:C ratio is >0.6, the half-life will be less than 100 years. It is therefore very important to determine the O:C ratio of biochar to illustrate the potential extent of stability of biochar

in soils. Also, the interaction and fate of organic contaminants with biochar in soil requires proper understanding in order to apply it as a soil amendment.

3.2. Fate and Behaviour of Organic Contaminants within Biochar-Amended Soils

HOCs are considered to be ubiquitous contaminants in nature and are often found in high concentrations at industrial sites, especially those associated with petroleum, gas-production and wood-preserving due to spills, leakages, processing, use and disposal [53]. Other sources include burning of fuels and vegetation, vehicular emissions, volcanic eruption, cigarette smoking, sewage discharge, leachate from garbage, livestock waste, shipping and boating activities and maintenance and forest fires [114]. Amendment of soils with biochar has the potential to be an inexpensive, relatively novel strategy to mitigate the risk of organic compound contamination and exposure in soils. In this regard, the studies described in this section elucidate the sorption, desorption and biodegradation of PAHs, dioxins, furans and pesticides in biochar-amended soils.

3.2.1. Sorption of Organic Contaminants

Several studies have shown that the presence of biochar in soils can enhance the sequestration of organic contaminants. For example, Chen *et al.* [115] showed that pine needle biochars, produced under increasing temperature of pyrolysis for six hours, contained increasing concentrations of carbon content and surface area due to destruction of aliphatic alkyl and ester groups. The sorption of naphthalene, nitrobenzene and *m*-dinitrobenzene increased non-linearly with the increase in the temperature of biochar production. Similarly, Bornemann *et al.* [92] reported increases in the sorption of benzene and toluene onto red gum charcoal produced at higher temperature. This was also supported by Chen and Yuan [116] in pine needle biochar-amended soils spiked with naphthalene, phenanthrene or pyrene. More recently, Oleszczuk *et al.* [117] reported that addition of either AC or biochar as an adsorbent can mitigate the mass transfer of contaminants from PAH-containing sewage sludge matrix into pore-water. Sewage sludge shows unique nutritional properties due to the presence of plant nutrients within its matrix; however, the presence of bioavailable PAHs can limit the effectiveness of use [118]. Using polyoxymethylene (POM) passive samplers, the increasing concentrations and contact-time of AC or biochar mixed with sewage sludge constantly reduced the freely dissolved PAH content of the sewage sludge due to diffusion of the PAHs from sewage sludge through water and humic layers to micropores of adsorbents [117]. This finding was similar to that of dioxin and furan-contaminated soils where biochar markedly decreased the passive uptake of the toxic contaminants into POM samplers with increase in contact-time and concentration [119]. The increasing heat treatment on biochar feedstock reduces volatile matter, enhances the carbonisation, aromatic structure formation and surface area of the resultant biochar that is highly microporous [92,116,120]. Noticeably, biochar contains both carbonised (glassy) and non-carbonised (rubbery) fractions, where the former is categorised with non-linear competitive adsorption of organic contaminants and the latter is associated with linear non-competitive partitioning of organic contaminants [115,116,121].

When solute concentration is taken into consideration, Chen *et al.* [115] and Chen and Yuan [116] showed that increasing concentrations of solute results into decreased sorption of solutes across all

ranges of biochar, thereby shifting adsorption to partitioning. However, the increased concentration of biochars categorically enhanced adsorption due to increased micropore quantity in amended soils.

The appropriate feedstock for biochar production as a soil amendment for contaminated land mitigation is still a bone of contention. Generally, biomass waste is desirable as a feedstock but research has shown that the type of feedstock used can equally affect the ability of biochar to sorb organic contaminants. With respect to this, Bornemann *et al.* [92] showed that biochar produced from *Phalaris* pasture grass had a lower sorptive capacity compared to that of red gum wood biochar. The authors attributed the lower sorptive capacity to a combined effect of lower surface area, higher mineral salts and lower lignin contents of the feedstock and biochar product, which would have affected sorption. Similarly, Oleszczuk *et al.* [117] showed that paper mill waste reduced freely dissolved PAHs to a greater extent compared to maize stover biochar due to the higher aromacity and carbonisation of the former. Generally, wood biochars contain more phenolic groups due to the higher lignin content of the feedstock and have higher surface areas [122,123]. Additionally, the difference in the particle size of biochar has been thought to have little or no effect on sorption of PAHs due to similar surface areas [124]; however, the smaller the particle size, the shorter the time for sorption equilibrium to be attained [121]. Despite the total reduction in uptake of dioxins and furans into POM samplers in AC or biochar-amended soils, smaller particle-sized amendments show more rapid mass transfer of contaminants to micropore sites [119]. Further, Chai *et al.* [119] illustrated that although intact coconut AC had a higher surface area, its granular and larger particle-sized forms reduced sorption efficiency when compared to its grounded form and other smaller particle-sized AC and biochars. Sorption strength is thus mainly governed by the internal nanoporosity as more time will be required for organic contaminants to reach micropore regions of larger particle-sized biochars [119,121,124].

Contaminated land tends to contain complex mixtures of both organic and/or inorganic contaminants [2,3,125,126]. The presence of co-contaminants may affect the sorption, desorption, bioaccessibility and biodegradation of the target compound. For example, Wang *et al.* [127] purchased wood biochar from a supermarket and subjected part of it to further charring under oxygen-limited conditions for 3 h in order to reduce the O functional groups. The sorptive potential of pyrene was assessed in a single system and in a bi-solute system comprising either of the following compounds: phenol, 2,2-methylene-bis (4-methyl-6-*tert*-butylphenol) (MMBP), phenanthrene and benzo (a) anthracene (BaA). There was a corresponding increase in the aromatic content by 20%, as well as increase in surface area, micropore volumes and polyaromatic sheet rearrangement with a disorder of organic carbon structure. This resulted in low phenol competitiveness to pyrene on non-treated rather than treated biochar due to its lower hydrophobicity, pore distribution, surface chemistry of sorbent and molecular size compared to pyrene. In support of this, the sorption of atrazine decreased in the presence of increasing concentrations of simazine in biochar produced from greenwaste mixture of maple, elm and oak woodchips and barks at 450 °C for an hour [121]. The authors discovered that it was similar for simazine sorption in presence of atrazine due to competitive sorption between the two pesticides on biochar. Based on these findings, biochar sorption of organic contaminants is governed by the feedstock, production process, biochar surface chemistry, nanopore distribution and particle size, sorbate concentration and physicochemical properties, aging period and soil properties. Noticeably, the higher production temperature and concentration of wood biochar and increased aging

periods show non-linear adsorption mechanism of sorption due to more carbonised and nanopore fractions. Similarly, the smaller the particle size, the more rapidly HOC equilibrium is reached.

3.2.2. Desorption Mechanism Studies

The desorption of PAHs from soils has been intensely studied in recent years [27,38,65,128]. Zhou *et al.* [128] studied the desorption of pyrene and phenanthrene from sawdust wood-derived charcoal produced at 400 °C for 4 and 8 h, respectively, to produce two pine-wood charcoal samples (PC2 and PC3). Charcoal characterisation results showed that PC3 was more aromatic with a greater binding force and had greater pore volume than that of PC2 but both had similar specific surface areas. Pre-loading charcoal with humic acids resulted in reduction in pore volume due to a pore-blocking mechanism and altered surface properties. Rapid desorption was observed on the PC2 at high concentrations (2000 mg L^{-1}), thus desorption takes a shorter time at higher pollution levels on such charcoal. However, upon 25 days aging of PAH-charcoal sample, PAH desorption rates reduced. Aging evidently gave time for the PAHs to locate difficult accessible sites and encourage HOC physical entrapment in irreversible sorption sites. Furthermore, the authors disclosed that desorption of phenanthrene was greater than that of pyrene due to their difference in properties, in which phenanthrene was thought to diffuse more rapidly than pyrene into nanopores due to a difference in molecular size.

More recently, Rhodes *et al.* [65] investigated desorption kinetics of phenanthrene from activated charcoal (AChar)-amended soils using hydroxypropyl-β-cyclodextrin (HPCD) sequential extractions. The different soil types were amended with AChar between 0.1% and 5% concentrations, where increase in concentrations of AChar resulted in a 7.8-fold decrease in rapidly desorbed fraction (%F_{rap}) and corresponding decrease in (slow desorbed fraction) %F_{slow}. Similarly, as the soil-PAH contact time increased, the %F_{rap}, which represents labile fractions of the compound [38] decreased due to strong pore sorption. The pore sites within such black carbons prove to be impervious to aqueous-based extraction solutions [129] and variations in soil physicochemical properties showed no effect on phenanthrene desorption in AChar-amended soils. Additionally, desorption of low concentrations of phenanthrene (≤5 μg L^{-1}) freshly sorbed to either AC-, biochar- or compost-soil suspensions onto a silicone O-ring was investigated by Marchal *et al.* [130]. The desorption data showed the freely dissolved phase, partitioning and potential biota uptake. Interestingly, the extent of phenanthrene desorption was dependent on the desorption media and was in the following order: compost > biochar > AC, due to higher surface area and volume of nanopores in AC and biochar [130].

Pyrimethanil desorption behaviour was assessed in soils containing red gum biochar produced at 450 °C (BC450) and 850 °C (BC850) by Yu *et al.* [131]. The data showed that as concentrations of biochar increased, the degree of non-linear sorption increased, whilst BC850 showed greater extents of sorption compared to BC450 and control soil. When desorption studies were carried out, >50% of pyrimethanil was desorbed from unamended (control) soil, whilst 13.5% and 1.49% of pyrimethanil was desorbed from 5.0% BC450 and 1.0% BC850, respectively. BC850 likewise showed greater effect on desorption due to its higher microporous nature compared to BC450. Strong sorption led to slow and irreversible desorption of the compound from microporous sorption sites, which can reduce plant

uptake of pesticides. In order to test this hypothesis, Yang *et al.* [132] investigated the effect of cotton straw biochar produced at 450 °C (BC450) and 850 °C (BC850) on the dissipation of chlorpyrifos and fipronil in soil-containing Chinese chives (*A. tuberosum*). Noticeably, pesticide dissipation decreased with increasing biochar concentration, in which a greater effect was observed in B850-amended soil compared to BC450. Following 35 days of incubation, 68% and 58% of chlorpyrifos and fipronil were lost from non-sterile control soil, respectively, whilst 28% and 24% of chlorpyrifos and fipronil were lost from sterile soils, respectively. However, the dissipation of the pesticides was higher in presence of plants than in soil only. The authors suggested that microbial degradation and plant uptake were key factors responsible for the dissipation of the pesticides. Interestingly, the presence of biochar in the soil increased the half-life of the pesticides under non-sterile conditions, in which 1% BC850 reduced the concentration of both pesticides in the plant and increased biomass production. This shows that biochar can serve as a soil amendment, reducing the availability of organic contaminants to biota in soil and the degree of reduction is governed by the biochar type, production process, biochar concentration and chemical property. In summary, increased aging periods, higher production temperature and concentration of biochar enhances sorption of HOCs and subsequently retards desorption of the HOCs thereby reducing the availability and uptake of the contaminants in soil.

3.2.3. Biodegradation

In assessing the bioavailable and bioaccessible fractions of PAHs, HPCD extraction has been shown and described to predict the rates and extents of microbial degradation of PAHs in soils [25,26,47,133–135]. Thus, it serves as a biomimetic tool to predict the bioaccessible portion of PAHs in soils [10]. It is believed that the increased sorption of organic contaminants will decrease the bioavailable/bioaccessible fraction of contaminant for uptake and biodegradation [128,131,132]. Rhodes *et al.* [14] first assessed the extractability of spiked PAHs using HPCD in black carbon (BC)-amended soils. Results showed that amount of extracted ^{14}C-phenanthrene decreased with an increase in black carbon concentration and contact time (Figure 3) with <1% extracted in soils amended with >2% BC. This was, however, suggested to be due to low displacement capacity of HPCD within BC matrices. Furthermore, there was good correlation between amount of ^{14}C-phenanthrene extracted and extents of mineralisation at BC concentrations of 0% and 0.1%. The authors concluded that at high concentrations of such BC, HPCD would not predict biodegradation of the PAH. With respect to Figure 1, the addition of biochar to soils will eventually result in decreases in desorbable and bioaccessible (biodegradable) fractions, whilst increasing the non-extractable fractions as illustrated in Figure 3.

Figure 3. The influence of contact time on the extractability and bioaccessibility of a contaminant in biochar-amended soil.
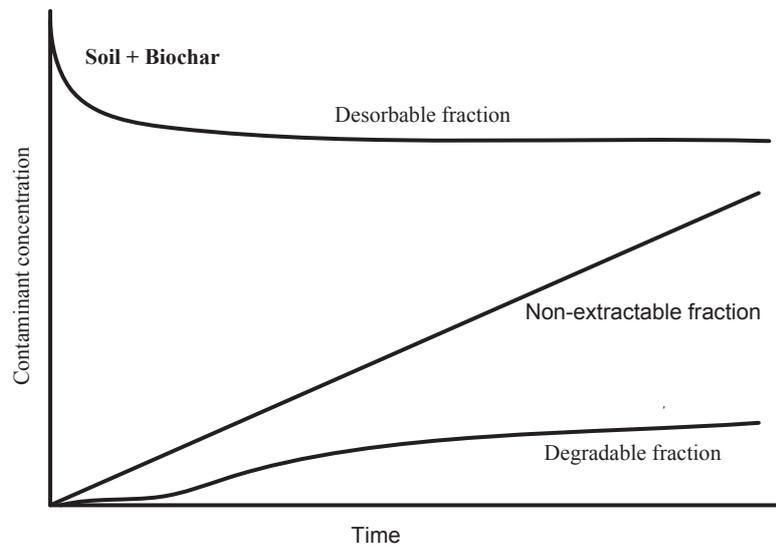
Similarly, Rhodes *et al.* [12] investigated biodegradation of ^{14}C-phenanthrene in soils amended with activated charcoal (AChar) and effect of pre-exposure on catabolic development upon mineralisation. Adaptation of indigenous microorganisms in the PAH spiked soils led to a reduction in lag phase with corresponding increase in extents of mineralisation upon aging. Additionally, the increase in lag phases, reduction in fastest rates and extents of ^{14}C-phenanthrene mineralisation was due to increase in concentrations of AChar. There was enhanced sorption and decline in bioaccessibile fraction of the PAH due to limited or slow desorption of ^{14}C-phenanthrene. In conclusion, the authors stated that higher concentrations of AChar reduce the bioaccessible pool of the contaminant resulting in retardation of the development of indigenous microbial catabolic activity within the soil. Figure 4 illustrates the potential effects of increasing biochar concentrations on the bioavailability and bioaccessibility of organic contaminants. Currently, there is limited information in the literature on the impact of biochar on the catabolic activity of PAHs during mineralisation. Marchal *et al.* [130] investigated the co-metabolic biodegradation of phenanthrene sorbed to suspensions containing either AC, biochar, or compost-amended soils using a *Sphingomonas* sp. inoculum. Interestingly, the authors discovered that sorption did not inhibit the biodegradation activity of phenanthrene by the bacterial inoculum due to the sufficient numbers of phenanthrene degraders, difference in growth media, and optimal assay conditions. Although the properties of the AC and biochar were not stated, the authors suggested that there is a time window for freshly spiked PAHs to be biodegraded. Biodegradation of spiked volatile petroleum hydrocarbons from NAPLs in wood chip derived-biochar (fast pyrolysis)-amended sandy soil was investigated by Bushnaf *et al.* [63] and found that biodegradation of water-dissolved available compounds was faster in biochar-amended soil. The adsorption of monoaromatic compounds onto biochar actually enhanced the biodegradation of branched and cycloalkanes, whilst the dissipation of the hydrocarbons was markedly reduced. This illustrates that in a mixed contaminated soil, biochar tends to reduce the availability of strongly sorbing compounds and allows degradation of less sorptive compounds [63]. In using earthworms to measure

bioavailability/uptake of dioxins and furans into biota, Chai *et al.* [119] demonstrated that both AC and biochar can reduce the total concentrations of the contaminants within biota. Currently, there is no universal approach for determining the bioavailability/bioaccessibility of organic contaminants in soil. Similarly, there is no universal approach to measure freely dissolved HOCs; however, using mild extractions and passive samplers such as (PDMS and POM) are vital, the chemical activity of the reversibly bound and freely dissolved (unbound) fractions of a contaminant in equilibrium can be transferred onto the sampler which provides information on bioconcentration in soils [10,29,48–50]. This would be vital in determining the direction of diffusion of hydrophilic, sorbing and strongly sorbing contaminants in a complex system [48]. In so doing, the diffusion rates and extents of contaminants in biochar-amended soils can be determined, whereby it is suggested that chemical activity can predict the potential partitioned and freely dissolved concentrations that are available for uptake. Although AC and biochar differ physico-chemically, the extent of sorption, reduction in bioaccessibility and chemical activity by biochar is less than that of AC but follow a similar trend. The advantage of biochar here is that it encourages microbial activity that also encourages contaminant catabolism [63,69], unlike AC [12].

Figure 4. Diagram showing organic chemical flux arising from (**A**) bioavailable, (**B**) bioaccessible and (**C**) non-bioaccessible fractions in soil amended with black carbon at increasing concentrations in presence of biodegradation [29]. An increasing concentration of biochar results in decrease in bioaccessible/bioavailable fractions and biodegradation in soil.
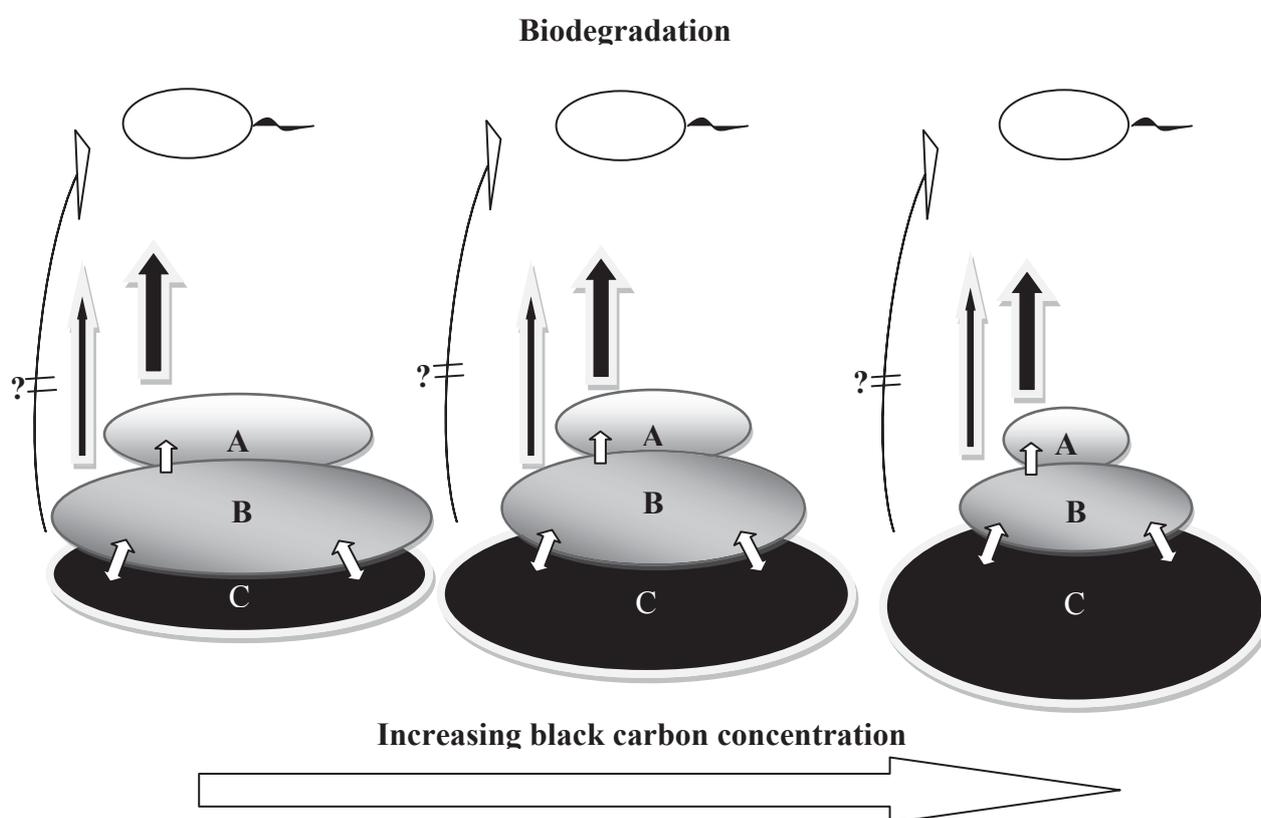
It is worthy of note that the sources and properties of HOCs differ considerably. For instance, PAHs naturally occur and are anthropogenically distributed, they are associated with soot, coal, coal tar and contain similar functional groups but are degradable [12,14,23]. Pesticides are often synthetic in nature and differ in functional groups and mode of action, some of which are banned due to toxicity and persistence in soils, whilst the degradability of pesticides has been linked to pH of the containing soil [136]. Dioxins and furans are unintentionally produced as byproducts from chemical processes associated with combustion of chlorine-containing materials [137]; they are very toxic and highly persistent in soil [138]. Since these compounds vary in source and properties, the level of sorption, bioavailability and desorption have been shown to vary in type of chemical due to structure and hydrophobicity [139,140]. Therefore, considerable investigation has to be undertaken to determine appropriate type and quality of biochar to be utilised for potential remediation of contaminated soils.

3.3. Application of Biochar in Remediation of Contaminated Soil

In order to remediate contaminated sites, bioremediation has often been employed successfully but, to a large extent, it has been assumed to be time consuming and costly. The utilisation of biochar in such contaminated sites is suggested to be an important tool to enhance remediation by governing the mobility and fate of the pollutants as a soil amendment. It is already known that biochar reduces bioaccessibility, chemical activity and ecotoxicity of organic compounds to receptors [15,52,126,141] and reduce risk of exposure to biota. When physical entrapment occurs, the parent molecule or its metabolite becomes less bioavailable upon aging, chemical bonding (covalent) may result in indistinguishable bound residues [29,36]. A key component of contaminated land mitigation is to identify and remove unacceptable risks or harm to human health and the environment. This paper suggests that with appropriate investigation and application, biochar will evidently be useful in sequestering and reducing associated risk of HOCs, and other inorganics in soils. Thus, it will reduce and disrupt pollutant linkages, the mobility or run-off of such substances that may cause harm or pollution to controlled waters and biological systems. Knowing that no two biochars are same, a major question is what type of biochar will be preferred for a certain contaminant and how long will it retain the contaminant in question when practically applied in the soil environment. In respect to contaminant concentrations and types, there exists a maximum solid-phase irreversible capacity that should be predicted based on biochar micropore distribution and it should be investigated to elucidate whether biochar can introduce more contaminants into soil [142]. Indeed, during the pyrolysis process, volatile organic compounds (VOCs), furans and PAHs can be found within biochar matrix in varying mixtures and concentrations [123,140,143,144]. Thus the presence of these compounds can pose concerns, having potentially deleterious impacts on biota and potentially increasing the concentration of HOCs in biochar-amended soils. However, the total quantities of these compounds can be controlled by selection of feedstock, oxygen availability, production temperature, combustion efficiency, post-production handling and storage under controlled conditions [123,140,145,146]. For instance, Spokas *et al.* [123] and Freddo *et al.* [145] showed that at higher temperature of pyrolysis, the total PAHs and VOCs reduced markedly, whilst shorter residence times produced higher PAH concentrations [140]. Although some wood derived biochars show reduced PAH concentrations, during slow pyrolysis, the PAHs generated escape to gaseous phase, whilst short residence time allows

the condensation of PAHs on biochar surfaces [140]. Despite the presence of PAHs on biochar surfaces, the total concentrations of PAHs in a wide range of biochars were comparable to background soil levels and well below concentrations found in coal, soot, urban dust and sewage sludge [140,143,145]. However, Hilber *et al.* [146] found extremely high concentrations of PAHs in elephant grass and coniferous wood derived biochars. The majority of studies on quantitative analysis of PAHs on biochar have been based on total concentrations; for example, Freddo *et al.* [145] and Hale *et al.* [140] showed that water-based extractions and bioavailable fractions (POM sampling) of PAHs on biochar were often below the limits of detection or much lower than the total concentrations because PAH fractions could become occluded within the biochar structure. When biochar is applied to agricultural soil, the eventual PAH concentrations will depend on background PAHs in the soil, sorbed PAHs on biochar, and concentration of biochar applied [144]. This explains why application of biochar into some soils has not resulted in the introduction of PAH contamination [130]. Thus, the feedstock, application rate, and production process, as well as post-handling of biochar still need to be investigated in order to know if and how biochar application will introduce contamination when applied to soil. Preferably, wood-derived biochar produced at high temperatures under slow pyrolysis will contain lower concentrations of PAHs [140,144,145]. It is, however, worthy of note that the quality (nanopore distribution and chemical properties) of biochar is of greater importance than the quantity, as it is suggested that the higher quantity can be more expensive and may have deleterious effects on the receiving soil due to the presence of intrinsic hydrocarbons [131,132,147].

Another question relates to the effectiveness of biochar addition due to potential biodegradation and release of pollutants. Long-term degradation studies of different types of biochar containing contaminants should be investigated to provide significant illustration in literature.

Based on the fact that biochar nutrient properties enhances plant growth and microbial activity and have shown to enhance biodegradation of bioaccessible contaminants [63,132,148,149], it can be used in a systematic concept to promote phytoremediation. The macropores serve as a route for adsorbate exposure to the micro- and meso-pore regions, and also as a habitat for microorganisms [61,62,150]. While locking up organic contaminants, the bioaccessible (reversibly bound and freely dissolved) fraction may become degraded by selected plants for phytoremediation, whilst biochar provide nutrients and moisture to enhance a rapid plant growth [132]. Yu *et al.* [151] showed that mineralisation of pesticides by plants was enhanced by the presence of biochar in soil, which is supported by Yang *et al.* [132]. Future studies should also investigate if during phytoremediation, which has been regarded as a long process can become rapid with different concentrations and types of biochar. Similarly, the microbial degradation of bioaccessible fractions of organic contaminants can be enhanced in the presence of biochar, whilst the volatilisation is mitigated as per Bushnaf *et al.* [63]. Stability of biochar has been shown to be long term [110], but the ability or duration of sequestering these pollutants is uncertain.

4. Conclusions

Frequent exploration of natural resources, industrial activities, transport, energy demand and increase in population results in persistent release of organic contaminants into the soil environment [2–4]. In particular, PAHs gain contact with soils and are subject to volatilisation,

biodegradation, photodegradation and physical transport [10,19]. The fate of HOCs in the environment is of prime importance in order to prevent severe contamination to the environment. As a result, the mobility of the organic compounds is governed by its physicochemical properties, environmental conditions, and the properties of the soil matrix [10,14,21]. Within soil, black carbon materials such as biochar influence the bioavailability and bioaccessibility of these compounds through sorption and entrapment. This influence can be observed through the rates and extents of sorption, desorption and biodegradation of HOCs in biochar-amended soils, whilst the biochar concentration, production conditions, feedstock and chemical properties are also determining factors [28,65,127]. Despite the presence of co-contaminants, biochar still strongly affected the total and bioavailable fractions of PAHs [126,127]. As a result, biochar can be a crucial tool to remove unacceptable risks by disrupting pollutant pathway of HOCs to humans and the environment. The minerals within biochar serve as source of nutrients to microorganisms and plants which can additionally aid the growth of microbes and plants used for biodegradation of PAHs [132,148,150,151]. However, the majority of studies have been proven to be positive only within confined laboratory conditions, thus extensive investigations are required on field contaminated land.

Acknowledgments

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