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Advances in research on the use of biochar in soil for remediation: a review

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Abstract

Purpose Soil contamination mainly from human activities remains a major environmental problem in the contemporary world. Significant work has been undertaken to position biochar as a low-cost material useful for the management of contaminants in various environmental media notably soil. Here, we review the increasing research on the use of biochar in soil for the remediation of some organic and inorganic contaminants.

Materials and methods Bibliometric analysis were carried out within the past 10 years to determine the increasing trend in research related to biochar in soil for contaminant remediation. Five exemplar contaminants were reviewed in both laboratory and field-based studies. These included two inorganic (i.e. As and Pb), and three organic classes (i.e. sulfamethoxazole, atrazine, and PAHs). The contaminants were selected based on bibliometric data and as representatives of their various contaminant classes. For example, As and Pb are potentially toxic elements (anionic and cationic, respectively) while sulfamethoxazole, atrazine, and PAHs represent antibiotics, herbicides and hydrocarbons, respectively.

Results and discussion The interaction between biochar and contaminants in soil is largely driven by biochar precursor material and pyrolysis temperature as well as some characteristics of the contaminants such as octanol-water partition coefficient (K_{OW}) and polarity. The structural and chemical characteristics of biochar in turn determine the major sorption mechanisms and define biochar's suitability for contaminant sorption. Based on the reviewed literature, a soil treatment plan is suggested to guide the application of biochar in various soil types (paddy soils, brownfield and mine soils) at different pH levels (4 – 5.5) and contaminant concentrations (< 50 and > 50 mg kg^{-1}).

Conclusions Research on biochar has grown over the years with significant focus on its properties, and how these affect biochar's ability to immobilize organic and inorganic contaminants in soil. Few of these studies have been field-based. More studies with greater focus on field-based soil remediation are therefore required to fully understand the behavior of biochar under natural circumstances. Other recommendations are made aimed at stimulating future research in areas where significant knowledge gaps exist.

Keywords Contaminants • Immobilization • Inorganic • Organic • Laboratory • Field • Sorption

1. Introduction

The contamination of soil by organic and inorganic contaminants is one of the major environmental challenges faced by the world. Growth in industrial activities, increased use of pesticides, herbicides, antibiotics, agricultural fertilizers, and fossil fuel consumption often leads to soil contamination with potential severe health risks to the human population. Both policy makers and scientists have continued to seek novel ways of managing contamination from organic and inorganic compounds in soil. Phytoremediation, precipitation, ion exchange, membrane filtration and coagulation are some of the ways that have been used for the treatment of pollution in soil and water (Ferniza-García et al. 2017; Paz-Ferreiro et al. 2014). However, these techniques are not always cost-effective and may end up generating contaminant-rich waste. This has in part prompted researchers to investigate the use of readily available biochar materials to mitigate contamination issues in soil (Lehmann et al. 2015; Qian et al. 2015; Yang et al. 2017).

Research relating to biochar has been on-going since the discovery of *terra preta* by James Orton in 1870 (Ahmad et al. 2014; Lehmann et al. 2009; Lehmann et al. 2015). As a result of its high permeability, biochar has also been demonstrated as an attractive material for the sorption of suspended particulate matter, capture of potentially toxic elements (PTEs) and the sorption and/or degradation of biological pathogens (Reddy et al. 2014). Biochar has also been reported as an effective material to improve soil properties and reduce the hazardous effects of soil acidification (Dai et al., 2017b). Researchers have performed elaborate tests on biochar derived from many different biomass materials (e.g. wood, yard wastes, leaves, bones, sludge, etc.). Until date, questions are still being raised whether biochar is a source or a sink of organic and inorganic contaminants (Hilber et al. 2017b). However, the majority of these studies have suggested that biochar has the ability to sorb most organic and inorganic contaminants from soil and water at rates depending mainly on specific biochar properties as underpinned by the type of biomass material used and pyrolysis temperature applied (Fabietti et al. 2010; Silvani et al. 2017).

Until recently, the addition of biochar to soil has largely focused on its ability to improve soil quality physically, chemically and biologically (Guo et al. 2016; Manyà, 2012) rather than its ability to remediate contamination. Many more studies have, (within the past 5 years), been carried out dealing with soil contamination and the use of biochar for remediation (Qian et al., 2015; Wang et al., 2017; Yang et al., 2017).

This review is aimed at assessing significant research contributions in the use of biochar for the management of five contaminants in soil (three organic and two inorganic). The contaminants [arsenic (As), lead (Pb), sulfamethoxazole (SMX), atrazine and polycyclic aromatic hydrocarbons (PAHs)] were selected based on bibliometric analysis as discussed in section 2 and as representatives of their various contaminant classes. For example, As is a metalloid representing inorganic anions, Pb represents inorganic cations, atrazine and sulfamethoxazole are mobile (polar/ionic) compounds representing herbicides and antibiotics, respectively while PAHs are nonpolar and hydrophobic representing hydrocarbon contaminants. The review focuses on the known properties of biochar and contaminants and how these interact in sorption or immobilization processes in soil. It differentiates sorption efficiencies in the laboratory or greenhouse and in the field under natural environmental conditions and outlines the challenges faced in the field application of biochar for soil remediation. The review also presents a treatment plan (based on assessed literature) aimed at guiding the use of biochar on contaminated soil at various pH levels. In addition to contaminant sorption, soil remediation may encompass aspects of phytoremediation, revegetation, and the complete restoration of several ecosystem services including biomass production and carbon sequestration. However, these aspects were well outside the scope of this review.

2. Bibliometric analysis

An assessment in 2015 found that, nearly 46% of studies on the use of biochar in contaminant remediation focused on its sorption ability for potentially toxic elements (PTEs) while 54% have focused on the sorption of organic pollutants and other nitrogen and phosphorus related contaminants (Tan et al. 2015). Clearly, there has been a surge in research involving the use of biochar in soil as sorbent over the past decade (**Fig. 2a, Table S1**). Three key search words (*Biochar, soil, [As or Pb or SMX or atrazine or PAHs]*) were used in ScienceDirect database to retrieve publications from 2009 to 2017 focusing on the removal of the five contaminants considered in this review. Retrieved data was further sorted out to ensure that the publications were strictly on remediation of the contaminants of concern by biochar. A total of 1,508 publications were found from 2009 to 2017 (**Table S1**) involving all the five contaminants. Total yearly publications on all the contaminants increased from only 7 in 2009 to 572 in 2017 highlighting the increasing research interest on soil remediation using biochar. Pb had the highest number of publications (532) while sulfamethoxazole (SMX) had the least publications (60) within the study period (**Table S1**).

Field experiments involving the use of biochar on the five contaminants of interest were fewer within the study period (2009 to 2017) with only 39 publications found in field studies. This number also grew from zero (0) in 2009 to 11 and 6 in 2016 and 2017, respectively. The highest number of field studies were done on PAHs (15) followed by Pb (11) (**Fig. 1**). This significantly lower number of field studies may be attributed to some environmental constraints (changing temperatures, rainfall, microbial activity and soil pH) impeding the application of biochar in the field. The analysis of publications on field work suggest that significant work is required to assess the efficiency of biochar in the field and to translate laboratory or greenhouse results to field realities, consistent with the conclusions of Hilber et al. (2017a). The number of publications between 2009 and 2017 grouped according to publication type (i.e. research articles, review articles, book chapters, encyclopedia, abstracts, editorials, short communications and others) for Pb and PAHs **are** shown on **Fig. 2b**. The distribution of publications according to type for all five contaminants is presented on **Fig. S1**. The majority of publications were on direct research work totaling 962 for all five contaminants and closely followed by review articles totaling 249 for all five contaminants of interest. The rest of the publications were made in the form of book chapters, encyclopedia, abstracts, editorials, short communications and others (**Fig. S1**).

3. Biochar characterization

3.1. Description

Biochar has varied descriptions but three aspects are re-current; (1) biochar is dark, porous and very rich in carbon (usually 40 to 90%), (2) it is prepared by heating organic material at temperatures above 250 °C and (3) it is prepared under conditions of little or no oxygen supply (Ahmad et al. 2014; Fellet et al. 2011; Liu et al. 2015; Wang et al. 2015a). As a pyrogenic material, biochar can be distinguished from black carbon and activated carbon by its structure and function (Zhang et al. 2013). Black carbon generally refers to all naturally formed carbonaceous material (e.g. soots, charcoals) (Hammes et al. 2007; Samsuri et al. 2013). Activated carbon is formed from high temperature (~ 800 ºC) or chemical treatment of carbonaceous materials (Ahiduzzaman et al., 2016; Park et al., 2013b), with added steps to ensure high porosity and surface area, such as adding catalysts and inert gases. Biochar is generally less of a pure carbonaceous material than activated carbon, and as such it can include more O-containing carboxyl, hydroxyl and phenolic functional groups and the presence of inorganic minerals (Ahmad et al. 2014; Liu et al. 2015). Pyrolysis processes can be wet or dry depending on whether or not water was used during the pyrolysis. In dry pyrolysis which produces biochar often referred to as pyrochars (Han et al. 2016), only heat and little or no oxygen supply is required whereas wet pyrolysis which produces hydrochars (Han et al. 2016) involves the use of water and high pressure (Libra et al. 2011). This review focuses on pyrochars produced from dry pyrolysis of biomass.

3.2. Chemical changes during dry pyrolysis

Biomass responds to increased heating by undergoing chemical bond modification where aliphatic bonds are converted to aromatic bonds in biochar (Xiao et al. 2014a). During pyrolysis, hemicellulose decomposes first, at temperatures between 200 and 260 °C, while cellulose and lignin decompose at temperatures ranging from 240 to 350 and 280 to 500 °C, respectively (Liu et al. 2015). The transformative processes begin with biomass appearing crystalline and then quickly turning into amorphous carbon with altered bonds and chemical composition. The latter then converts into biochar with stacked sheets of poorly structured polyaromatic hydrocarbon sheets (graphene) which is finally consolidated to very strong graphitic sheets (Nartey and Zhao, 2014).

3.3. Surface chemistry

The surface chemistry of biochar is complex with heterogeneous chemical compositions which often depend on the type of biomass material and pyrolysis conditions. Biochar surface exhibits acidity (mainly supplied by carboxyl and hydroxyl groups) and basicity (mainly supplied by O and N functional groups and C−π electrons and some minerals like CaO, MgO, and $CaCO_3$) (Pignatello et al. 2017) in conjunction with hydrophilic and hydrophobic properties (Kookana et al. 2011). Fundamentally, the structure of biochar is supported by carbon (C) arranged hexagonally in a ‘honeycomb’ pattern without oxygen or hydrogen (Lehmann and Joseph, 2015). Heteroatoms (e.g. N, S, O, P) are often present while inorganic minerals (e.g. Mg, Na, Ca, Si, and K) and some PTEs (e.g. Al, Cd, As, and Pb) may also be present in small amounts (Freddo et al. 2012). During pyrolysis, K and Cl tend to vaporize easily at lower temperatures (< 300 ºC), while P, N, Mg, S, and Ca tend to be covalently bound to complex organic compounds and can only vaporize at higher temperatures (> 500 ºC) (Kookana et al. 2011). Increasing temperatures favour the release of gases such as CO_2, CO and NO_x as carbon-rich compounds decompose (Liu et al. 2015). Hydroxyl and carboxylic functional groups are most abundant in biochars derived from fast pyrolysis (rapid heating of biomass at moderate to high temperatures (~700 ºC)) while C-H groups become dominant in biochars produced from slow pyrolysis (gradual heating of biomass over a wide range of temperatures (250 – 900 ºC)) (Tripathi et al., 2016). Other functional groups on the surfaces of biochar may include nitriles, carbonyls, peptides, phenols, quinones, lactones, and pyrones (Liu et al. 2015) which may be fewer compared to other organic matter like humus (Hale et al. 2016).

3.4. Stability in soil

Large deposits of dark char in the amazon basin have existed for thousands of years (Lehmann et al. 2011). The presence of this material and its persistence in soil for long periods of time is indicative of its high resistance to biological decay (McLaughlin et al. 2009; Zhu et al. 2016). When biochar is incorporated in soil, its half-life may be up to several thousand years (Wu et al. 2013). The resistance to decay and persistence in soil may be advantageous in a sorption system as it would imply the immobilization of strongly-sorbed contaminants for a significant amount of time. The H/C ratio of biochar has been suggested to be a very important indicator of biochar's stability in soil, potentially because it is an indicator of aromaticity (Han et al. 2016). Biochars with H/C ratios below 0.7 are considered very stable, presumably because aromatic structures are slower to degrade. The stability (and aromaticity) of biochars is influenced not only by the type of feedstock and pyrolysis temperature but also biochar's interaction with soil under specific pedo-climatic conditions (Herath et al. 2015).

What happens to the biochar beyond tens of thousands of years as reported in the literature (Lehmann et al. 2011) remains uncertain. While Xu et al. (2014) and Zhu et al. (2016) suggested some minimal microbial action on the biochar, Spokas et al. (2014) suggests that, over time, the biochar disintegrates into micro and nano-scale fragments that are capable of infiltrating into soil. This disintegration has been reported to occur as the result of repeated swelling and cracking of biochar's graphitic sheets, leading to a crumbling of the physical structure (Spokas et al. 2014). Extremely small and mobile biochar particles, which would be similar to colloidal black carbon particles, are capable of becoming mobilized in the subsurface (Enell et al. 2016; Wang et al. 2013). Singh et al. (2014) also suggested that some of the recalcitrant carbon, over longer periods of time, gets mineralized or may turn into organic matter when biotic and abiotic oxidation takes place under conditions of high soil temperature and moisture.

3.5. Suitability for contaminant sorption

Sorption is a physicochemical transfer process in which materials (contaminants) are partitioned between the sorbent and aqueous phases (Yavari et al. 2015). Some properties of the sorbent including surface area, pore sizes/volume, CEC, pH, surface functional groups, molecular structure, hydrophobicity, solubility, polarity and minerals are crucial for this transfer process (Yavari et al. 2015). The suitability of biochar as a sorbent hinges not only on these properties and its resistance to decomposition and mineralization, but also on its low-cost availability from a wide range of precursors notably agricultural by-products (plant husk, plant straw, pine bark, sawdust, bagasse, fruit wastes, weeds, dried aquatic plants), sewage sludge and even automobile tyres (Gupta et al. 2015). Yavari et al. (2015) reviewed that the sorption capacity of organic matter is enhanced 10 – 1000 times after charring to products like biochar through pyrolysis. The structural and chemical composition of biochar (which can easily be engineered) often correlate well with its function as a sorbent. Large pore sizes and pore volumes with high CO_2 measured surface areas (often greater than 100 m^2 g^{-1}) equip biochar with high sorption tendencies (Liu et al. 2015; Lehmann and Joseph, 2015). Pyrolysis temperature is the underlying factor that determines pore distribution (including pore size and pore volume) (Rawal et al. 2016; Uchimiya et al., 2011a) and specific surface area (SSA) of biochars (Hale et al. 2016; Xiao et al. 2014a; Zama et al. 2017). This high polyaromaticity and nanoporosity (Pignatello et al. 2017) as well as hydrophobicity and high surface area make biochar physically a sorbent with qualities similar to, but not as substantial as, activated carbon for non-polar substances (Huggins et al. 2016). However, unlike activated carbon, biochar's polarity and abundant surface functional groups can also intensify the number of sorption sites for polar or ionic substances, including metals.

4. Biochar's interaction with As, Pb, SMX, atrazine and PAHs in soil

4.1. Arsenic (As)

Bibliometric analysis found 302 publications and 6 field-based studies focusing on the removal of As by biochar in soil (**Table S1**). Arsenic is a metalloid oxo-anion existing in the natural environment as arsenite [As(III)] and arsenate [As(V)] usually in combination with sulfur, oxygen and iron (Ungureanu et al. 2015). Soil easily adsorbs As(V) although its ability to retain the anion is relatively poor (Agrafioti et al. 2014). The oxidation state of As has a great role to play in its sorption or immobilization in soil. This observation was made by Pan et al. (2015) and Yokoyama et al. (2012) who noticed that the ratio of the coefficients of distribution of As(III) and As(V) on calcite ($K_{As(V)}/K_{As(III)}$) at neutral pH was larger than 2100. Wang et al. (2015b) also had similar observations but added that the relatively easy removal of As(V) from the environment is also attributable to its higher mobility.

Many different types of biochars (notably sewage sludge, rice straw/husk, and manure) have been tested for As removal in soil and the majority of them have been counter-productive (increasing pore water As concentration)

(Yamaguchi et al. 2011). Studies in the laboratory or greenhouse under controlled conditions of pH, temperature, moisture etc. have reported significantly high concentrations of As in pore water or plant tissues following the addition of biochar. For example, Zheng et al. (2012) reported a 327% increase in As concentration in rice shoot following the amendment of rice husk and straw biochars pyrolysed at 500 °C while Beesley et al. (2013) reported up to 300% increase in As pore water concentration following soil amendment with orchard prune residue biochar produced at 500 °C. In both studies, initial soil As concentration was 77 µg g^{-1} and 6000 mg g^{-1}, respectively. According Beesley et al. (2013), biochar's framework (porosity) harbours conditions that create a net negative redox potential and in such circumstances, less As is sorbed to biochar while the majority is mobile. In addition, the presence of As mainly as oxo-anions also limits ion exchange interactions on the predominantly anionic biochar surfaces (Yang et al. 2016), particularly because biochar addition in soil often increases pH which decreases positively charged sorption sites on the biochar (Baig et al. 2014). Zheng et al. (2012) also cited the presence of Si and P in soil which may out-compete As for sorption sites on biochar leaving As mobile.

To improve As sorption, researchers have frequently modified biochars with oxides and hydroxides of Fe and Mn. For example, Yu et al. (2017) recently modified corn straw biochar produced at 600 °C with MnO to remove As in contaminated soils (47.2 – 73.0 mg g^{-1}). The results showed that modification significantly decreased As concentration in the roots, stems, leaves and grains from 356, 3.93, 4.88, and 0.349 mg g^{-1}, respectively in control (without biochar) to 241, 3.08, 3.77 and 0.328 mg g^{-1}, respectively in soil treated with 0.5% modified biochar. This represented a percentage decrease of 40.8, 44.3, 33.2, and 17.7%, respectively. Similar results have been reported when other researchers used Fe-modified/Fe-rich biochars for the removal of As (Rajapaksha et al. 2016; Samsuri et al. 2013)

Field-based studies aimed at using biochar for the sorption or immobilization of As under natural environmental conditions are rare. Only 3 field studies were found on ScienceDirect database focusing on As removal in field soils using biochar. In the field, the addition of unmodified biochar in soil encounters similar trends like laboratory or greenhouse studies where As mobility is enhanced following the addition of biochar. For example the NH_4NO_3 extractable concentration of As in paddy soil (34 µg g^{-1}) significantly increased by 73.3% when rice straw biochars pyrolysed at 500 °C were added at 20 t ha^{-1} in a 4 months study (Zheng et al. 2015). Increase in As concentration in pore water or plant tissue in the field has been found to be at least 2 orders of magnitude less than that reported in laboratory or greenhouse studies due to environmental constraints (Zheng et al. 2015) (Table S2) discussed in section 5.

Studies have also shown that As lacks the ability to engage in complexation and precipitation reactions with biochar (Zama et al., 2017). This explains why pristine biochar does not do well in As removal. However when biochar is modified (e.g. Fe modification), some complexes such as Mn(Fe)–O-As and Fe–O–C (Yang et al. 2016) may be formed on the surfaces of biochar which increases the density of positively charged sites at low pH values (< 4.5) and in turn increases the sorption of As (Yang et al. 2016). Manning et al. (2002) observed that As(III) is easily oxidized to As(V) in the presence of MnO_2 (equation 1). Modifying biochar with MnO_2 therefore enhances the removal of As(III) and As(V) by converting As(III) to As(V) which is easily sorbed (Yu et al., 2017; Wang et al., 2015b; Gude et al., 2017)

$$MnO_2 + H_3AsO_3 + 2H^+ \longrightarrow Mn^{2+} + H_3AsO_4 + H_2O \qquad (1)$$

Hartley et al. (2009) also observed the influence of pH and the presence of entities like P and Si on the sorption of As by biochar. Lower pH values (i.e. pH < 5) favour the release of H^+ which may enhance electrostatic attraction with the predominantly anionic As specie in soil. Phosphorus (often present as PO_4 ions) has chemical similarities with As and would compete with As for sorption sites on the biochar (Hartley et al. 2009). The presence of PO_4 therefore limits the sorption of As which is often released into the surrounding soil solution.

4.2. Lead (Pb)

According to bibliometric analysis, lead (Pb) has been the highest PTE studied for its interaction with biochar in soil. Up to 532 publications and 11 field-based, studies were found focusing on Pb removal by biochar in soil (**Table S1**). It is a common contaminant present in most urban and suburban soils in significant quantities (ATSDR, 2011). Many different types of biochars (wood-based, husk-based, sewage sludge, bone-based and yard wastes) at various pyrolysis temperatures (mainly 300 – 700 ºC) have been experimented on Pb sorption in soil. All these biochars (both modified and un-modified) have been very effective in the sorption removal of Pb in environmental media (averaging 90% sorption rates in water and 60% in soil) (Li et al. 2016). Compared to most PTEs, Pb is relatively easier to immobilize possibly because of its involvement in multiple sorption mechanisms with biochar (i.e. pore filling, formation of complexes and precipitates, and ion exchange mechanisms) (Han et al. 2016; Xu et al. 2016).

Apart from pyrolysis temperature and feedstock type which influence the removal of Pb (Uchimiya et al., 2012), laboratory or greenhouse experiments involving biochar and Pb sorption in soil have shown that soil pH, particle size and biochar amount also play key roles in Pb removal (Xu and Zhao, 2013; Uchimiya, 2014). These properties have been extensively tested and known to affect Pb mobility in soil although the high affinity between most biochars and Pb often compensates for these effects. In an experiment carried out by Houben et al. (2013) on a heavily Pb contaminated soil (~3110 mg kg^{-1}), miscanthus straw biochar applied at 10% (w/w) decreased bioavailable Pb in pore water by 92%. This was attributed to the increase in soil pH from 5.62 to 6.70 after biochar addition. Similar effects were observed when Lu et al. (2014) added 5% (w/w) of rice straw biochars, pyrolysed at 500 °C, to a sandy loam moderately acidic (pH ~5.7) paddy soils contaminated with Pb (527 mg kg^{-1}) and other metals. The study suggested that a combination of increasing pH (~ 6.2), high biochar rate (up to 78 t ha^{-1}) and small particle size (< 0.25 mm) may have contributed to the 71% of reduction in Pb concentration in the *Sedum plumbizincicola* shoots. Many more studies have reported similar trends in Pb sorption in controlled laboratory/greenhouse condition.

The trend of Pb removal in the field soil (where concentrations decrease with biochar addition under field conditions) is similar to laboratory or greenhouse trends. However, sorption amounts differ in field trials (consistently lower than laboratory or greenhouse amounts even under similar conditions) due to differences in soil pH and initial Pb concentrations, which are harder to control in the field. In a five-year field experiment, Pb was immobilized in soil by wheat straw biochar mainly in the form of stabilized carbonates, organic and residual forms (Cui et al. 2016) (Table S2). Abundant functional groups and complex structures in the biochar played key roles in the stabilization of Pb by 3.7 – 19.8% while improving soil microstructure and increasing soil pH and soil organic matter. Most field studies have used greater than 10 t ha^{-1} of biochar to achieve averagely 50% Pb immobilization. For example, Zheng et al. (2015) used 20 t ha^{-1} of rice straw biochar to achieve 40.7% Pb removal (NH_4NO_3 extractable) while Bian et al. (2014) used 10, 20 and 40 t ha^{-1} of wheat straw biochar to achieve 33.3, 79.6 and 59.1% Pb removal, respectively ($CaCl_2$ extractable) (Table S2). Initial Pb concentrations and type of extractant may have influenced extracted amounts and in both experiments, extracted concentrations were consistently lower, compared to laboratory or greenhouse studies.

Physical processes such as pore filling have been rarely reported as major mechanisms for Pb removal in soil. Researchers have frequently cited non-specific chemisorption mechanisms like ion exchange (Uchimiya, 2014), complexation and precipitation (**Fig. 3**) with inorganic components (e.g. CO_3^{2-}, SO_4^{2-}) as the main mechanisms driving Pb sorption in soil (Chi et al. 2017; Li et al. 2017; Park et al. 2013a). Soil pH tends to influence most of these processes (Uchimiya, 2014). **Fig. S2** indicates the removal of organic and inorganic contaminants by typical processes such as microbial breakdown (**Fig. S2a**) and complexation reactions (**Fig. S2b**), respectively.

Ion exchange is sorption mechanism involving weak reversible reactions (Alfen, 2014). Usually, inorganic mineral cations (e.g. Mg^{2+}, Na^+, Ca^{2+}, and K^+) are scattered on the surfaces and pores of biochar and tend to increase with increasing pyrolysis temperatures due to increased ash content (Lehmann et al. 2009). Contaminant cations such as Pb^{2+} can easily displace these mineral cations, which are bound to anionic sites on the biochar, leading to sorption of the contaminants. A major characteristic of ion exchange is charge balance and selective replacement (Sposito, 2008). Typically one mole of Pb^{2+} would exchange with two moles of K^+ to ensure charge balance and ions held together by weak electrostatic forces on the surfaces of biochar are replaced by contaminant ions of the same charge but with a higher charge density (Alfen, 2014). For example, Pb^{2+} might replace K^+ (equation 2), which in turn might replace Na^+ because of its larger charge density (Ahmed et al., 1998). However, Alfen, (2014) reported that although ions of higher charge density are preferably sorbed, outcomes depend on the relative concentration of the ions in the system.

The formation of precipitates such as lead phosphate and hydrocerussite (Equations 3 and 4, respectively) often formed between Pb^{2+} and mineral ions present on the surfaces of biochar represents another major mechanism driving Pb sorption on biochar (Tran et al. 2016) (**Fig. 3**). Very often, minerals such as calcite ($CaCO_3$), althausite (Mg_2PO_4OH), and caminite ($Mg_3(SO_4)_2(OH)_2$) present on biochar surfaces (Wang et al. 2015a) release ions such as PO_4^{3-}, SO_4^{2-}, and CO_3^{2-}, which undergo precipitation and co-precipitation reactions with Pb. These sorption processes may also be affected by the pH of the soil solution.

$$2K^+ + Pb^{2+}_{(soil)} \rightleftharpoons Pb^{2+} + 2K^+_{(soil)} \tag{2}$$

$$6HPO_4^{2-} + 9Pb + 6OH^- \longrightarrow Pb_9(PO_4)_6 + 6H_2O \tag{3}$$

$$2HCO_3^- + 3Pb^{2+} + 4OH^- \longrightarrow Pb_3(CO_3)_2 + 2H_2O \tag{4}$$

$$2(=FeOH) + Pb^{2+} \longrightarrow (-FeO)_2Pb^+ + 2H^+ \tag{5}$$

The formation of monodentate and bidentate complexes with Pb ions (equation 5) is also a major mechanism for Pb sorption by biochar (Najar et al. 2010; Sposito, 2008). A large amount of functional groups including hydroxyls, carboxyls, nitriles, ketones, and alkyls often develops on the surfaces of biochar at optimal pyrolysis temperatures (< 500 ^{o}C) (Uchimiya et al. 2011b) when anomeric O-C-O and O-alkylated groups undergo cleavage in addition to the formation of fused-ring aromatic C-O groups (Li et al. 2013; Nartey and Zhao, 2014). Higher pH values (> 5.0) in soil solution influences the deprotonation of functional groups with a higher chance of coordination with Pb ions (Li et al. 2016). Moreover, at higher pH (> 5.0), Tsai et al. (2012) observed that Pb begins to hydrolyze as Pb $(OH)^{+}$ which also improves its sorption on biochar. **Fig. S2b** illustrates Pb^{2+} binding to a carboxylic group on the surface of biochar. Pb sorption on biochar may also follow a single Langmuir model, which describes surface sorption through coordination of Pb d-electron to C═C (π-electron) and —O—Pb bonds (Cao et al. 2009).

4.3. Sulfamethoxazole (SMX) ($C_{10}H_{11}N_3O_3S$)

Sulfamethoxazole is the most commonly detected sulfonamide-based antibiotic in soil (Li et al. 2015; Shimabuku et al. 2016). It is used in this review to represent the antibiotic class of contaminants. Within the past 10 years, many publications have been made on a wide range of antibiotic contaminants based on sciencedirect database. However only 60 have focused on SMX and biochar in soil (**Table S1**) amongst which none were field-based. SMX has been found to cause widespread aquifer contamination due to its high mobility in soil (Avisar et al. 2009; Lian et al. 2014; Tamtam et al. 2011). It is widely used in livestock treatment especially in New Zealand (Srinivasan and Sarmah, 2015) and is almost ubiquitously present in groundwater. Its physical properties are outlined on **Table 1**.

In the laboratory or greenhouse, biochar has been fairly good in SMX sorption with reports of up to 50% sorption efficiency. Bamboo, pine sawdust, corncobs, sugarcane bagasse, and wood-based biochars are some examples frequently used in SMX removal. For instance, Srinivasan and Sarmah (2015) reported significant increases in SMX sorption when green waste, corncob and pine sawdust biochars pyrolysed at 350 to 700 °C were added to a silt loam soil at 0.5 and 1% (w/w). Pine sawdust had the highest sorption affinity for SMX which was attributed to its large surface area (795 $m^2\ g^{-1}$) and lesser exchangeable cations which make the biochar surface less hydrophilic. Apart from surface area, Zheng et al. (2013) also observed that soil pH also affected SMX sorption considerably. At pH 1.0, more than 86.3% of cationic SMX was sorbed and biochar surfaces became positively charged. When the pH values were between 2.0 and 5.0, the dominant SMX species sorbed onto biochars was neutral and biochar surfaces became positive while pH values greater than 6.0 resulted to more anionic SMX species (> 70%) with stronger negative biochar surfaces. SMX has very low K_d values (0.6 - 3.1 L kg^{-1}) and differences in K_d values between biochar and SMX may also affect SMX sorption in soil. All biochars such as bamboo, Brazilian pepper wood, sugarcane bagasse, and hickory wood with higher K_d values (2 - 104 L kg^{-1}) (Yao et al. 2012) would have the ability to immobilize SMX in soil solution.

Pore-filling, cation exchange, and electrostatic interactions have been suggested as the major mechanisms influencing SMX sorption in soil (Zheng et al. 2013). Pyrolysis temperature and pH of soil are crucial for these sorption processes (Reemtsma et al. 2016; Zheng et al. 2013). As explained by Zheng et al. (2013), SMX charge state easily switches between negative, neutral and positive depending on the pH of the soil and this greatly influences sorption characteristics especially ion exchange. Both Zheng et al. (2013) and Lian et al. (2014) have underscored the importance of charge assisted H-bonding in SMX sorption which ensures anionic SMX sorption even at higher pH values (> 7.0). At pH 5.0, where SMX tends to be neutral, sorption is ensured by hydrophobic interaction, π–π EDA interaction and pore-filling. However, SMX's K_{OW} at 0.89 (**Table 1**) has a contrary indication that SMX is more hydrophilic and partitioning into hydrophobic biochar surfaces is rarely a major mechanism for SMX sorption. Lower temperature biochars (~250 ºC) contain more O-containing functional groups and when the pK_a of such biochars nears that of SMX ($pK_a = 5.7$), sorption is enhanced. Inorganic fractions are often more abundant on biochar at higher temperatures. These inorganic fractions tend to complex very strongly with SMX and other antibiotics but such complexation reactions have rarely been reported as major mechanisms for SMX sorption.

4.4. Atrazine (2-Chloro 4-ethylamino 6-isopropylamino-s-triazine)

Atrazine is a mobile polar contaminant used in this review to represent the triazine family of contaminants. It is an herbicide commonly used for weed suppression, and has physical properties that mirror most herbicides (**Table 1)**. Various sorbents including activated carbon (Tan et al. 2016), organic matter, humics and minerals (Deng et al. 2014) have been used in the past to capture atrazine. According to the bibliometric analysis, up to 150 publications focusing on biochar and atrazine sorption in soil have been made between 2009 and 2017 (**Table S1**). Amongst these, only 4 publications were field-based.

The removal of atrazine by biochar in the laboratory or greenhouse has also been largely successful. Wood and manure-based biochars (e.g. pine wood and dairy waste manure) have been frequently used for atrazine removal which is significantly affected by soil DOC and pH. For example, at low pH values ($pH < 3$), cassava waste biochar prepared at 350 - 750 °C and applied at 1% sorbed up to 86.6% of atrazine in an artificially contaminated krasnozem soil (20 mg L^{-1}) (Deng et al. 2014). In a related study, southern crabgrass, common lambsquarter, lettuce and wheat biochars were effective in removing atrazine by 89, 34, 100, and 45%, respectively although its herbicidal activity was also greatly reduced (Soni et al. 2015). However, the decrease in its herbicidal activity was dependent on soil DOC and pH. Increasing the DOC fraction of soil increases the chances of partitioning into the organic C fraction and surface sorption which plays a key role in atrazine removal (Cao et al. 2011). Compared to unmodified manioc waste biochar made at 750 ^{o}C, $FeCl_3$ modified manioc waste biochars demonstrated a higher sorption capacity for atrazine by 17.5 times in tropical soils implying that biochar modification can be very beneficial for atrazine sorption (Deng et al., 2014).

Reports have shown no significant difference in the sorption of atrazine in the field and laboratory or greenhouse. In a field study to determine the influence of biochar on atrazine immobilization, Soni et al. (2015) added 0.5 kg m^{-2} of biochar produced from pine wood chips at 800 °C to atrazine contaminated soil and reported 75% decrease in atrazine concentration (Table S2). The slope of atrazine immobilization was 16 times higher in biochar amended soils than soil alone when linear regression analysis was done implying that biochar had a high affinity for atrazine. However, the addition of biochar also decreased the control of broadleaf weed from 70% in soil without biochar to 5% in soil containing atrazine and biochar. This implied that the addition of biochar significantly weakened the performance of atrazine as an herbicide. Delwiche et al. (2014) also carried out field studies (Table S2) to assess the leachability of atrazine under increasingly heterogeneous soil conditions. The study used biochar from peat pyrolysed at 700 and 750 °C by flash pyrolysis and observed that the peak atrazine concentration in groundwater reduced by 58% following the addition of 10 t ha^{-1} of biochar. Unexpectedly, the percentage decrease in atrazine in the field study was not significantly different from that obtained in the laboratory (55%) implying that field conditions did not have any significant influence on the performance of pine wood chip biochar in atrazine sorption (Delwiche et al. 2014).

Pore-filling and electrostatic interactions appear to be the major mechanisms driving atrazine sorption in soil (**Fig. 3a**). Atrazine is polar and can accept or donate electrons during reactions with amino groups. Its polarity and solubility (**Table 1**) also mean that atrazine can easily form covalent bonds with polar biochar surfaces in complexation interactions. However at low pH, biochar surfaces protonate which may influence the sorption of the slightly basic atrazine (pKa = 1.7) through electrostatic attractions. Loganathan et al. (2009) noted that the sorption of atrazine (K_{OW} ~1.72) involved sorption on carbonized surfaces and partitioning into the residual organic matter of char (biochar). Hao et al. (2013) reported a negative correlation between carbon normalized sorption coefficient (K_{OC}) and H/C and (O+N)/C when corn cobs biochar produced at 350 - 650 °C was applied to atrazine contaminated soil also implying that aromatic carbon and hydrophobic surfaces were influential in atrazine sorption. Pore-filling was also suggested by Hao et al. (2013 as a key mechanism influencing atrazine removal in soil. For ionic organic contaminants or ionic and ionizable molecules like atrazine, there are additional sorption interactions such as cationic or anionic exchange interactions (**Fig. 3**) to charged moieties on the biochar surface or mineral impurities (Droge and Goss, 2012; Droge and Goss, 2013). The intensity of these interactions can be dependent on the pH as well as counterions in the pore water, as the pH can affect the ionization state of both biochar and molecules, and both pH and counterions can effect ion-exchange processes of organic ions (Arp et al. 2017).

4.5. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a class of neutral organic compounds with multiple fused aromatic rings produced. It is used in this review to represent hydrocarbons which cause widespread contamination in soil, water and air (Zhang et al. 2015), and possess a wide range of mobility and health risks. Given that PAHs are also a class of compounds within the hydrocarbons family, significant research has been undertaken involving biochar and PAHs in soil. The sciencedirect database found 464 publications within the past 10 years with focus on PAHs removal by biochar in soil (**Table S1**). Amongst the contaminants selected in this review, PAHs had the highest number of field studies (up to 15) carried out mainly between 2015 and 2017. Some physical characteristics of PAHs, likely to influence their sorption on biochar, are presented on **Table 1**.

The interaction between biochar and a wide range of PAHs in the laboratory or greenhouse has been reported extensively in literature with varied and high removal efficiencies. However, these removal efficiencies are affected by some biochar and soil properties including the nature of pyrolysis, particle size and microbial community (Waqas et al. 2015). For example, Ogbonnaya et al. (2016) investigated the efficiency of wood-derived biochar made by slow pyrolysis and gasification and observed that biochar produced by slow pyrolysis was better at immobilizing ^{14}C-naphthalene in soil than biochar produced by gasification. This could be attributed to the presence of a larger amount of pores and organic functional groups on slowly pyrolysed biochar 450 - 500 °C (ramped at 10 °C min^{-1}) compared to gasified biochar at 900 - 1000 °C. The influence of particle size was investigated by Zand and Grathwoh (2016) on the immobilization and leaching of Σ16 PAHs from contaminated soils in column experiments using crushed and pulverized forest wood biochars. The addition of 5% crushed biochar (2 mm) decreased 80% PAHs in leachates while 5% pulverized biochar (1 μm) amendment decreased up to 98% PAHs in leachates, implying that smaller sized biochar is better at immobilizing PAHs possibly because of its larger surface area. The study also observed that crushed biochar increased the mobility of higher molecular weight PAHs (i.e. pyrene, benzo(b)fluoranthene, and indeno (1,2,3-cd)) which depended on DOC for their transportation unlike pulverized biochar which depended on colloids formed after biochar addition. Recently, Xiong et al. (2017) investigated the influence of a microbe-biochar composite (*Mycobacterium gilvum* and rice straw biochar) on the remediation of PAHs contaminated coke plant soil. The authors observed superior degradation of phenanthrene, fluoranthene and pyrene by 62.6, 52.1 and 62.1%, respectively after the treatment with microbe-biochar composite. This increase in PAHs degradation compared to less than 47.3% when free cells alone and biochar alone were used could be attributed to enhanced mass transfer of PAHs from the soil to biochar (acting as sink) and the subsequent degradation of these PAHs by the immobilized *M. gilvum* (Xiong et al. 2017). Modifying biochar may also increase the sorption of PAHs in soil. Reports have indicated that more than 90% of PAHs are often removed from soil when biochar is modified with base substances. For example, base modification of rice straw, wood and bamboo biochars produced at temperatures below 500 °C using NaOH was shown to significantly increase the removal of phenanthrene in soil by 72%. According to Feng and Zhu (2018), this was because base modification increased the Koc of extractable biochar by up to 60% – 751%.

In field experiments, the influence of microbial activity on PAHs degradation has been significantly highlighted. For example, Stefaniuk et al. (2017) recently experimented the removal of Σ16PAHs by willow (*Salix viminalis*) biochar on podzolic soil (Σ16PAHs concentration ~128.8 μg kg^{-1}) (Table S2) and in the 18 months field experiment, there was no significant change in Σ16PAHs concentration for the first 12 months. However, after the 12th month, up to 45% reduction in Σ16PAHs concentration in soil was recorded especially when biochar was added at the rate of 2.5%. The study suggested that during the first 12 months, microbial activity, which is crucial for PAHs degradation, focused on available soil organic matter (SOM). As SOM reduced, degradation of the harder PAHs then accelerated. The majority of the biochars produced at 400 - 700 °C often come with Σ16PAHs concentrations ranging from 0.4 - 1987 mg kg^{-1}, and 12 - 81 ng L^{-1}, respectively. However, Hilber et al. (2017b) and Rombolà et al. (2015) noted that the majority of these PAHs bound in the biochar (used for soil remediation) were not bioavailable. The biochars acted mainly as contaminant sinks rather than sources of PAHs. In an experiment carried out by Hilber et al. (2017b), the PAHs of 25 out of 33 biochar samples were resistant to desorption.

Unlike SMX and atrazine, PAHs have a higher K_{OW} (> 3.5) (**Table 1**) indicating its hydrophobic nature and the possibility of partitioning into hydrophobic biochar surfaces as one of the leading mechanisms for PAHs sorption. However, studies have reported non-specific van der Waal and specific electron-donor-acceptor (EDA) interactions such as π-π interactions (Anyika et al. 2015) and H-bonding (Goss and Schwarzenbach, 2001) as key mechanisms for PAHs sorption. According to Pignatello et al. (2017), π electron clouds of arenes may engage in non-covalent interactions with cations, anions, proton-donor molecules, and the π electron cloud of other arenes (**Fig. 3a**). The formation of coplanar interactions between biochar polyaromatic sheets and neutral or charged arene contaminants is the most important π-interactions.

The breakdown of PAHs contaminants by microbial activity may also constitute a major mechanism for their removal in soil (**Fig. S2a**). The activity of large populations of microbes, often present in soil, may be enhanced by the addition of biochar, which offers a platform for the microbes to degrade PAHs. The biochar also helps in shuttling electrons between molecules and microbes (Pignatello et al. 2017; Zhao et al. 2016). Ni et al. (2017) recently investigated the mechanisms in which biochar reduces the bioaccumulation of PAHs in carrot (*Daucus carota*) and observed that corn straw and bamboo biochars pyrolysed at 300 and 700 °C, respectively decreased bioaccumulation of PAHs in carrot due to the presence of *Arthrobacter* and *Flavobacterium* in soil which play significant roles in microbial PAH degradation processes. They suggested that biochar application to soil can enhance the growth of indigenous microbes which degrade PAHs and reduce their bioavailability and bioaccumulation. Biochar interaction with microbes can be summarized in seven different ways. These include biochar as a habitat for microbes, promoting enzyme activity, improving soil properties, source of signaling molecules for microbial communication, adsorption of nutrients through CEC, toxicity to microbes and enhancing soil contaminant degradation (Kołtowski et al., 2017; Zhu et al., 2017). The redox potential of biochar facilitates microbial degradation of organic contaminants (Yu et al., 2015; Chen et al., 2014). The strategy here, is using biochars as pretreatments to immobilize and concentrate organic contaminants such as PAHs in soil. After the pretreatment, an inoculation with PAH-degrading microbes such as *Phanerochaete chrysosporium, Pleurotus Ostreatus, Pseudomonas putida, Pseudomonas aeruginosa,* and *Acinetobacter radioresistens* is done which completes the final degradation of the PAHs in soil (Chen and Ding, 2012; Galitskaya et al., 2016).

Han et al. (2016) presented the specific role of amorphous alkyl, aryl and aromatic C in the sorption of PAHs such as pyrene. Alkyl C appears to have properties similar to kerogen with flexible alkyl domains structurally compatible with organic compounds and offering conducive sorption sites for contaminants (Han et al. 2016). Aromatic C through its aromatic π system likely acts as π electron donors or acceptors towards contaminants. Some organic contaminants like acetaminophen and carbamazepine may also contain electron donating groups (e.g. –OH, and –NH_2) which aid in sorbing PAHs onto the biochar through EDA interactions (Han et al. 2016).

5. Challenges in field application of biochar

As observed in section 4, the field application of biochar frequently led to lower contaminant sorption compared to laboratory or greenhouse biochar application. There appear to be little optimization of biochar in soil when applied directly in the field under natural conditions. This may be due to environmental factors like temperature, wind, moisture, rainfall, soil microbes, pH etc., which are often hard to control (Ogbonnaya and Semple, 2013; Ter Laak et al. 2006). Apart from these environmental constraints, scientists also worry about the likelihood of biochar inhibiting the actions of some beneficial chemicals and a source of contamination itself. The efficiency of DNA extraction in soil was also shown to be affected by biochar addition. This can affect the precise estimation and comparison of soil microbial abundance and diversity. This however depended on pyrolysis temperature, extractable C, and incubation with soil (Dai et al., 2017a).

The influence of temperatures on the sorption capacity of biochar has been reported in some laboratory or greenhouse studies. For example, at 25 ^{o}C, Liu et al. (2017) reported a sorption capacity of 14.9 mg g^{-1} for As(V) on rice straw biochar made at 450 ^{o}C. However when the temperature increased to 45 ^{o}C, the sorption capacity increased correspondingly to 17.9 mg g^{-1} indicating that increase in temperature increases sorption capacities. Soil temperature constantly fluctuates with respect to daytime temperatures, nighttime and across seasonal temperatures. Studies directed towards understanding the influence of temperature on the performance of biochar in the field are rare but it can be inferred from laboratory studies that changing temperatures affect biochar performance in the field.

Rainfall and wind conditions also affect biochar sorption capacities under field conditions. Heavy rainfall and runoffs may cause leaching and percolation of tiny biochar particles deeper into soil or floating larger particles away, separating them from contaminants which significantly reduces their likelihood of contact and sorption.

Fractions of biochar may be lost during application under windy conditions in the field. Major (2010) estimated that 2% of biochar is lost while loading a spreader, 3% is lost during transportation and about 30% is lost during spreading amounting to almost 30% of biochar loss during field application with significant cost effects. The presence of microbes in soil can also affect biochar performance through degradation of biochar particles in the short term or long term. Sorbed contaminants may be re-released into soil once biochar is degraded through microbial action.

Several studies notably Hale et al. (2012), Han et al. (2016), Hilber et al. (2012) and Yavari et al. (2015), have all discussed the possibility of biochar being a source of contaminant itself in soil. During pyrolysis, compounds such as PAHs, dioxins and PCBs may develop in biochar together with some heavy metals like Pb, Cd, Cu, Zn, and Al from the original biomass material (Hilber et al. 2017a). These compounds are often not available for microbial breakdown as they remain tightly bound to biochar matrices through π-π interactions (Yavari et al. 2015). The type of pyrolysis, feedstock and time determine the concentration of these compounds in biochar (Hale et al. 2012). Quicker production methods (e.g. flash pyrolysis and gasification) often result to biochars with elevated PAHs and dioxin concentrations (~45 $\mu g\ g^{-1}$ and 92 $pg\ g^{-1}$, respectively). Han et al. (2016) cautioned that this should always be taken into consideration before using biochar for contaminant remediation although Hilber et al. (2017b) noted that PAHs in biochar is usually desorption resistant and can only become bioavailable at higher concentrations (> 10 $mg\ kg^{-1}$).

Another setback in the application of biochar in the field is its potential to reduce the efficacy of some herbicides and pesticides applied in soil such as atrazine (Yavari et al. 2015). As described above, biochar has a high sorption affinity for atrazine which easily becomes immobilized through chemical and physical sorption onto biochar. In soil, the entrapped herbicide or pesticide may significantly decrease its efficiency in weed or pest control. For example, Nag et al. (2011) realized that atrazine dosage required to reduce ryegrass weed biomass by 50% increased by 3.5 times following the addition of 1% wheat straw biochar produced at 450 ºC. This implies that the use of biochar may increase herbicide use and the overall cost of application and may result to the evolution of herbicide resistant weed (Yavari et al. 2015).

6. Selecting biochars for the treatment of contaminated soils

Despite the large volume of information available on biochar sorption/immobilization of organic and inorganic contaminants in soil, fundamental questions remain un-answered notably, "which biochar (including its characteristics) is most suitable for the removal of target contaminants". So far, it is extremely challenging to select the 'best' biochar for a particular contaminant in soil (a situation hinged to the significant variability in biochar feedstock, pyrolysis temperatures, particle sizes, pH, elemental content, surface area, ash content, and even nature of modification). The methods of biochar production (wet or dry pyrolysis, gasification, slow or fast pyrolysis, flash pyrolysis) also produce biochars with different properties. The rates of biochar application, contact times and environmental factors (pH, temperature, rainfall, wind, moisture, redox etc.) all have an impact on the performance of biochar as a sorbent. Suggestions have however been made based on some estimated soil conditions such as soil type, level of contamination and pH for the selection of biochars and biochar properties most suitable for the sorption or immobilization of As, Pb, SMX, Atrazine or PAHs in soil (**Table 2**). Two biochar types were suggested for each contaminant and for each biochar type, pyrolysis temperature was considered a primary determining factor for sorption capacity. Other variables considered in the selection were pH and application rate (**Table 2**).

Arsenic (As)*:* Rice straw and sewage sludge biochars prepared at 400 - 500 ^{o}C were suggested for As remediation in soil (**Table 2**). Rice straw biochar can easily be modified with Fe or Mn (hydr)oxides and it contains Si which easily precipitates with As to products like Gonardite [$(Na, Ca, K)_2 (Si, Al)_5O_{10}.3H_2O$] (Treacy and Higgins, 2007) or simply inhibits the transfer of As to plant tissues (Chen et al. 2017). Without modification, sewage sludge biochar may contain some oxides and hydroxides of Fe and Mn, which have been very effective in the removal of As in contaminated soils (Rajapaksha et al. 2016). The modification of biochar for the removal of As in soil is highly recommended given that pristine biochar rarely sorbs As. It rather increases its mobility. Many researchers have also recommended chemical modification, where chemical agents such as KOH (Jin et al. 2014), Ca (Agrafioti et al. 2014), Si, clay (Yao et al. 2014) are used to change the surface functionality of biochar in favour of As or other metals sorption (Liu et al. 2015; Rajapaksha et al. 2016). It is important to make biochars at relatively low pyrolysis temperatures (< 500 ^{o}C) which have less ash and low pH which favours oxo-anionic As sorption.

Lead (Pb): The sorption of Pb hinges on complexation, ion exchange and precipitation reactions. The availability of functional groups and inorganic ions are therefore important. Wood-based biochars are suitable because of their characteristic large surface areas, porous structure resulting from thermal cracking and unequal shrinking of interior and exterior woody masses during pyrolysis (Yavari et al. 2015) and abundance of surface functional groups. Dairy manure biochar is also suitable especially for Pb sorption because of the presence of PO_4^{3-} ions which easily precipitate with Pb into more stable $Pb_5(PO_4)_3OH$ (Cao et al. 2011). It is important to pyrolyze these biochars at 500 – 600 ºC (**Table 2**) to have a high surface area and still retain most surface functional groups which enhance complexation with Cd and Pb. At 600 °C, more inorganic minerals develop on biochar surfaces to increase pH which favours Cd^{2+} and Pb^{2+} sorption by enhancing cation exchange (Zama et al. 2017)

SMX: Wood and manure-based biochars with high porosity may be most suitable for SMX sorption through pore-filling. A suitable biochar for SMX sorption should also have abundant functional groups to enhance polar interactions between polar SMX and biochar. Lower temperature biochars (< 400 ºC) which have many functional groups are therefore preferred (**Table 2**). Some studies even recommend pyrolysis temperatures as low as 150 ºC (Sun et al. 2011). The biochars may also be associated with inorganic minerals (e.g. Mg, Ca) which also enhance SMX sorption (Yao et al. 2012). Low pH (< 5) is preferred, however, the formation of charge assisted H-bond on low temperature biochars also enhances sorption of SMX even at higher pH values (Lian et al. 2014)

Atrazine: Like SMX, wood and manure-based biochars are suitable for atrazine removal because of their high porosity which favours pore-filing. These biochars should also be pyrolysed at low temperature (e.g. 300 °C) to retain some residual organic matter where atrazine is easily partitioned (Loganathan et al. 2009). Manure biochars are also rich in minerals and high surface carbon which is suitable for the sorption of atrazine.

PAHs: For the sorption of PAHs, wood-based biochars pyrolysed at higher temperatures (500 - 800 ºC) (Table 2) are most suitable because they offer hydrophobic surfaces on which PAHs are easily partitioned (Fang et al. 2013). Sun et al. (2013) suggested that the biochars could be de-ashed to remove excess minerals and opening up many more hydrophobic sorption sites for PAHs. Although the hydrophobicity of sewage sludge biochar is not significant, it is still highly recommended for the sorption of PAHs because sewage sludge can easily stimulate soil microbial activity with the growth of microorganisms capable of degrading PAHs (Ter Laak et al. 2006).

7. Conclusions and future perspectives

Research on biochar has grown over the years with significant focus on its properties and how they affect its ability to immobilize both organic and inorganic contaminants. Biochar remains an impressive alternative in soil remediation. Few biochars may be inefficient in soil contaminant removal especially in As remediation but the majority of biochars achieve significant sorption results (often greater than 50%) when used in the soil remediation. The interaction between biochar and contaminants is governed by processes such as electrostatic attraction, precipitation, complexation and microbial activity and these strongly depend on biochar’s precursor material, pyrolysis temperature and the characteristics of the contaminants such as K_{OW} and polarity. The sorption of contaminants in the laboratory or greenhouse under controlled conditions is always significantly higher than sorption in the field under natural conditions. In the field, temperature, rainfall, wind, pH etc., are harder to control and have significant influence on the sorption capacity of biochars.

Many studies have been done on biochar interaction with biochar in soil. However very few of these studies have been field-based. More studies with greater focus on soil remediation in the field under natural conditions are therefore required to fully understand the behavior of biochar under such circumstances. A wide range of biochars with different physicochemical properties have been tested for their sorption capacities on contaminants both in soil and water. There is no conclusive evidence that 'best' biochars for target contaminants exist. Significant work is required to ensure case-specific and precision in the use of biochar with respect to biochar type, preparation conditions, application rate, application time, and recovery procedures. The quantity and quality as well as the type of biochar that can be accommodated by a particular soil type without interrupting its normal function also needs further investigation. While it is important to fully understand the mechanisms of retention of contaminant ions on biochar, it is also important to understand the coordination of these mechanisms (i.e. whether they work independently on each other or complementarily). Further work is also needed to clarify this aspect. Currently, what happens to diverse biochar particles over long time scales remains uncertain given that biochar is highly resistant to biological decay. More long-term, real-time studies are required to understand the transportation and transformation of nanoscale biochar particles.

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Tables and Figures

Advances in research on the use of biochar in soil for remediation: A review

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Table captions

Table 1. Physicochemical properties of SMX, atrazine and PAHs related to their sorption on biochar in soil

Table 2. Recommended biochar treatment plan for different soil types contaminated by As, Pb, SMX, atrazine and PAHs

Figures captions

Figure 1. Number of publications on field studies in removal of As, Pb, SMX, atrazine and PAHs in soil between 2009 and 2017 (Data source: ScienceDirect database).

Figure 2. Bibliometric distribution of publications according to year (a) and type (b) in laboratory or greenhouse studies on inorganic (Pb) and organic (PAHs) contaminant removal in soil by biochar

Figure 3. Summary of major mechanisms and processes that influence the removal of As, Pb, SMX, atrazine and PAHs in soil. (**a**) removal of organic contaminants, (**b**) removal of inorganic contaminants

Table 1

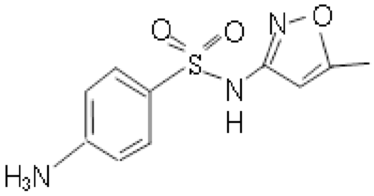
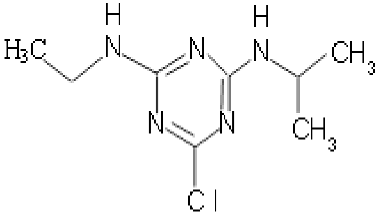
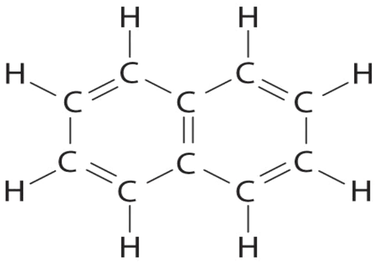
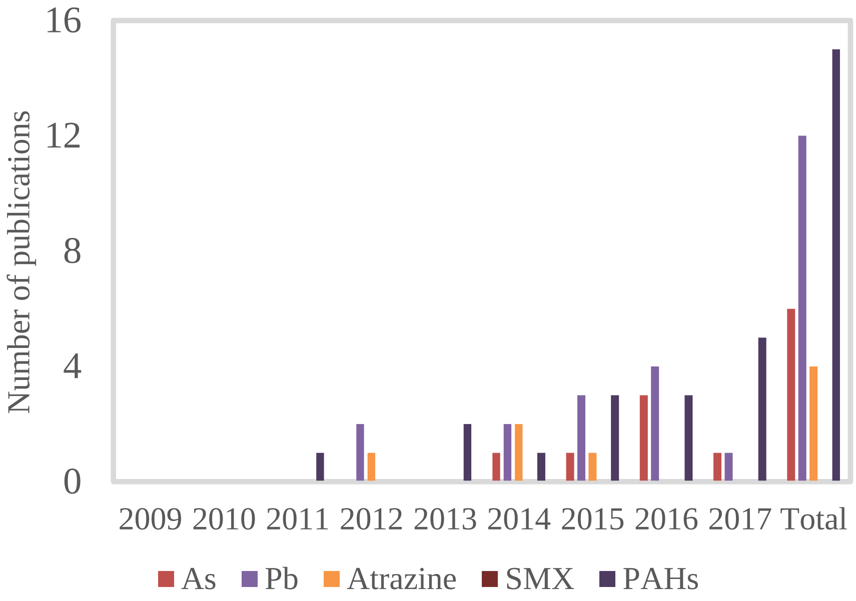
Contaminant	Chemical formula	Chemical structure	Polarity	Aqueous Solubility	Partition coefficients		References
					Log K_{ow}	Log K_{oc}	
SMX	$C_{10}H_{11}N_3O_3S$		Polar	Soluble (<1 mg ml^{-1}) at 25 °C	0.89		NCBI, (2001)
Atrazine	$C_8H_{14}ClN_5$		Polar	Soluble (34.7 mg L^{-1}) at 22 °C	2.71	1.96	ATSDR, (2003)
PAHs (e.g. naphthalene)	$C_{10}H_8$		Neutral (nonpolar)	Weak solubility (Insoluble at higher molecular weight)	> 3.5		Hale et al. (2016)

Table 2

Contaminant	**Soil options**			**Recommended biochar treatment**				**Expected sorption rate (%)**
	Soil type	**pH**	**Approx. contamination (mg kg^{-1})**	**Beneficial feedstock**	**Pyrolysis Temp. (°C)**	**Application rate (% w/w)**	**Favourable pH range**	
As	Paddy and non-paddy soils	5 – 6.5	10- 50	Rice straw Sewage sludge	400 - 500	0.5– 1	3 - 4	> 50
	Brownfield and mine soils	4 – 6	50^{+}	Rice straw Sewage sludge	400 - 500	2	2 - 3	> 50
Pb	Paddy and non-paddy soils	5 – 6.5	5- 50	Wood Dairy manure	500 - 600	0.5 - 1	5 - 5.5	> 65
	Brownfield and mine soils	5	50^{+}	Wood Dairy manure	500 - 600	2	5 - 5.5	> 65
SMX	Paddy and non-paddy soils	5 – 6.5	20 - 50	Wood Manure	250 - 400	0.5 - 1	< 5	> 60
Atrazine	Paddy and non-paddy soils	5 – 6.5	20 - 50	Wood Manure	250 - 400	0.5 - 1	< 5	> 60
PAHs	Paddy and non-paddy soils	5 – 6.5	20 - 50	Wood Sewage sludge	500 - 800	0.5- 1	5 - 6	> 60

Fig. 1


Number of publications
16
12
8
4
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2009
2010
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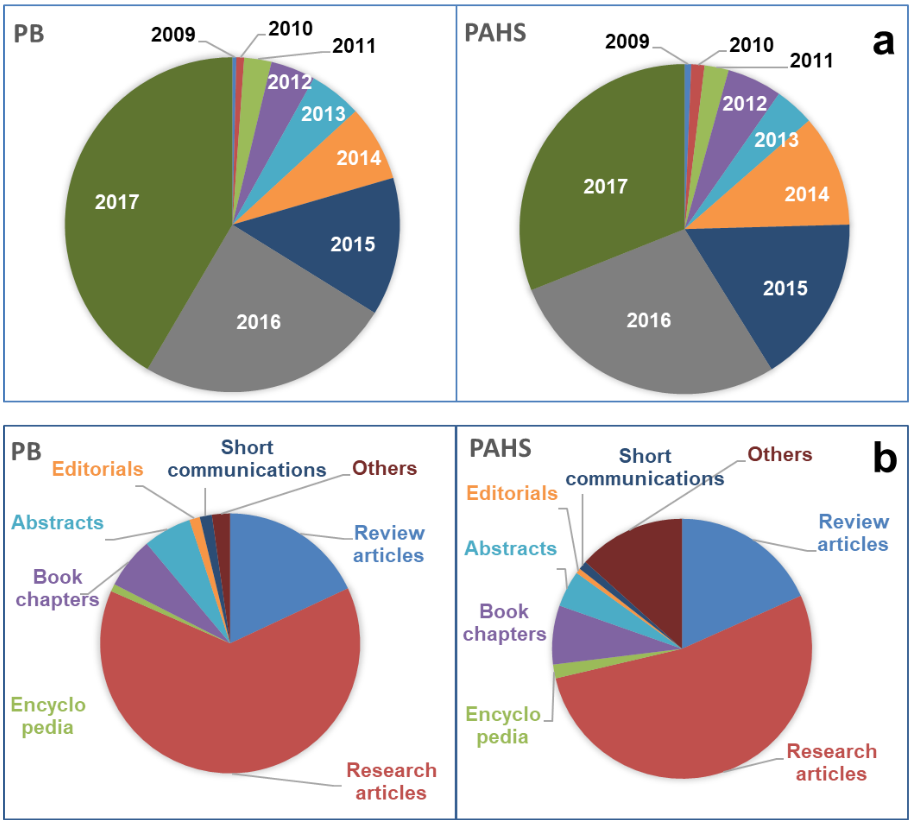
Total
As
Pb
Atrazine
SMX
PAHs

Fig. 2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Abstracts
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Book chapters
Encyclo pedia
Research articles
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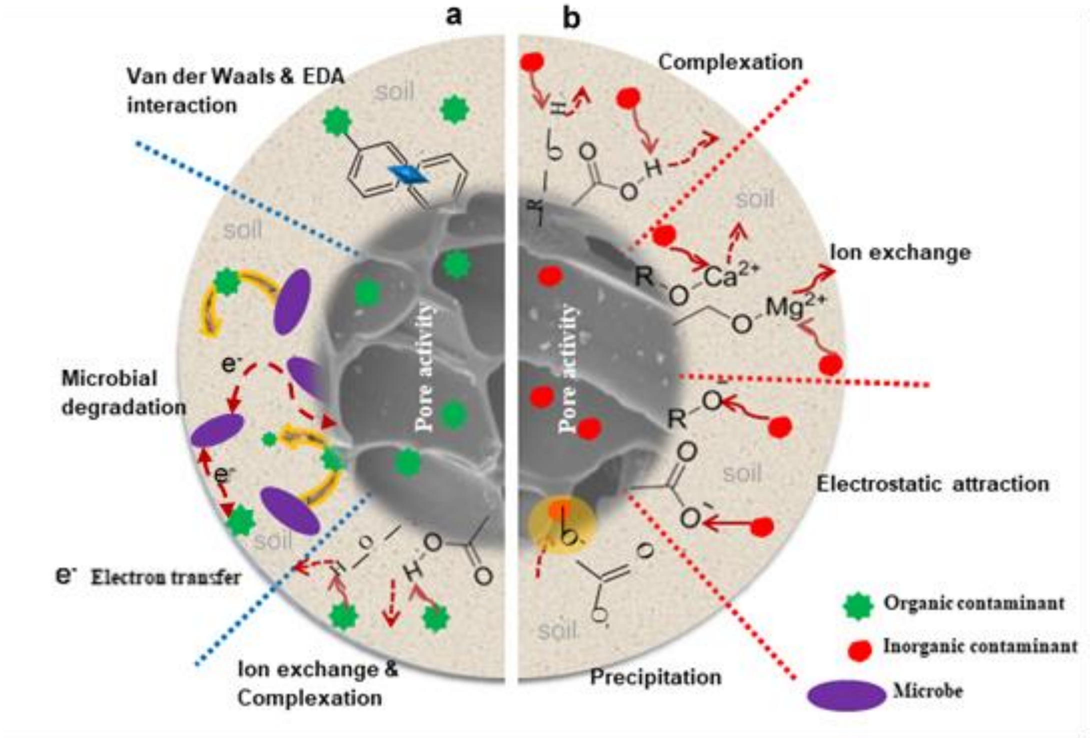
Fig. 3


a
b
Van der Waals & EDA interaction
soil
Microbial degradation
e⁻
e⁻ Electron transfer
Ion exchange & Complexation
Pore activity
Pore activity
Complexation
Ion exchange
R
O
Ca2+
Mg2+
Electrostatic attraction
Precipitation
Organic contaminant
Inorganic contaminant
Microbe