

1 SOILS, SEC # • REVIEW ARTICLE

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

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23 **Abstract**

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

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

35 **Results and discussion** The interaction between biochar and contaminants in soil is largely driven by biochar
36 precursor material and pyrolysis temperature as well as some characteristics of the contaminants such as octanol-
37 water partition coefficient (K_{OW}) and polarity. The structural and chemical characteristics of biochar in turn
38 determine the major sorption mechanisms and define biochar's suitability for contaminant sorption. Based on the
39 reviewed literature, a soil treatment plan is suggested to guide the application of biochar in various soil types
40 (paddy soils, brownfield and mine soils) at different pH levels (4 – 5.5) and contaminant concentrations (< 50 and
41 > 50 mg kg⁻¹).

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

47

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

49 **1. Introduction**

50 The contamination of soil by organic and inorganic contaminants is one of the major environmental challenges
51 faced by the world. Growth in industrial activities, increased use of pesticides, herbicides, antibiotics, agricultural
52 fertilizers, and fossil fuel consumption often leads to soil contamination with potential severe health risks to the
53 human population. Both policy makers and scientists have continued to seek novel ways of managing
54 contamination from organic and inorganic compounds in soil. Phytoremediation, precipitation, ion exchange,
55 membrane filtration and coagulation are some of the ways that have been used for the treatment of pollution in
56 soil and water (Ferniza-García et al. 2017; Paz-Ferreiro et al. 2014). However, these techniques are not always
57 cost-effective and may end up generating contaminant-rich waste. This has in part prompted researchers to
58 investigate the use of readily available biochar materials to mitigate contamination issues in soil (Lehmann et al.
59 2015; Qian et al. 2015; Yang et al. 2017).

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

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

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

89 2. Bibliometric analysis

90 An assessment in 2015 found that, nearly 46% of studies on the use of biochar in contaminant remediation focused
91 on its sorption ability for potentially toxic elements (PTEs) while 54% have focused on the sorption of organic
92 pollutants and other nitrogen and phosphorus related contaminants (Tan et al. 2015). Clearly, there has been a
93 surge in research involving the use of biochar in soil as sorbent over the past decade (**Fig. 2a, Table S1**). Three
94 key search words (*Biochar, soil, [As or Pb or SMX or atrazine or PAHs]*) were used in ScienceDirect database to
95 retrieve publications from 2009 to 2017 focusing on the removal of the five contaminants considered in this review.
96 Retrieved data was further sorted out to ensure that the publications were strictly on remediation of the
97 contaminants of concern by biochar. A total of 1,508 publications were found from 2009 to 2017 (**Table S1**)
98 involving all the five contaminants. Total yearly publications on all the contaminants increased from only 7 in
99 2009 to 572 in 2017 highlighting the increasing research interest on soil remediation using biochar. Pb had the
100 highest number of publications (532) while sulfamethoxazole (SMX) had the least publications (60) within the
101 study period (**Table S1**).

102 Field experiments involving the use of biochar on the five contaminants of interest were fewer within the study
103 period (2009 to 2017) with only 39 publications found in field studies. This number also grew from zero (0) in
104 2009 to 11 and 6 in 2016 and 2017, respectively. The highest number of field studies were done on PAHs (15)
105 followed by Pb (11) (**Fig. 1**). This significantly lower number of field studies may be attributed to some
106 environmental constraints (changing temperatures, rainfall, microbial activity and soil pH) impeding the
107 application of biochar in the field. The analysis of publications on field work suggest that significant work is
108 required to assess the efficiency of biochar in the field and to translate laboratory or greenhouse results to field
109 realities, consistent with the conclusions of Hilber et al. (2017a). The number of publications between 2009 and
110 2017 grouped according to publication type (i.e. research articles, review articles, book chapters, encyclopedia,
111 abstracts, editorials, short communications and others) for Pb and PAHs are shown on **Fig. 2b**. The distribution
112 of publications according to type for all five contaminants is presented on **Fig. S1**. The majority of publications
113 were on direct research work totaling 962 for all five contaminants and closely followed by review articles totaling
114 249 for all five contaminants of interest. The rest of the publications were made in the form of book chapters,
115 encyclopedia, abstracts, editorials, short communications and others (**Fig. S1**).

116 **3. Biochar characterization**

117 **3.1. Description**

118 Biochar has varied descriptions but three aspects are re-current; (1) biochar is dark, porous and very rich in carbon
119 (usually 40 to 90%), (2) it is prepared by heating organic material at temperatures above 250 °C and (3) it is
120 prepared under conditions of little or no oxygen supply (Ahmad et al. 2014; Fellet et al. 2011; Liu et al. 2015;
121 Wang et al. 2015a). As a pyrogenic material, biochar can be distinguished from black carbon and activated carbon
122 by its structure and function (Zhang et al. 2013). Black carbon generally refers to all naturally formed carbonaceous
123 material (e.g. soots, charcoals) (Hammes et al. 2007; Samsuri et al. 2013). Activated carbon is formed from high
124 temperature (~ 800 °C) or chemical treatment of carbonaceous materials (Ahiduzzaman et al., 2016; Park et al.,
125 2013b), with added steps to ensure high porosity and surface area, such as adding catalysts and inert gases. Biochar
126 is generally less of a pure carbonaceous material than activated carbon, and as such it can include more O-
127 containing carboxyl, hydroxyl and phenolic functional groups and the presence of inorganic minerals (Ahmad et
128 al. 2014; Liu et al. 2015). Pyrolysis processes can be wet or dry depending on whether or not water was used
129 during the pyrolysis. In dry pyrolysis which produces biochar often referred to as pyrochars (Han et al. 2016), only

130 heat and little or no oxygen supply is required whereas wet pyrolysis which produces hydrochars (Han et al. 2016)
131 involves the use of water and high pressure (Libra et al. 2011). This review focuses on pyrochars produced from
132 dry pyrolysis of biomass.

133

134 **3.2. Chemical changes during dry pyrolysis**

135 Biomass responds to increased heating by undergoing chemical bond modification where aliphatic bonds are
136 converted to aromatic bonds in biochar (Xiao et al. 2014a). During pyrolysis, hemicellulose decomposes first, at
137 temperatures between 200 and 260 °C, while cellulose and lignin decompose at temperatures ranging from 240 to
138 350 and 280 to 500 °C, respectively (Liu et al. 2015). The transformative processes begin with biomass appearing
139 crystalline and then quickly turning into amorphous carbon with altered bonds and chemical composition. The
140 latter then converts into biochar with stacked sheets of poorly structured polyaromatic hydrocarbon sheets
141 (graphene) which is finally consolidated to very strong graphitic sheets (Nartey and Zhao, 2014).

142

143 **3.3. Surface chemistry**

144 The surface chemistry of biochar is complex with heterogeneous chemical compositions which often depend on
145 the type of biomass material and pyrolysis conditions. Biochar surface exhibits acidity (mainly supplied by
146 carboxyl and hydroxyl groups) and basicity (mainly supplied by O and N functional groups and C- π electrons and
147 some minerals like CaO, MgO, and CaCO₃) (Pignatello et al. 2017) in conjunction with hydrophilic and
148 hydrophobic properties (Kookana et al. 2011). Fundamentally, the structure of biochar is supported by carbon (C)
149 arranged hexagonally in a 'honeycomb' pattern without oxygen or hydrogen (Lehmann and Joseph, 2015).
150 Heteroatoms (e.g. N, S, O, P) are often present while inorganic minerals (e.g. Mg, Na, Ca, Si, and K) and some
151 PTEs (e.g. Al, Cd, As, and Pb) may also be present in small amounts (Freddo et al. 2012). During pyrolysis, K and
152 Cl tend to vaporize easily at lower temperatures (< 300 °C), while P, N, Mg, S, and Ca tend to be covalently bound
153 to complex organic compounds and can only vaporize at higher temperatures (> 500 °C) (Kookana et al. 2011).
154 Increasing temperatures favour the release of gases such as CO₂, CO and NO_x as carbon-rich compounds
155 decompose (Liu et al. 2015). Hydroxyl and carboxylic functional groups are most abundant in biochars derived
156 from fast pyrolysis (rapid heating of biomass at moderate to high temperatures (~700 °C)) while C-H groups
157 become dominant in biochars produced from slow pyrolysis (gradual heating of biomass over a wide range of
158 temperatures (250 – 900 °C)) (Tripathi et al., 2016). Other functional groups on the surfaces of biochar may

159 include nitriles, carbonyls, peptides, phenols, quinones, lactones, and pyrones (Liu et al. 2015) which may be fewer
160 compared to other organic matter like humus (Hale et al. 2016).

161

162 **3.4. Stability in soil**

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

173 What happens to the biochar beyond tens of thousands of years as reported in the literature (Lehmann et al. 2011)
174 remains uncertain. While Xu et al. (2014) and Zhu et al. (2016) suggested some minimal microbial action on the
175 biochar, Spokas et al. (2014) suggests that, over time, the biochar disintegrates into micro and nano-scale fragments
176 that are capable of infiltrating into soil. This disintegration has been reported to occur as the result of repeated
177 swelling and cracking of biochar's graphitic sheets, leading to a crumbling of the physical structure (Spokas et al.
178 2014). Extremely small and mobile biochar particles, which would be similar to colloidal black carbon particles,
179 are capable of becoming mobilized in the subsurface (Enell et al. 2016; Wang et al. 2013). Singh et al. (2014) also
180 suggested that some of the recalcitrant carbon, over longer periods of time, gets mineralized or may turn into
181 organic matter when biotic and abiotic oxidation takes place under conditions of high soil temperature and
182 moisture.

183 **3.5. Suitability for contaminant sorption**

184 Sorption is a physicochemical transfer process in which materials (contaminants) are partitioned between the
185 sorbent and aqueous phases (Yavari et al. 2015). Some properties of the sorbent including surface area, pore

186 sizes/volume, CEC, pH, surface functional groups, molecular structure, hydrophobicity, solubility, polarity and
187 minerals are crucial for this transfer process (Yavari et al. 2015). The suitability of biochar as a sorbent hinges not
188 only on these properties and its resistance to decomposition and mineralization, but also on its low-cost availability
189 from a wide range of precursors notably agricultural by-products (plant husk, plant straw, pine bark, sawdust,
190 bagasse, fruit wastes, weeds, dried aquatic plants), sewage sludge and even automobile tyres (Gupta et al. 2015).
191 Yavari et al. (2015) reviewed that the sorption capacity of organic matter is enhanced 10 – 1000 times after charring
192 to products like biochar through pyrolysis. The structural and chemical composition of biochar (which can easily
193 be engineered) often correlate well with its function as a sorbent. Large pore sizes and pore volumes with high
194 CO₂ measured surface areas (often greater than 100 m² g⁻¹) equip biochar with high sorption tendencies (Liu et al.
195 2015; Lehmann and Joseph, 2015). Pyrolysis temperature is the underlying factor that determines pore distribution
196 (including pore size and pore volume) (Rawal et al. 2016; Uchimiya et al., 2011a) and specific surface area (SSA)
197 of biochars (Hale et al. 2016; Xiao et al. 2014a; Zama et al. 2017). This high polyaromaticity and nanoporosity
198 (Pignatello et al. 2017) as well as hydrophobicity and high surface area make biochar physically a sorbent with
199 qualities similar to, but not as substantial as, activated carbon for non-polar substances (Huggins et al. 2016).
200 However, unlike activated carbon, biochar's polarity and abundant surface functional groups can also intensify the
201 number of sorption sites for polar or ionic substances, including metals.

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

203 **4.1. Arsenic (As)**

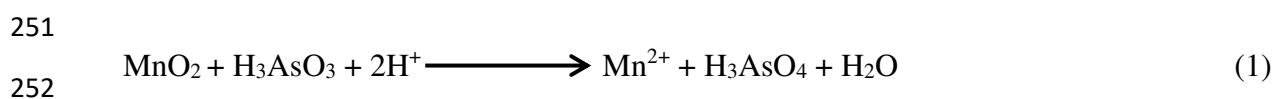
204 Bibliometric analysis found 302 publications and 6 field-based studies focusing on the removal of As by biochar
205 in soil (**Table S1**). Arsenic is a metalloid oxo-anion existing in the natural environment as arsenite [As(III)] and
206 arsenate [As(V)] usually in combination with sulfur, oxygen and iron (Ungureanu et al. 2015). Soil easily adsorbs
207 As(V) although its ability to retain the anion is relatively poor (Agrafioti et al. 2014). The oxidation state of As
208 has a great role to play in its sorption or immobilization in soil. This observation was made by Pan et al. (2015)
209 and Yokoyama et al. (2012) who noticed that the ratio of the coefficients of distribution of As(III) and As(V) on
210 calcite ($K_{As(V)}/K_{As(III)}$) at neutral pH was larger than 2100. Wang et al. (2015b) also had similar observations but
211 added that the relatively easy removal of As(V) from the environment is also attributable to its higher mobility.
212 Many different types of biochars (notably sewage sludge, rice straw/husk, and manure) have been tested for As
213 removal in soil and the majority of them have been counter-productive (increasing pore water As concentration)

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

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

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

243 Studies have also shown that As lacks the ability to engage in complexation and precipitation reactions with
244 biochar (Zama et al., 2017). This explains why pristine biochar does not do well in As removal. However when
245 biochar is modified (e.g. Fe modification), some complexes such as Mn(Fe)–O-As and Fe–O–C (Yang et al. 2016)
246 may be formed on the surfaces of biochar which increases the density of positively charged sites at low pH values
247 (< 4.5) and in turn increases the sorption of As (Yang et al. 2016). Manning et al. (2002) observed that As(III) is
248 easily oxidized to As(V) in the presence of MnO₂ (equation 1). Modifying biochar with MnO₂ therefore enhances
249 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
250 al., 2015b; Gude et al., 2017)



253 Hartley et al. (2009) also observed the influence of pH and the presence of entities like P and Si on the sorption of
254 As by biochar. Lower pH values (i.e. pH < 5) favour the release of H⁺ which may enhance electrostatic attraction
255 with the predominantly anionic As specie in soil. Phosphorus (often present as PO₄ ions) has chemical similarities
256 with As and would compete with As for sorption sites on the biochar (Hartley et al. 2009). The presence of PO₄
257 therefore limits the sorption of As which is often released into the surrounding soil solution.

258

259 **4.2. Lead (Pb)**

260 According to bibliometric analysis, lead (Pb) has been the highest PTE studied for its interaction with biochar in
261 soil. Up to 532 publications and 11 field-based, studies were found focusing on Pb removal by biochar in soil
262 (**Table S1**). It is a common contaminant present in most urban and suburban soils in significant quantities (ATSDR,
263 2011). Many different types of biochars (wood-based, husk-based, sewage sludge, bone-based and yard wastes) at
264 various pyrolysis temperatures (mainly 300 – 700 °C) have been experimented on Pb sorption in soil. All these
265 biochars (both modified and un-modified) have been very effective in the sorption removal of Pb in environmental
266 media (averaging 90% sorption rates in water and 60% in soil) (Li et al. 2016). Compared to most PTEs, Pb is
267 relatively easier to immobilize possibly because of its involvement in multiple sorption mechanisms with biochar
268 (i.e. pore filling, formation of complexes and precipitates, and ion exchange mechanisms) (Han et al. 2016; Xu et
269 al. 2016).

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

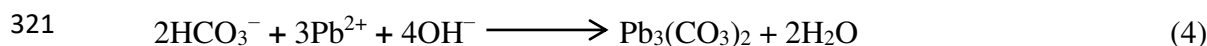
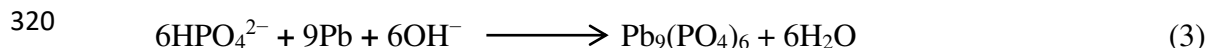
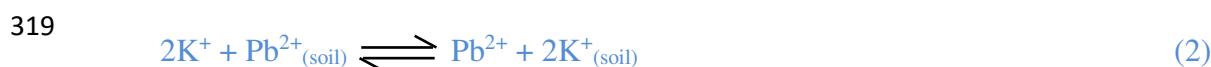
283 The trend of Pb removal in the field soil (where concentrations decrease with biochar addition under field
284 conditions) is similar to laboratory or greenhouse trends. However, sorption amounts differ in field trials
285 (consistently lower than laboratory or greenhouse amounts even under similar conditions) due to differences in
286 soil pH and initial Pb concentrations, which are harder to control in the field. In a five-year field experiment, Pb
287 was immobilized in soil by wheat straw biochar mainly in the form of stabilized carbonates, organic and residual
288 forms (Cui et al. 2016) (Table S2). Abundant functional groups and complex structures in the biochar played key
289 roles in the stabilization of Pb by 3.7 – 19.8% while improving soil microstructure and increasing soil pH and soil
290 organic matter. Most field studies have used greater than 10 t ha^{-1} of biochar to achieve averagely 50% Pb
291 immobilization. For example, Zheng et al. (2015) used 20 t ha^{-1} of rice straw biochar to achieve 40.7% Pb removal
292 (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,
293 79.6 and 59.1% Pb removal, respectively (CaCl_2 extractable) (Table S2). Initial Pb concentrations and type of
294 extractant may have influenced extracted amounts and in both experiments, extracted concentrations were
295 consistently lower, compared to laboratory or greenhouse studies.

296 Physical processes such as pore filling have been rarely reported as major mechanisms for Pb removal in soil.
297 Researchers have frequently cited non-specific chemisorption mechanisms like ion exchange (Uchimiya, 2014),

298 complexation and precipitation (**Fig. 3**) with inorganic components (e.g. CO_3^{2-} , SO_4^{2-}) as the main mechanisms
 299 driving Pb sorption in soil (Chi et al. 2017; Li et al. 2017; Park et al. 2013a). Soil pH tends to influence most of
 300 these processes (Uchimiya, 2014). **Fig. S2** indicates the removal of organic and inorganic contaminants by typical
 301 processes such as microbial breakdown (**Fig. S2a**) and complexation reactions (**Fig. S2b**), respectively.

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

313 The formation of precipitates such as lead phosphate and hydrocerussite (Equations 3 and 4, respectively) often
 314 formed between Pb^{2+} and mineral ions present on the surfaces of biochar represents another major mechanism
 315 driving Pb sorption on biochar (Tran et al. 2016) (**Fig. 3**). Very often, minerals such as calcite (CaCO_3), althausite
 316 ($\text{Mg}_2\text{PO}_4\text{OH}$), and caminite ($\text{Mg}_3(\text{SO}_4)_2(\text{OH})_2$) present on biochar surfaces (Wang et al. 2015a) release ions such
 317 as PO_4^{3-} , SO_4^{2-} , and CO_3^{2-} , which undergo precipitation and co-precipitation reactions with Pb. These sorption
 318 processes may also be affected by the pH of the soil solution.



323 The formation of monodentate and bidentate complexes with Pb ions (equation 5) is also a major mechanism for
324 Pb sorption by biochar (Najar et al. 2010; Sposito, 2008). A large amount of functional groups including hydroxyls,
325 carboxyls, nitriles, ketones, and alkyls often develops on the surfaces of biochar at optimal pyrolysis temperatures
326 (< 500 °C) (Uchimiya et al. 2011b) when anomeric O-C-O and O-alkylated groups undergo cleavage in addition
327 to the formation of fused-ring aromatic C-O groups (Li et al. 2013; Nartey and Zhao, 2014). Higher pH values (>
328 5.0) in soil solution influences the deprotonation of functional groups with a higher chance of coordination with
329 Pb ions (Li et al. 2016). Moreover, at higher pH (> 5.0), Tsai et al. (2012) observed that Pb begins to hydrolyze as
330 Pb (OH)⁺ which also improves its sorption on biochar. **Fig. S2b** illustrates Pb²⁺ binding to a carboxylic group on
331 the surface of biochar. Pb sorption on biochar may also follow a single Langmuir model, which describes surface
332 sorption through coordination of Pb d-electron to C=C (π -electron) and —O—Pb bonds (Cao et al. 2009).

333 **4.3. Sulfamethoxazole (SMX) (C₁₀H₁₁N₃O₃S)**

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

342 In the laboratory or greenhouse, biochar has been fairly good in SMX sorption with reports of up to 50% sorption
343 efficiency. Bamboo, pine sawdust, corncobs, sugarcane bagasse, and wood-based biochars are some examples
344 frequently used in SMX removal. For instance, Srinivasan and Sarmah (2015) reported significant increases in
345 SMX sorption when green waste, corncob and pine sawdust biochars pyrolysed at 350 to 700 °C were added to a
346 silt loam soil at 0.5 and 1% (w/w). Pine sawdust had the highest sorption affinity for SMX which was attributed
347 to its large surface area (795 m² g⁻¹) and lesser exchangeable cations which make the biochar surface less
348 hydrophilic. Apart from surface area, Zheng et al. (2013) also observed that soil pH also affected SMX sorption
349 considerably. At pH 1.0, more than 86.3% of cationic SMX was sorbed and biochar surfaces became positively
350 charged. When the pH values were between 2.0 and 5.0, the dominant SMX species sorbed onto biochars was

351 neutral and biochar surfaces became positive while pH values greater than 6.0 resulted to more anionic SMX
352 species (> 70%) with stronger negative biochar surfaces. SMX has very low K_d values (0.6 - 3.1 L kg⁻¹) and
353 differences in K_d values between biochar and SMX may also affect SMX sorption in soil. All biochars such as
354 bamboo, Brazilian pepper wood, sugarcane bagasse, and hickory wood with higher K_d values (2 - 104 L kg⁻¹) (Yao
355 et al. 2012) would have the ability to immobilize SMX in soil solution.

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

370

371 **4.4. Atrazine (2-Chloro 4-ethylamino 6-isopropylamino-s-triazine)**

372 Atrazine is a mobile polar contaminant used in this review to represent the triazine family of contaminants. It is an
373 herbicide commonly used for weed suppression, and has physical properties that mirror most herbicides (**Table**
374 **1**). Various sorbents including activated carbon (Tan et al. 2016), organic matter, humics and minerals (Deng et
375 al. 2014) have been used in the past to capture atrazine. According to the bibliometric analysis, up to 150
376 publications focusing on biochar and atrazine sorption in soil have been made between 2009 and 2017 (**Table S1**).
377 Amongst these, only 4 publications were field-based.

378 The removal of atrazine by biochar in the laboratory or greenhouse has also been largely successful. Wood and
379 manure-based biochars (e.g. pine wood and dairy waste manure) have been frequently used for atrazine removal

380 which is significantly affected by soil DOC and pH. For example, at low pH values (pH < 3), cassava waste biochar
381 prepared at 350 - 750 °C and applied at 1% sorbed up to 86.6% of atrazine in an artificially contaminated
382 krasnozem soil (20 mg L⁻¹) (Deng et al. 2014). In a related study, southern crabgrass, common lambsquarter,
383 lettuce and wheat biochars were effective in removing atrazine by 89, 34, 100, and 45%, respectively although its
384 herbicidal activity was also greatly reduced (Soni et al. 2015). However, the decrease in its herbicidal activity was
385 dependent on soil DOC and pH. Increasing the DOC fraction of soil increases the chances of partitioning into the
386 organic C fraction and surface sorption which plays a key role in atrazine removal (Cao et al. 2011). Compared to
387 unmodified manioc waste biochar made at 750 °C, FeCl₃ modified manioc waste biochars demonstrated a higher
388 sorption capacity for atrazine by 17.5 times in tropical soils implying that biochar modification can be very
389 beneficial for atrazine sorption (Deng et al., 2014).

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

404 Pore-filling and electrostatic interactions appear to be the major mechanisms driving atrazine sorption in soil (**Fig.**
405 **3a**). Atrazine is polar and can accept or donate electrons during reactions with amino groups. Its polarity and
406 solubility (**Table 1**) also mean that atrazine can easily form covalent bonds with polar biochar surfaces in
407 complexation interactions. However at low pH, biochar surfaces protonate which may influence the sorption of

408 the slightly basic atrazine ($pK_a = 1.7$) through electrostatic attractions. Loganathan et al. (2009) noted that the
409 sorption of atrazine ($K_{ow} \sim 1.72$) involved sorption on carbonized surfaces and partitioning into the residual organic
410 matter of char (biochar). Hao et al. (2013) reported a negative correlation between carbon normalized sorption
411 coefficient (K_{oc}) and H/C and (O+N)/C when corn cobs biochar produced at 350 - 650 °C was applied to atrazine
412 contaminated soil also implying that aromatic carbon and hydrophobic surfaces were influential in atrazine
413 sorption. Pore-filling was also suggested by Hao et al. (2013) as a key mechanism influencing atrazine removal in
414 soil. For ionic organic contaminants or ionic and ionizable molecules like atrazine, there are additional sorption
415 interactions such as cationic or anionic exchange interactions (**Fig. 3**) to charged moieties on the biochar surface
416 or mineral impurities (Droge and Goss, 2012; Droge and Goss, 2013). The intensity of these interactions can be
417 dependent on the pH as well as counterions in the pore water, as the pH can affect the ionization state of both
418 biochar and molecules, and both pH and counterions can effect ion-exchange processes of organic ions (Arp et al.
419 2017).

420 **4.5. Polycyclic aromatic hydrocarbons (PAHs)**

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

429 The interaction between biochar and a wide range of PAHs in the laboratory or greenhouse has been reported
430 extensively in literature with varied and high removal efficiencies. However, these removal efficiencies are
431 affected by some biochar and soil properties including the nature of pyrolysis, particle size and microbial
432 community (Waqas et al. 2015). For example, Ogbonnaya et al. (2016) investigated the efficiency of wood-derived
433 biochar made by slow pyrolysis and gasification and observed that biochar produced by slow pyrolysis was better
434 at immobilizing ^{14}C -naphthalene in soil than biochar produced by gasification. This could be attributed to the
435 presence of a larger amount of pores and organic functional groups on slowly pyrolysed biochar 450 - 500 °C
436 (ramped at 10 °C min⁻¹) compared to gasified biochar at 900 - 1000 °C. The influence of particle size was

437 investigated by Zand and Grathwoh (2016) on the immobilization and leaching of $\Sigma 16$ PAHs from contaminated
438 soils in column experiments using crushed and pulverized forest wood biochars. The addition of 5% crushed
439 biochar (2 mm) decreased 80% PAHs in leachates while 5% pulverized biochar (1 μm) amendment decreased up
440 to 98% PAHs in leachates, implying that smaller sized biochar is better at immobilizing PAHs possibly because
441 of its larger surface area. The study also observed that crushed biochar increased the mobility of higher molecular
442 weight PAHs (i.e. pyrene, benzo(b)fluoranthene, and indeno (1,2,3-cd)) which depended on DOC for their
443 transportation unlike pulverized biochar which depended on colloids formed after biochar addition. Recently,
444 Xiong et al. (2017) investigated the influence of a microbe-biochar composite (*Mycobacterium gilvum* and rice
445 straw biochar) on the remediation of PAHs contaminated coke plant soil. The authors observed superior
446 degradation of phenanthrene, fluoranthene and pyrene by 62.6, 52.1 and 62.1%, respectively after the treatment
447 with microbe-biochar composite. This increase in PAHs degradation compared to less than 47.3% when free cells
448 alone and biochar alone were used could be attributed to enhanced mass transfer of PAHs from the soil to biochar
449 (acting as sink) and the subsequent degradation of these PAHs by the immobilized *M. gilvum* (Xiong et al. 2017).
450 Modifying biochar may also increase the sorption of PAHs in soil. Reports have indicated that more than 90% of
451 PAHs are often removed from soil when biochar is modified with base substances. For example, base modification
452 of rice straw, wood and bamboo biochars produced at temperatures below 500 °C using NaOH was shown to
453 significantly increase the removal of phenanthrene in soil by 72%. According to Feng and Zhu (2018), this was
454 because base modification increased the Koc of extractable biochar by up to 60% – 751%.

455 In field experiments, the influence of microbial activity on PAHs degradation has been significantly highlighted.
456 For example, Stefaniuk et al. (2017) recently experimented the removal of $\Sigma 16$ PAHs by willow (*Salix viminalis*)
457 biochar on podzolic soil ($\Sigma 16$ PAHs concentration $\sim 128.8 \mu\text{g kg}^{-1}$) (Table S2) and in the 18 months field
458 experiment, there was no significant change in $\Sigma 16$ PAHs concentration for the first 12 months. However, after the
459 12th month, up to 45% reduction in $\Sigma 16$ PAHs concentration in soil was recorded especially when biochar was
460 added at the rate of 2.5%. The study suggested that during the first 12 months, microbial activity, which is crucial
461 for PAHs degradation, focused on available soil organic matter (SOM). As SOM reduced, degradation of the
462 harder PAHs then accelerated. The majority of the biochars produced at 400 - 700 °C often come with $\Sigma 16$ PAHs
463 concentrations ranging from 0.4 - 1987 mg kg^{-1} , and 12 - 81 ng L^{-1} , respectively. However, Hilber et al. (2017b)
464 and Rombolà et al. (2015) noted that the majority of these PAHs bound in the biochar (used for soil remediation)
465 were not bioavailable. The biochars acted mainly as contaminant sinks rather than sources of PAHs. In an

466 experiment carried out by Hilber et al. (2017b), the PAHs of 25 out of 33 biochar samples were resistant to
467 desorption.

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

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

494 Han et al. (2016) presented the specific role of amorphous alkyl, aryl and aromatic C in the sorption of PAHs such
495 as pyrene. Alkyl C appears to have properties similar to kerogen with flexible alkyl domains structurally
496 compatible with organic compounds and offering conducive sorption sites for contaminants (Han et al. 2016).
497 Aromatic C through its aromatic π system likely acts as π electron donors or acceptors towards contaminants.
498 Some organic contaminants like acetaminophen and carbamazepine may also contain electron donating groups
499 (e.g. $-\text{OH}$, and $-\text{NH}_2$) which aid in sorbing PAHs onto the biochar through EDA interactions (Han et al. 2016).

500 **5. Challenges in field application of biochar**

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

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

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

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

527 Several studies notably Hale et al. (2012), Han et al. (2016), Hilber et al. (2012) and Yavari et al. (2015), have all
528 discussed the possibility of biochar being a source of contaminant itself in soil. During pyrolysis, compounds such
529 as PAHs, dioxins and PCBs may develop in biochar together with some heavy metals like Pb, Cd, Cu, Zn, and Al
530 from the original biomass material (Hilber et al. 2017a). These compounds are often not available for microbial
531 breakdown as they remain tightly bound to biochar matrices through π - π interactions (Yavari et al. 2015). The type
532 of pyrolysis, feedstock and time determine the concentration of these compounds in biochar (Hale et al. 2012).
533 Quicker production methods (e.g. flash pyrolysis and gasification) often result to biochars with elevated PAHs and
534 dioxin concentrations ($\sim 45 \mu\text{g g}^{-1}$ and 92 pg g^{-1} , respectively). Han et al. (2016) cautioned that this should always
535 be taken into consideration before using biochar for contaminant remediation although Hilber et al. (2017b) noted
536 that PAHs in biochar is usually desorption resistant and can only become bioavailable at higher concentrations ($>$
537 10 mg kg^{-1}).

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

546 **6. Selecting biochars for the treatment of contaminated soils**

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

560 **Arsenic (As):** Rice straw and sewage sludge biochars prepared at 400 - 500 °C were suggested for As remediation
561 in soil (**Table 2**). Rice straw biochar can easily be modified with Fe or Mn (hydr)oxides and it contains Si which
562 easily precipitates with As to products like Gonardite [(Na, Ca, K)₂ (Si, Al)₅O₁₀.3H₂O] (Treacy and Higgins, 2007)
563 or simply inhibits the transfer of As to plant tissues (Chen et al. 2017). Without modification, sewage sludge
564 biochar may contain some oxides and hydroxides of Fe and Mn, which have been very effective in the removal of
565 As in contaminated soils (Rajapaksha et al. 2016). The modification of biochar for the removal of As in soil is
566 highly recommended given that pristine biochar rarely sorbs As. It rather increases its mobility. Many researchers
567 have also recommended chemical modification, where chemical agents such as KOH (Jin et al. 2014), Ca
568 (Agrafioti et al. 2014), Si, clay (Yao et al. 2014) are used to change the surface functionality of biochar in favour
569 of As or other metals sorption (Liu et al. 2015; Rajapaksha et al. 2016). It is important to make biochars at relatively
570 low pyrolysis temperatures (< 500 °C) which have less ash and low pH which favours oxo-anionic As sorption.

571 **Lead (Pb):** The sorption of Pb hinges on complexation, ion exchange and precipitation reactions. The availability
572 of functional groups and inorganic ions are therefore important. Wood-based biochars are suitable because of their
573 characteristic large surface areas, porous structure resulting from thermal cracking and unequal shrinking of
574 interior and exterior woody masses during pyrolysis (Yavari et al. 2015) and abundance of surface functional
575 groups. Dairy manure biochar is also suitable especially for Pb sorption because of the presence of PO₄³⁻ ions

576 which easily precipitate with Pb into more stable $Pb_5(PO_4)_3OH$ (Cao et al. 2011). It is important to pyrolyze these
577 biochars at 500 – 600 °C (**Table 2**) to have a high surface area and still retain most surface functional groups which
578 enhance complexation with Cd and Pb. At 600 °C, more inorganic minerals develop on biochar surfaces to increase
579 pH which favours Cd^{2+} and Pb^{2+} sorption by enhancing cation exchange (Zama et al. 2017)

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

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

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

597

598 **7. Conclusions and future perspectives**

599 Research on biochar has grown over the years with significant focus on its properties and how they affect its ability
600 to immobilize both organic and inorganic contaminants. Biochar remains an impressive alternative in soil
601 remediation. Few biochars may be inefficient in soil contaminant removal especially in As remediation but the
602 majority of biochars achieve significant sorption results (often greater than 50%) when used in the soil remediation.
603 The interaction between biochar and contaminants is governed by processes such as electrostatic attraction,
604 precipitation, complexation and microbial activity and these strongly depend on biochar's precursor material,

605 pyrolysis temperature and the characteristics of the contaminants such as K_{OW} and polarity. The sorption of
606 contaminants in the laboratory or greenhouse under controlled conditions is always significantly higher than
607 sorption in the field under natural conditions. In the field, temperature, rainfall, wind, pH etc., are harder to control
608 and have significant influence on the sorption capacity of biochars.

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

623

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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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1019 **Table captions**

1020 **Table 1.** Physicochemical properties of SMX, atrazine and PAHs related to their sorption on
1021 biochar in soil

1022 **Table 2.** Recommended biochar treatment plan for different soil types contaminated by As,
1023 Pb, SMX, atrazine and PAHs

1024 **Figures captions**

1025 **Figure 1.** Number of publications on field studies in removal of As, Pb, SMX, atrazine and
1026 PAHs in soil between 2009 and 2017 (Data source: ScienceDirect database).

1027 **Figure 2.** Bibliometric distribution of publications according to year (a) and type (b) in
1028 laboratory or greenhouse studies on inorganic (Pb) and organic (PAHs) contaminant removal
1029 in soil by biochar

1030 **Figure 3.** Summary of major mechanisms and processes that influence the removal of As, Pb,
1031 SMX, atrazine and PAHs in soil. (a) removal of organic contaminants, (b) removal of
1032 inorganic contaminants

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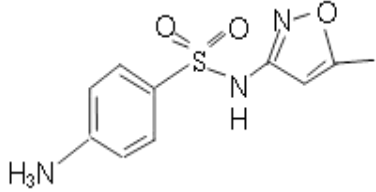
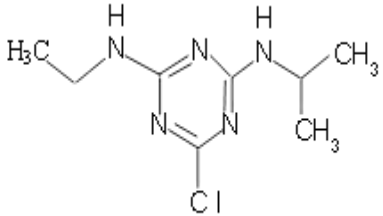
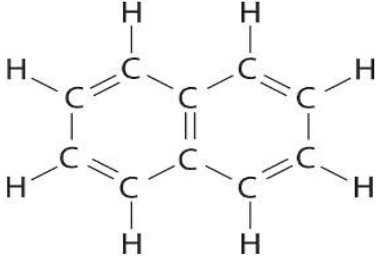
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Table 1

Contaminant	Chemical formula	Chemical structure	Polarity	Aqueous Solubility	Partition coefficients		References
					Log K _{ow}	Log K _{oc}	
SMX	C ₁₀ H ₁₁ N ₃ O ₃ S		Polar	Soluble (<1 mg ml ⁻¹) at 25 °C	0.89		NCBI, (2001)
Atrazine	C ₈ H 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)

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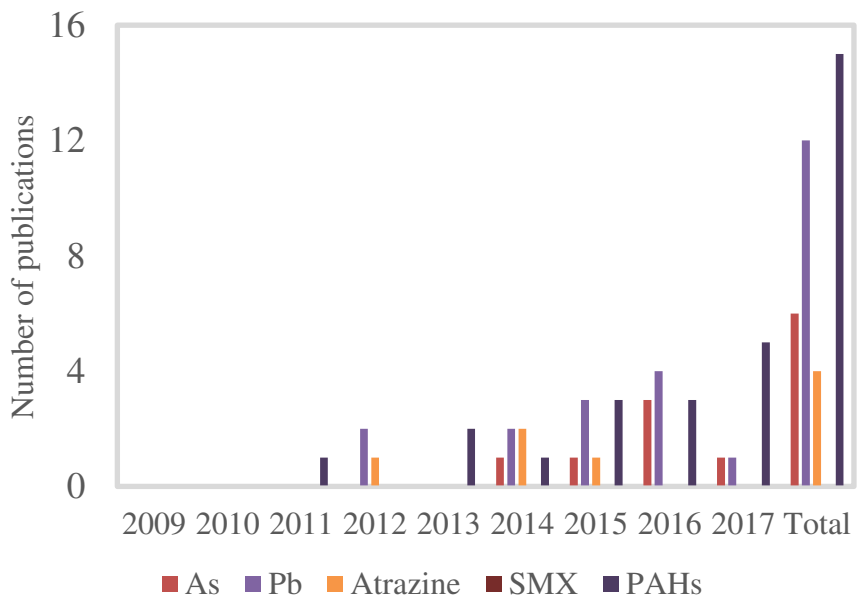
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Table 2

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

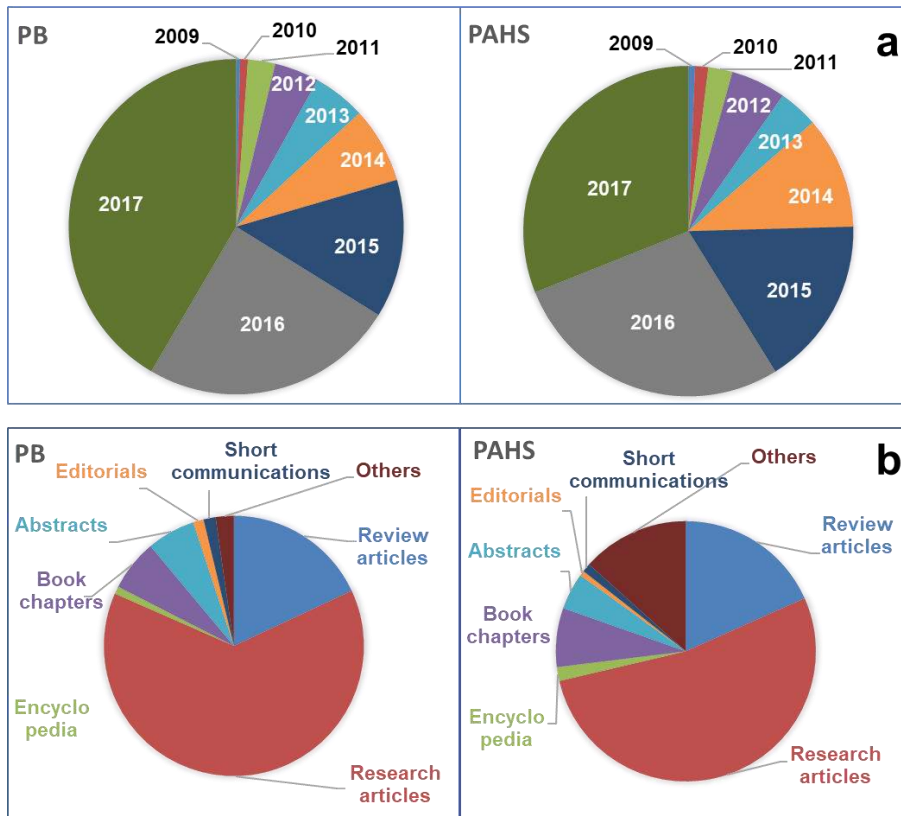
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Fig. 2



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Fig. 3

