

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<sup>-1</sup>).

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- $\pi$  electrons and  
147 some minerals like CaO, MgO, and CaCO<sub>3</sub>) (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 CO<sub>2</sub>, CO and NO<sub>x</sub> 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 CO<sub>2</sub> measured surface areas (often greater than 100 m<sup>2</sup> g<sup>-1</sup>) 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)**

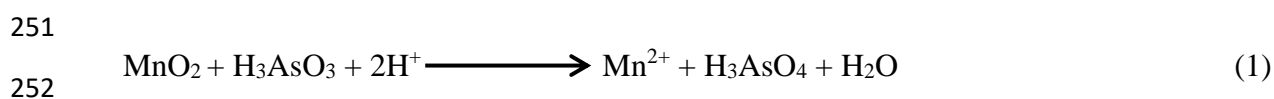
204 Bibliometric analysis found 302 publications and 6 field-based studies focusing on the removal of As by biochar  
205 in soil (**Table S1**). Arsenic is a metalloid oxo-anion existing in the natural environment as arsenite [As(III)] and  
206 arsenate [As(V)] usually in combination with sulfur, oxygen 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  $\text{mg g}^{-1}$ , 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  $\text{mg g}^{-1}$ ). 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  $\text{mg g}^{-1}$ , respectively in control  
230 (without biochar) to 241, 3.08, 3.77 and 0.328  $\text{mg g}^{-1}$ , 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  $\text{NH}_4\text{NO}_3$   
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  $\text{t ha}^{-1}$  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 MnO<sub>2</sub> (equation 1). Modifying biochar with MnO<sub>2</sub> 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<sup>+</sup> which may enhance electrostatic attraction  
255 with the predominantly anionic As specie in soil. Phosphorus (often present as PO<sub>4</sub> 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 PO<sub>4</sub>  
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  $\sim 5.7$ ) paddy soils contaminated with Pb ( $527 \text{ mg kg}^{-1}$ ) and other  
279 metals. The study suggested that a combination of increasing pH ( $\sim 6.2$ ), high biochar rate (up to  $78 \text{ t ha}^{-1}$ ) 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.

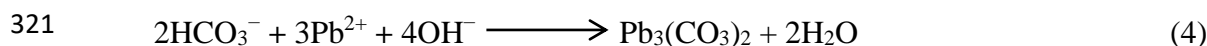
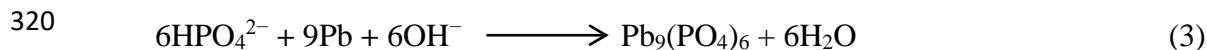
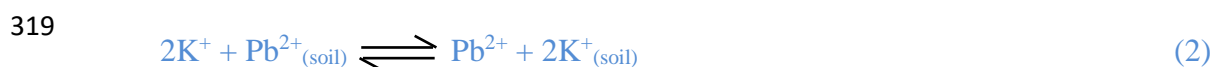
283 The trend of Pb removal in the field soil (where concentrations decrease with biochar addition under field  
284 conditions) is similar to laboratory or greenhouse trends. However, sorption amounts differ in field trials  
285 (consistently lower than laboratory or greenhouse amounts even under similar 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  $10 \text{ t ha}^{-1}$  of biochar to achieve averagely 50% Pb  
291 immobilization. For example, Zheng et al. (2015) used  $20 \text{ t ha}^{-1}$  of rice straw biochar to achieve 40.7% Pb removal  
292 ( $\text{NH}_4\text{NO}_3$  extractable) while Bian et al. (2014) used 10, 20 and  $40 \text{ t ha}^{-1}$  of wheat straw biochar to achieve 33.3,  
293 79.6 and 59.1% Pb removal, respectively ( $\text{CaCl}_2$  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.  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ) 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.  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ ) 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  $\text{Pb}^{2+}$  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  $\text{Pb}^{2+}$  would exchange with two moles of  $\text{K}^+$  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,  $\text{Pb}^{2+}$  might replace  $\text{K}^+$  (equation 2),  
 310 which in turn might replace  $\text{Na}^+$  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  $\text{Pb}^{2+}$  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 ( $\text{CaCO}_3$ ), 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  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$ , 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; Narthey 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)<sup>+</sup> which also improves its sorption on biochar. **Fig. S2b** illustrates Pb<sup>2+</sup> 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 ( $\pi$ -electron) and —O—Pb bonds (Cao et al. 2009).

#### 333 **4.3. Sulfamethoxazole (SMX) (C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>S)**

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 m<sup>2</sup> g<sup>-1</sup>) 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<sup>-1</sup>) 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<sup>-1</sup>) (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,  $\pi$ - $\pi$  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<sup>-1</sup>) (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, FeCl<sub>3</sub> 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<sup>-2</sup> 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<sup>-1</sup> 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  $\mu\text{m}$ ) 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 12<sup>th</sup> 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  $\text{mg kg}^{-1}$ , and 12 - 81  $\text{ng L}^{-1}$ , 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  $\pi$ - $\pi$  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),  $\pi$  electron clouds of arenes may engage in  
473 non-covalent interactions with cations, anions, proton-donor molecules, and the  $\pi$  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  $\pi$ -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 (Koftowski 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  $\pi$  system likely acts as  $\pi$  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<sup>-1</sup> 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<sup>-1</sup> 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  $\pi$ - $\pi$  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  $92 \text{ pg g}^{-1}$ , 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  $10 \text{ mg kg}^{-1}$ ).

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)<sub>2</sub>(Si, Al)<sub>5</sub>O<sub>10</sub>.3H<sub>2</sub>O] (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 PO<sub>4</sub><sup>3-</sup> 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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627

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## 630 **References**

631 Agrafioti E, Kalderis D, Diamadopoulos E (2014). Arsenic and chromium removal from water using biochars  
632 derived from rice husk, organic solid wastes and sewage sludge. *J. Environ. Manage.* 133, 309 – 314



633 Agrafioti E, Kalderis D, Diamadopoulos E (2014). Ca and Fe modified biochars as adsorbents of arsenic and  
634 chromium in aqueous solutions. *J. Environ. Manage.* 146, 444-450

635 Ahiduzzaman M, Islam, AS (2016). Preparation of porous bio-char and activated carbon from rice husk by leaching  
636 ash and chemical activation. *SpringerPlus*, 5, 1248.

637 Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage MS, Lee S, Ok Y. S., (2014).  
638 Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, 99, 19–23.

639 Ahmed S, Chughtai S, Keane MA (1998). The removal of cadmium and lead from aqueous solution by ion  
640 exchange with Na-Y zeolite. *Sep Purif Technol*, 13, 57-64.

641 Alfen NKV, Ed., (2014). *Encyclopedia of Agriculture and Food Systems*. Davis USA,

642 Anyika C, Majid ZA, Ibrahim Z, Zakaria MP, Yahya A (2015). The impact of biochars on sorption and  
643 biodegradation of polycyclic aromatic hydrocarbons in soils—a review. *Environ Sci Pollut R*, 22, 3314-  
644 3341

645 Arp HPH, Brown TN, Berger U, Hale S, (2017). Ranking REACH registered neutral, ionizable and ionic organic  
646 chemicals based on their aquatic persistency and mobility. *Environ. Sci: Proc. Imp.* 19, 939-955.

647 ATSDR (Agency for Toxic Substances and Disease Registry) (2003). Toxicological profile for Atrazine US  
648 Department of Human and Health Services,

649 ATSDR (Agency for Toxic Substances and Disease Registry) (2011). Toxicological profile for Cadmium. US  
650 Department of Human and Health Services,

651 Avisar D, Lester Y, Ronen D (2009). Sulfamethoxazole contamination of a deep phreatic aquifer. *Sci Total*  
652 *Environ.* 407, 4278-4282.

653 Baig SA, Sheng T, Sun C, Xue X, Tan L, Xu X (2014). Arsenic removal from aqueous solutions using Fe<sub>3</sub>O<sub>4</sub>-  
654 HBC composite: Effect of calcination on adsorbents performance. *PLoS One*, 9, e100704.

655 Beesley L, Marmiroli M, Pagano L, Pighi V, Fellet G, Fresno T, Vamerali T, Bandiera M, Marmiroli N (2013).  
656 Biochar addition to an arsenic contaminated soil increases arsenic concentrations in the pore water but  
657 reduces uptake to tomato plants (*Solanum lycopersicum*). *Sci. Total Environ.* 454-455, 598-603

658 Beesley L, Moreno-Jiménez E, Gomez-Eyles JL (2010). Effects of biochar and greenwaste compost amendments  
659 on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted  
660 soil. *Environ Pollut*, 158, 2282-2287.

661 Bian R, Joseph S, Cui L, Pan G, Li L, Liu X, Zhang A, Rutledge H, Wonge S, Chia C, Marjo C, Gong B, Munroe  
662 P, Donne S (2014). A three-year experiment confirms continuous immobilization of cadmium and lead in  
663 contaminated paddy field with biochar amendment. *J. Hazard Mater.* 272, 121–128

664 Cao X, Ma L, Gao B, Harris W (2009). Dairy-manure derived biochar effectively sorbs lead and Atrazine. *Environ.*  
665 *Sci. Technol.* 43, 3285–3291

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

668 Chen B, Ding J (2012). Biosorption and biodegradation of phenanthrene and pyrene in sterilized and unsterilized  
669 soil slurry systems stimulated by *Phanerochaete chrysosporium*. *J Hazard Mater*, 229, 159-169.

670 Chen B, Yuan M (2011). Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar.  
671 *J Soil Sediments.* 11, 62-71

672 Chen D, Guo H, Li R, Li L, Pan G, Chang A, Joseph S (2016). Low uptake affinity cultivars with biochar to tackle  
673 Cd-tainted rice—a field study over four rice seasons in Hunan, China. *Sci. Total Environ*, 541, 1489-1498.

674 Chen H, Gao B, Li H, Ma L (2011). Effects of pH and ionic strength on sulfamethoxazole and ciprofloxacin  
675 transport in saturated porous media. *J. Contam. Hydrol.* 126, 29-36

676 Chen SS, Rotaru AE, Shrestha PM, Malvankar NS, Liu FH, Fan W, Nevin KP, Lovley DR (2014). Promoting  
677 interspecies electron transfer with biochar. *Sci Rep* 4: 5019.

678 Chen Y, Han YH, Cao Y, Zhu YG, Rathinasabapathi B, Ma LQ (2017). Arsenic transport in rice and biological  
679 solutions to reduce arsenic risk from rice. *Front. Plant Sci.*, 8.

680 Chi T, Zuo J, Liu F (2017). Performance and mechanism for cadmium and lead adsorption from water and soil by  
681 corn straw biochar. *Front Env Sci Eng*, 11, 15.

682 Cui L, Pan G, Li L, Bian R, Liu X, Yan J, Quan G, Ding C, Chen T, Liu Y, Liu Y (2016). Continuous  
683 immobilization of cadmium and lead in biochar amended contaminated paddy soil: A five-year field  
684 experiment. *Ecol. Eng.*, 93, 1-8.

685 Cui L, Yan J, Yang Y, Li L, Quan G, Ding C, Chen T, Fu Q, Chang A (2013). Influence of biochar on microbial  
686 activities of heavy metals contaminated paddy fields. *BioResource*, 8, 5536-5548.

687 Dai Z, Webster TM, Enders A, Hanley KL, Xu J, Thies JE, Lehmann J (2017a). DNA extraction efficiency from  
688 soil as affected by pyrolysis temperature and extractable organic carbon of high-ash biochar. *Soil Biology*  
689 *and Biochemistry*, 115, 129-136.

690 Dai Z, Zhang X, Tang C, Muhammad N, Wu J, Brookes PC, Xu J (2017b). Potential role of biochars in decreasing  
691 soil acidification-A critical review. *Sci.Total Environ*, 581, 601-611.

692 Delwiche KB, Lehmann J, Walter MT (2014). Atrazine leaching from biochar-amended soils. *Chemosphere*, 95,  
693 346–352

694 Deng H, Yu H, Chen M, Ge C (2014). Sorption of atrazine in tropical soil by biochar prepared from cassava waste.  
695 *BioResourc.* 9, 6627-6643

696 Droge S, Goss KU (2012). Effect of sodium and calcium cations on the ion-exchange affinity of organic cations  
697 for soil organic matter. *Environ Sci. Technol.* 46, 5894–5901.

698 Droge ST, Goss KU (2013). Ion-exchange affinity of organic cations to natural organic matter: influence of amine  
699 type and nonionic interactions at two different pHs. *Environ Sci Technol.* 47, 798-806

700 Enell A, Lundstedt S, Arp HP, Josefsson S, Cornelissen G, Kleja DB (2016). Combining Leaching and Passive  
701 Sampling to Measure the Mobility and Distribution between Porewater, DOC, and Colloids of Native Oxy-  
702 PAHs, N-PACs, and PAHs in Historically Contaminated Soil. *Environ Sci Technol*, 50, 11797-11805

703 Fabietti G, Biasioli M, Barberis R, Marsan FA (2010). Soil contamination by organic and inorganic pollutants at  
704 the regional scale: the case of Piedmont, Italy. *J. Soils Sed.*, 10, 290–300

705 Fang Q, Chen B, Lin Y, Guan Y (2013). Aromatic and hydrophobic surfaces of wood-derived biochar enhance  
706 perchlorate adsorption via hydrogen bonding to oxygen-containing organic groups, *Environ. Sci. Technol.*  
707 48, 279–288

708 Fellet G, Marchiol L, Vedove GD, Peressotti A (2011). Application of biochar on mine tailings: Effects and  
709 perspectives for land reclamation. *Chemosphere*, 83, 1262-1267

710 Feng Z, Zhu L (2018). Sorption of phenanthrene to biochar modified by base. *Front Environ Sci Eng*, 12, 1.

711 Ferniza-García F, Amaya-Chávez A, Roa-Morales G, Barrera-Díaz CE (2017). Removal of Pb, Cu, Cd, and Zn  
712 present in aqueous solution using coupled electrocoagulation-phytoremediation treatment. *Inter.J.*  
713 *ElecChem.*

714 Freddo A, Cai C, Reid BJ (2012). Environmental contextualization of potential toxic elements and polycyclic  
715 aromatic hydrocarbons in biochar. *Environ Pollut.* 171, 18–24.

716 Galitskaya P, Akhmetzyanova L, Selivanovskaya S (2016). Biochar-carrying hydrocarbon decomposers promote  
717 degradation during the early stage of bioremediation. *Biogeoscience*, 13, 5739.

718 Goss KU, Schwarzenbach RP (2001). Linear free energy relationships used to evaluate equilibrium partitioning of  
719 organic compounds. *Environ Sci Technol.* 35, 1-9.

720 Gude JCJ, Rietveld LC, Van Halem D (2017). As (III) oxidation by MnO<sub>2</sub> during groundwater treatment. *Water*  
721 *Res.* 111, 41-51.

722 Guo M, Uchimiya SM, He Z (2016). Agricultural and environmental applications of biochar: Advances and  
723 barriers. *Soil Sci. Society of America Inc.*, 495-504

724 Gupta VK, Nayak A, Agarwal S (2015). Bio-adsorbents for remediation of heavy metals: current status and their  
725 future prospects. *Environ. Eng R.*, 20, 1-18.

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

728 Hale SE, Arp HPH, Kupryianchyk D, Cornelissen G (2016). A synthesis of parameters related to the binding of  
729 neutral organic compounds to charcoal. *Chemosphere*, 144, 65-74

730 Hale SE, Lehmann J, Rutherford D, Zimmerman AR, Bachmann RT, Shitumbanuma V, Toole A, Sundkvist K L,  
731 Arp HPH, Cornelissen G (2012). Quantifying the total and bioavailable Polycyclic Aromatic Hydrocarbons  
732 and Dioxins in biochars. *Environ, Sci. Technol.* 46, 2830-2838

733 Hammes K, Schmidt MW, Smernik RJ, Currie LA, Ball WP, Nguyen TH, Louchouart P, Houel S, Gustafsson Ö.,  
734 Elmquist M, Cornelissen G (2007). Comparison of quantification methods to measure fire-derived  
735 (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and  
736 the atmosphere. *Global Biogeochem Cy*, 21, GB3016.

737 Han L, Ro KS, Sun K, Sun H, Wang Z, Libra JA, Xing B (2016). New evidence for high sorption capacity of  
738 hydrochar for hydrophobic organic pollutants. *Environ. Sci. Technol.* 50, 13274–13282

739 Han X, Liang CF, Li TQ, Wang K, Huang HG, Yang XE (2013). Simultaneous removal of cadmium and  
740 sulfamethoxazole from aqueous solution by rice straw biochar. *J. Zhejiang Univ. Sci. B.* 14, 640-649

741 Hao F, Zhao X, Ouyang W, Lin C, Chen S, Shan Y, Lai X (2013). Molecular structure of corncob-derived biochars  
742 and the mechanism of atrazine sorption. *Agron J*, 105, 773-782.

743 Hartley W, Dickinson NM, Riby P, Lepp NW (2009). Arsenic mobility in brownfield soils amended with green  
744 waste compost or biochar and planted with *Miscanthus*. *Environ Pollut*, 157, 2654-2662.

745 Herath HMSK, Camps-Arbestain M, Hedley MJ, Kirschbaum MUF, Wang T, Hale R (2015). Experimental  
746 evidence for sequestering C with biochar by avoidance of CO<sub>2</sub> emissions from original feedstock and  
747 protection of native soil organic matter. *Gcb Bioenergy*, 7, 512-526.

748 Hilber I, Bastos AC, Loureiro S, Soja G, Marsz A, Cornelissen G, Bucheli TD (2017a). The different faces of  
749 biochar: contamination risk versus remediation tool. *J. Environ Eng Land. Manage*, 1-19.

750 Hilber I, Blum F, Leifeld J, Schmidt HP, Bucheli TD (2012). Quantitative determination of PAHs in biochar: a  
751 prerequisite to ensure its quality and safe application. *J Agr Food Chem*, 60, 3042-3050.

752 Hilber I, Mayer P, Gouliarmou V, Hale SE, Cornelissen G, Schmidt HP, Bucheli TD (2017b). Bioavailability and  
753 bioaccessibility of polycyclic aromatic hydrocarbons from (post-pyrolytically treated) biochars.  
754 *Chemosphere*, 174, 700-707.

755 Houben D, Evrard L, Sonnet P (2013). Beneficial effects of biochar application to contaminated soils on the  
756 bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (*Brassica napus*), *Biomass*  
757 *Bioenerg*, 57, 196–204

758 Huggins TM, Haeger A, Biffinger JC, Ren ZJ (2016). Granular biochar compared with activated carbon for  
759 wastewater treatment and resource recovery. *Water Res*, 94, 225-232

760 Jin H, Capareda S, Chang Z, Gao J, Xu Y, Zhang J (2014). Biochar pyrolytically produced from municipal solid  
761 wastes for aqueous As(V) removal: adsorption property and its improvement with KOH activation.  
762 *Bioresour. Technol.* 169, 622 - 629

763 Khan S, Cai C, Waqas M, Arp HPH, Zhu YG (2013). Sewage sludge biochar influence upon rice (*Oryza sativa* )  
764 yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil. *Environ. Sci. Technol.*  
765 47, 8624-8632

766 Kołtowski M, Charmas B, Skubiszewska-Zięba J, Oleszczuk P (2017). Effect of biochar activation by different  
767 methods on toxicity of soil contaminated by industrial activity. *Ecotox Environ Safe*, 136, 119-125.

768 Kookana RS, Sarmah AKL, Zwieten V, Krull E, Singh B (2011). Biochar application to soil: agronomic and  
769 environmental benefits and unintended consequences. *Adv. Agro.*, 112, 103-143

770 Lehmann J, Joseph S, Eds. (2009). *Biochar for Environmental Management: science and technology*, 1<sup>st</sup>, ed.,  
771 Earthscan, London

772 Lehmann J, Joseph S, Eds. (2015). *Biochar for environmental management: science, technology and*  
773 *implementation*, 2<sup>nd</sup>, ed., Routledge, London and Newyork,

774 Lehmann J, Rillig MC, Thies J, Masiello CA, Hockaday WC, Crowley D (2011). Biochar effects on soil biota- A  
775 review. *Soil Biol Biochem.* 43, 1812-1836

776 Li H, Dong X, Silva EB, Oliveira LM, Chen Y, Ma LQ (2017). Mechanisms of metal sorption by biochars: Biochar  
777 characteristics and modifications. *Chemosphere.* 178, 466-478

778 Li H, Liu Y, Chen Y, Wang S, Wang M, Xie T, Wang G (2016a). Biochar amendment immobilizes lead in rice  
779 paddy soils and reduces its phyto-availability. *Sci Rep.* 6, 31616

780 Li T, Han X, Liang C, Shohag MJ, Yang X (2015). Sorption of sulphamethoxazole by the biochars derived from  
781 rice straw and alligator flag. *Environ Technol.* 36, 245-253

782 Li X, Shen Q, Zhang D, Mei X, Ran W, Xu Y, Yu G (2013). Functional groups determine biochar properties (pH  
783 and EC) as studied by two-dimensional <sup>13</sup>C NMR correlation Spectroscopy. *PLoS One.* 8, e65949

784 Li Y, Shao J, Wang X, Deng Y, Yang H, Chen H (2014). Characterization of modified biochars derived from  
785 bamboo pyrolysis and their utilization for target component (Furfural) adsorption. *Energy Fuels*, 28, 5119–  
786 5127

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

789 Libra JA, Ro KS, Kammann C, Funke A, Berge ND, Neubauer Y, Titirici MM, Fühner C, Bens O, Kern J,  
790 Emmerich KH (2011). Hydrothermal carbonization of biomass residuals: a comparative review of the  
791 chemistry, processes and applications of wet and dry pyrolysis. *Biofuels*, 2, 71-106.

792 Liu S, Huang B, Chai L, Liu Y, Zeng G, Wang X, Wei Z, Meirong S, Jiaqin D, Zhou Z (2017), Enhancement of  
793 As (v) adsorption from aqueous solution by a magnetic chitosan/biochar composite. *RSC Advances*, 7,  
794 10891-10900.

795 Liu WJ, Jiang H, Yu HQ (2015). Development of biochar-based functional materials: Toward a sustainable  
796 platform carbon material. *Chem. Rev.*, 115, 12251–12285

797 Loganathan VA, Feng Y, Sheng GD, Clement TP (2009). Crop-residue-derived char influences sorption,  
798 desorption and bioavailability of atrazine in soils. *Soil Sci. Soc J*, 73, 967-974.

799 Lu K, Yang X, Shen J, Robinson B, Huang H, Liu D, Bolan N, Pei J Wang H (2014). Effect of bamboo and rice  
800 straw biochars on the bioavailability of Cd, Cu, Pb and Zn to *Sedum plumbizincicola*. *Agr Eco. Environ*,  
801 191, 124-132.

802 Major J (2010). Guidelines on practical aspects of biochar application to field soil in various soil management  
803 systems. International Biochar Initiative, 8.

804 Manning BA, Fendorf SE, Bostick B, Suarez DL (2002). Arsenic (III) oxidation and arsenic (V) adsorption  
805 reactions on synthetic birnessite. *Environ Sci Technol*, 36, 976-981.

806 Manyà JJ (2012). Pyrolysis for biochar purposes: A review to establish current knowledge gaps and research needs.  
807 *Environ. Sci. Technol.*, , 46, 7939–7954

808 McLaughlin H, Anderson PS, Shields FE, Reed TB (2009). All biochars are not created equal, and how to tell  
809 them apart. IBI Conference, Boulder Colorado,

810 Nag SK, Kookana R, Smith L, Krull E, Macdonald LM, Gill G (2011). Poor efficacy of herbicides in biochar-  
811 amended soils as affected by their chemistry and mode of action. *Chemosphere*, 84, 1572-1577.

812 Najar AM, Tidmarsh IS, Ward MD (2010). Lead (II) complexes of bis-and tris-bidentate compartmental ligands  
813 based on pyridyl-pyrazole and pyridyl-triazole fragments: coordination networks and a discrete dimeric  
814 box. *Cryst Eng Comm*, 12, 3642-3650.

815 Nartey O, Zhao B (2014). Biochar preparation, characterization and adsorptive capacity and its effects on  
816 bioavailability of contaminants: An overview. *Adv. Mat. Sci. Engr.*

817 Ni N, Song Y, Shi R, Liu Z, Bian Y, Wang F, Yang X, Gu C, Jiang X (2017). Biochar reduces the bioaccumulation  
818 of PAHs from soil to carrot (*Daucus carota* L.) in the rhizosphere: A mechanism study. *Sci Total Environ*,  
819 601, 1015-1023.

820 Ogbonnaya U, Semple KT (2013). Impact of biochar on organic contaminants in soil: a tool for mitigating risk?  
821 *Agron*, 3, 349-375.

822 Ogbonnaya UO, Thomas J, Fasina SA, Semple KT (2016). Impact of two contrasting biochars on the bio-  
823 accessibility of <sup>14</sup>C-naphthalene in soil. *Environ Technol Innov*. 6, 80–93

824 Pan JJ, Jiang J, Qian W, Xu R (2015). Arsenate adsorption from aqueous solution onto Fe(III)-modified crop straw  
825 biochars. *Environ. Eng. Sci.* 32, 922-929

826 Park J H, Choppala G, Lee SJ, Bolan N, Chung JW, Edraki M (2013a). Comparative sorption of Pb and Cd by  
827 biochars and its implication for metal immobilization in soils. *Water Air Soil Pollut*. 224, 1711.

828 Park J, Hung I, Gan Z, Rojas OJ, Lim KH, Park S (2013b). Activated carbon from biochar: influence of its  
829 physicochemical properties on the sorption characteristics of phenanthrene. *Bioresource technol*, 149, 383-  
830 389.

831 Paz-Ferreiro J, Lu H, Fu S, Mendez A, Gasco G (2014). Use of phytoremediation and biochar to remediate heavy  
832 metal polluted soils: a review. *Solid Earth*, 5, 65-75

833 Pignatello JJ, Mitch WA, Xu W (2017). Activity and reactivity of pyrogenic carbonaceous matter toward organic  
834 compounds. *Environ. Sci. Technol.*, 51, 8893-8908. Qian, K., Kumar, A., Zhang, H., Bellmer, D., Huhnke,  
835 R., 2015. Recent advances in the utilization of biochar. *Renew. Sustain. Energy Rev.* 1055-1064

836 Rajapaksha AU, Chen SS, Tsang DCW, Zhang M, Vithanage M, Mandal S, Gao B, Bolan NS, Ok YS (2016).  
837 Engineered/designer biochar for contaminant removal/immobilization from soil and water: Potential and  
838 implication of biochar modification. *Chemosphere*, 148, 276–291

839 Rawal A, Joseph SD, Hook JM, Chia CH, Munroe PR, Donne S, Lin Y, Phelan D, Mitchell DR, Pace B, Horvat  
840 J, Webber JB (2016). Mineral–biochar composites: Molecular structure and porosity. *Environ Sci Technol.*  
841 50, 7706-7714

842 Reddy K, Xie T, Dastgheibi S (2014). Evaluation of biochar as a potential filter media for the removal of mixed  
843 contaminants from urban storm water runoff. *J. Environ. Eng.* 140, 1943-7870

844 Reemtsma T, Berger U, Arp HPH, Gallard H, Knepper TP, Neumann M, Quintana JB, Voogt PD (2016). Mind  
845 the Gap: Persistent and mobile organic compounds-water contaminants that slip through. *Environ. Sci.*  
846 *Technol.* 50, 10308–10315

847 Rombolà AG, Meredith W, Snape CE, Baront, S, Genesio L, Vaccari FP, Franco M, Fabbri D (2015). Fate of soil  
848 organic carbon and polycyclic aromatic hydrocarbons in a vineyard soil treated with biochar. *Environ Sci*  
849 *Technol*, 49, 11037-11044.

850 Samsuri AW, Zadeh FS, Bardan BJ (2013). Adsorption of As(III) and As(V) by Fe coated biochars and biochars  
851 produced from empty fruit bunch and rice husk. *J. Environ Chem Eng.* 1, 981-988

852 Shan D, Deng S, Zhao T, Wang B, Wang Y, Huang J, Yu G, Wingle J, Wiesner MR (2016). Preparation of ultrafine  
853 magnetic biochar and activated carbon for pharmaceutical adsorption and subsequent degradation by ball  
854 milling. *J. Hazard Mater.* 305, 156–163

855 Shimabuku KK, Kearns JP, Martinez JE, Mahoney RB, Moreno-Vasquez L, Summers RS (2016). Biochar sorbents  
856 for sulfamethoxazole removal from surface water, stormwater, and wastewater effluent. *Water Res.* 96, 236-  
857 245.

858 Silvani L, Vrchotova B, Kastanek P, Demnerova K, Pettiti I, Papini MP (2017). Characterizing biochar as  
859 alternative sorbent for oil spill remediation. *Sci. Rep.*, 7.



860 Singh B, Fang Y, Cowie BCC, Thomsen L (2014). NEXAFS and XPS characterization of carbon functional groups  
861 of fresh and aged biochars. *Org. Geochem.* 77, 1–10

862 Soni N, Leon RG, Erickson JE, Ferrell JA, Silveira ML (2015). Biochar decreases atrazine and pendimethalin  
863 preemergence herbicidal activity. *Weed Technol.* 29, 359–366

864 Spokas KA, Novak JM, Masiello CA, Johnson MG, Colosky EC, Ippolito JA, Trigo C (2014). Physical  
865 disintegration of biochar: An overlooked process. *Environ. Sci. Technol. Lett.* 1, 326–332

866 Sposito G (2008). *The Chemistry of Soils*. Oxford University Press, New York,

867 Srinivasan P, Sarmah AK (2015). Characterisation of agricultural waste-derived biochars and their sorption  
868 potential for sulfamethoxazole in pasture soil: A spectroscopic investigation. *Sci Total Environ* 502, 471–  
869 480

870 Stefaniuk M, Oleszczuk P, Różyło K (2017). Co-application of sewage sludge with biochar increases  
871 disappearance of polycyclic aromatic hydrocarbons from fertilized soil in long term field experiment. *Sci.*  
872 *Total. Environ.* 599, 854-862.

873 Sun K, Kang M, Zhang Z, Jin J, Wang Z, Pan Z, Dongyu X, Fengchang Wu, Xing B (2013). Impact of deashing  
874 treatment on biochar structural properties and potential sorption mechanisms of phenanthrene. *Environ. Sci.*  
875 *Technol.* 47, 11473-11481.

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

878 Tamtam F, Oort F, Bot B, Dinh T, Mompelat S, Chevreuil M, Lamy I, Thiry M (2011). Assessing the fate of  
879 antibiotic contaminants in metal contaminated soils four years after cessation of long-term waste water  
880 irrigation. *Sci. Total Environ.* 409, 540–547

881 Tan G, Sun W, Xu Y, Wang H, Xu N (2016). Sorption of mercury(II) and atrazine by biochar, modified biochars  
882 and biochar based activated carbon in aqueous solution. *Bioresourc Technol.* 211, 727–735

883 Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y, Yang Z (2015). Application of biochar for the removal of pollutants  
884 from aqueous solutions. *Chemosphere.* 125, 70-85

885 Ter Laak TL, Barendregt A, Hermens JL (2006). Freely dissolved pore water concentrations and sorption  
886 coefficients of PAHs in spiked, aged, and field-contaminated soils. *Environ Sci Technol*, 40, 2184-2190.

887 Tran HN, You SJ, Chao HP (2016). Effect of pyrolysis temperatures and times on the adsorption of cadmium onto  
888 orange peel derived biochar. *Waste Manag. Res.* 34, 129-138.

889 Treacy MM, Higgins JB (2007). Collection of simulated XRD powder patterns for zeolites fifth (5<sup>th</sup>) revised  
890 edition. Elsevier

891 Tripathi M, Sahu JN, Ganesan P (2016). Effect of process parameters on production of biochar from biomass waste  
892 through pyrolysis: A review. *Re Sus Energ Rev.* 55, 467-481.

893 Tsai WT, Liu SC, Chen HR, Chang YM, Tsai YL (2012). Textural and chemical properties of swine-manure-  
894 derived biochar pertinent to its potential use as a soil amendment. *Chemosphere.* 89,198-203

895 Uchimiya M (2014). Influence of pH, ionic strength, and multidentate ligand on the interaction of Cd with biochars.  
896 *ACS Sustain. Chem. Eng.* 4, 2019-2027

897 Uchimiya M, Chang S, Klasson KT (2011b). Screening biochars for heavy metal retention in soil: role of oxygen  
898 functional groups. *J. Hazard Mater.* 190, 432-441.

899 Uchimiya M, Wartelle LH, Klasson KT, Fortier CA, Lima IM (2011a). Influence of pyrolysis temperature on  
900 biochar property and function as a heavy metal sorbent in soil. *J Agr Food Chem*, 59, 2501-2510.

901 Uchimiya, M., Bannon, D. I., Wartelle, L. H., Lima, I. M., Klasson, K. T. (2012). Lead retention by broiler litter  
902 biochars in small arms range soil: impact of pyrolysis temperature. *J. Agric. Food Chem*, 60, 5035-5044

903 Ungureanu G, Santos S, Boaventura R, Botelho C (2015). Arsenic and antimony in water and wastewater:  
904 Overview of removal techniques with special reference to latest advances in adsorption. *J. Environ. Manag.*  
905 151, 326-342

906 Wang D, Zhang W, Hao X, Zhou D (2013). Transport of biochar particles in saturated granular media: Effects of  
907 pyrolysis temperature and particle size. *Environ. Sci. Technol.*, 47, 821–828

908 Wang F, Ji R, Jiang Z, Chen W (2014). Species-dependent effects of biochar amendment on bioaccumulation of  
909 atrazine in earthworms. *Environ Pollut.* 186, 241–247

910 Wang M, Zhu Y, Cheng L, Anderson B, Zhao X, Wang D, Ding A (2017). Review on utilization of biochar for  
911 metal-contaminated soil and sediment remediation. *J. Environ Sci.*

912 Wang N, Xue XM, Juhasz AL, Chang ZZ, Li HB (2016). Biochar increases arsenic release from an anaerobic  
913 paddy soil due to enhanced microbial reduction of iron and arsenic, *Environ. Pollut.* 220, 514-522

914 Wang S, Gao B, Li Y, Mosa A, Zimmerman AR, Ma LQ, Harrisb WG, Migliaccio KW (2015a). Manganese oxide-  
915 modified biochars: Preparation, characterization, and sorption of arsenate and lead. *Bioresourc Technol.*  
916 181, 13–17

917 Wang X, Peng B, Tan C, Ma L, Rathinasabapathi B (2015b). Recent advances in arsenic bioavailability, transport,  
918 and speciation in rice. *Environ Sci Pollut Res.* 22, 5742–5750

919 Wang Z, Liu G, Zheng H, Li F, Ngo HH, Guo W, Liu C, Chen L, Xing B (2014). Investigating the mechanisms  
920 of biochar's removal of lead from solution. *Bioresour Technol.* 177, 308-317.

921 Waqas M, Li G, Khan S, Shamshad I, Reid BJ, Qamar Z, Chao C (2015). Application of sewage sludge and sewage  
922 sludge biochar to reduce polycyclic aromatic hydrocarbons (PAH) and potentially toxic elements (PTE)  
923 accumulation in tomato. *Environ Sci Pollut R*, 22, 12114-12123.

924 Wu M, Pan B, Zhang D, Xiao D, Li H, Wang C, Ning P (2013). The sorption of organic contaminants on biochars  
925 derived from sediments with high organic carbon content. *Chemosphere*, 90, 782–788.

926 Xiao L, Bi E, Du B, Zhao X, Xing C (2014a). Surface characterization of maize straw- derived biochars and their  
927 sorption performance for MTBE and benzene. *Environ. Earth Sci.* 71, 5195-5205

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

930 Xiong B, Zhang Y, Hou Y, Arp HPH, Reid BJ, Cai C (2017). Enhanced biodegradation of PAHs in historically  
931 contaminated soil by *M. gilvum* inoculated biochar. *Chemosphere*, 182, 316-324.

932 Xu HJ, Wang XH, Li H, Yao HY, Su JQ, Zhu YG (2014). Biochar impacts soil microbial community composition  
933 and nitrogen cycling in an acidic soil planted with rape. *Environ. Sci. Technol.*, 48, 9391–9399

934 Xu P, Sun C X, Ye XZ, Xiao WD, Zhang Q, Wang Q (2016). The effect of biochar and crop straws on heavy metal  
935 bioavailability and plant accumulation in a Cd and Pb polluted soil. *Ecotox Environ Safe.* 132, 94–100

936 Xu RK, Zhao AZ (2013). Effects of biochars on the adsorption of Cu(II), Pb(II) and Cd(II) by three variable charge  
937 soils from southern China. *Environ. Sci. Pollut Res*, 20, 8491-8501

938 Yamaguchi N, Nakamura T, Dong D, Takahashi Y, Amachi S, Makino T (2011). Arsenic release from flooded  
939 paddy soils is influenced by speciation, Eh, pH, and iron dissolution. *Chemosphere.* 83, 925-932

940 Yang DING, Yunguo LIU, Shaobo LIU, Huang X, Zhongwu LI, Xiaofei TAN, Guangming ZENG, Lu ZHOU,  
941 (2017). Potential benefits of biochar in agricultural soils: A review. *Pedosphere*, 27, 645-661.

942 Yang F, Zhao L, Gao B, Xu X, Cao X (2016). The interfacial behavior between biochar and soil minerals and its  
943 effect on biochar stability. *Environ. Sci. Technol.*, 50, 2264–2271

944 Yang X, Liu J, McGrouther K, Huang H, Lu K, Guo X, He L, Lin X, Che L, Ye Z, Wang H (2016). Effect of  
945 biochar on the extractability of heavy metals (Cd, Cu, Pb, and Zn) and enzyme activity in soil. *Environ*  
946 *Science Pollut Res* 23, 974-984.

947 Yao Y, Gao B, Chen H, Jiang L, Inyang M, Zimmerman AR, Cao X, Yang L, Xue Y, Li H (2012). Adsorption of  
948 sulfamethoxazole on biochar and its impact on reclaimed water irrigation. *J. Hazard. Mater.* 209–210, 408–  
949 413

950 Yao Y, Gao B, Fang J, Zhang M, Chen H, Zhou Y, Creamer AE, Sun Y, Yang L (2014). Characterization and  
951 environmental applications of clay–biochar composites. *Chem Eng J.* 242, 136–143

952 Yavari S, Malakahmad A, Sapari NB (2015). Biochar efficiency in pesticides sorption as a function of production  
953 variables—a review. *Environ Sci Pollut R*, 22, 13824-13841.

954 Yokoyama Y, Tanaka K, Takahashi Y (2012). Differences in the immobilization of arsenite and arsenate by calcite.  
955 *Geochim Cosmochim Ac*, 91, 202-219.

956 Yu L, Yuan Y, Tang J, Wang Y, Zhou S (2015). Biochar as an electron shuttle for reductive dechlorination of  
957 pentachlorophenol by *Geobacter sulfurreducens*. *Sci. Rep.* 5, 16221.

958 Yu Z, Qiu W, Wang F, Lei M, Wang D, Song Z (2017). Effects of manganese oxide-modified biochar composites  
959 on arsenic speciation and accumulation in an indica rice (*Oryza sativa*) cultivar. *Chemosphere*, 168, 341-  
960 349.

961 Zama EF, Zhu YG, Reid BJ, Sun GX (2017). The role of biochar properties in influencing the sorption and  
962 desorption of Pb(II), Cd(II) and As(III) in aqueous solution. *J. Clean Prod.*, 148, 127-136.

963 Zand AD, Grathwoh P (2016). Enhanced immobilization of polycyclic aromatic hydrocarbons in contaminated  
964 soil using forest wood-derived biochar and activated carbon under saturated conditions, and the importance  
965 of biochar particle size. *Pol. J. Environ. Stud.* 25, 427-441

966 Zhang W, Zheng J, Zheng P, Qiu R (2015). Atrazine immobilization on sludge derived biochar and the interactive  
967 influence of coexisting Pb(II) or Cr(VI) ions. *Chemosphere.* 134, 438-445

968 Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, Bolan NS, Pei J, Huang H (2013). Using biochar for remediation  
969 of soils contaminated with heavy metals and organic pollutants. *Environ Sci Pollut R*, 20, 8472-8483

970 Zhang Y, Fan J, Fu M, Ok YS, Hou Y, Cai C (2017). Adsorption antagonism and synergy of arsenate(V) and  
971 cadmium(II) onto Fe-modified rice straw biochars. *Environ Geochem Hlth*, 1-12.

972 Zhao L, Cao X, Zheng W, Scott JW, Sharma BK, Chen X (2016). Coprolysis of biomass with phosphate  
973 fertilizers to improve biochar carbon retention, slow nutrient release, and stabilize heavy metals in soil.  
974 ACS Sustain. Chem. Eng., 4, 1630–1636

975 Zheng H, Wang Z, Zhao J, Herbert S, Xing B (2013). Sorption of antibiotic sulfamethoxazole varies with biochars  
976 produced at different temperatures. Environ Pollut. 181, 60-67

977 Zheng R, Chen Z, Cai C, Tie B, Liu X, Reid BJ, Huang Q, Lei M, Sun G, Baltrėnaitė E (2015). Mitigating heavy  
978 metal accumulation into rice (*Oryza sativa*) using biochar amendment—a field experiment in Hunan, China.  
979 Environ Sci Pollut Res, 22, 11097-11108.

980 Zheng RL, Cai C, Liang JH, Huang Q, Chen Z, Huang YZ, Arp HP, Sun GX (2012). The effects of biochars from  
981 rice residue on the formation of iron plaque and the accumulation of Cd, Zn, Pb, As in rice (*Oryza sativa*)  
982 seedlings. Chemosphere, 89, 856–862

983 Zhu X, Chen B, Zhu L, Xing B (2017). Effects and mechanisms of biochar-microbe interactions in soil  
984 improvement and pollution remediation: A review. Environ Pollut, 227, 98-115.

985 Zhu YG, Su JQ, Cao Z, Xue K, Quensen J, Guo GX, Yang YF, Zhou J, Chu HY, Tiedje JM (2016). A buried  
986 Neolithic paddy soil reveals loss of microbial functional diversity after modern rice cultivation. Sci. Bull.  
987 61, 1052–1060

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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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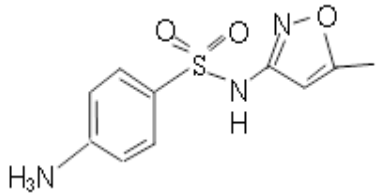
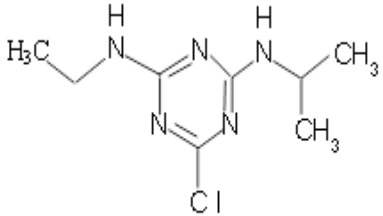
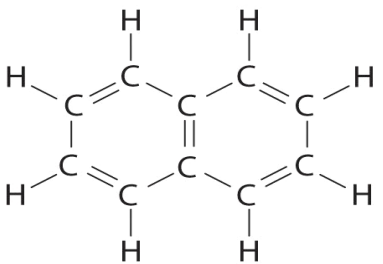
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**Table 1**

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

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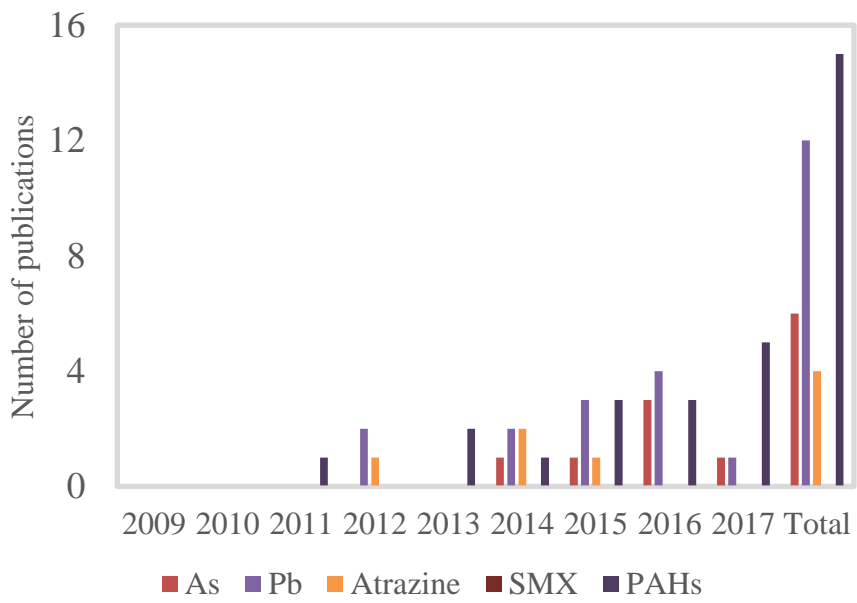


**Table 2**

| Contaminant | Soil options              |         | Recommended biochar treatment                |                             |                      |                          |                     | Expected sorption rate (%) |
|-------------|---------------------------|---------|--|-----------------------------|----------------------|--------------------------|---------------------|----------------------------|
|             | Soil type                 | pH      | Approx. contamination (mg kg <sup>-1</sup> ) | 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<br>Sewage sludge | 400 - 500            | 0.5– 1                   | 3 - 4               | > 50                       |
|             | Brownfield and mine soils | 4 – 6   | 50 <sup>+</sup>                              | Rice straw<br>Sewage sludge | 400 - 500            | 2                        | 2 - 3               | > 50                       |
| Pb          | Paddy and non-paddy soils | 5 – 6.5 | 5- 50  | Wood<br>Dairy manure        | 500 - 600            | 0.5 - 1                  | 5 - 5.5             | > 65                       |
|             | Brownfield and mine soils | 5       | 50 <sup>+</sup>                              | Wood<br>Dairy manure        | 500 - 600            | 2                        | 5 - 5.5             | > 65                       |
| SMX         | Paddy and non-paddy soils | 5 – 6.5 | 20 - 50                                      | Wood<br>Manure              | 250 - 400            | 0.5 - 1                  | < 5                 | > 60                       |
| Atrazine    | Paddy and non-paddy soils | 5 – 6.5 | 20 - 50                                      | Wood<br>Manure              | 250 - 400            | 0.5 - 1                  | < 5                 | > 60                       |
| PAHs        | Paddy and non-paddy soils | 5 – 6.5 | 20 - 50                                      | Wood<br>Sewage sludge       | 500 - 800            | 0.5- 1                   | 5 - 6               | > 60                       |

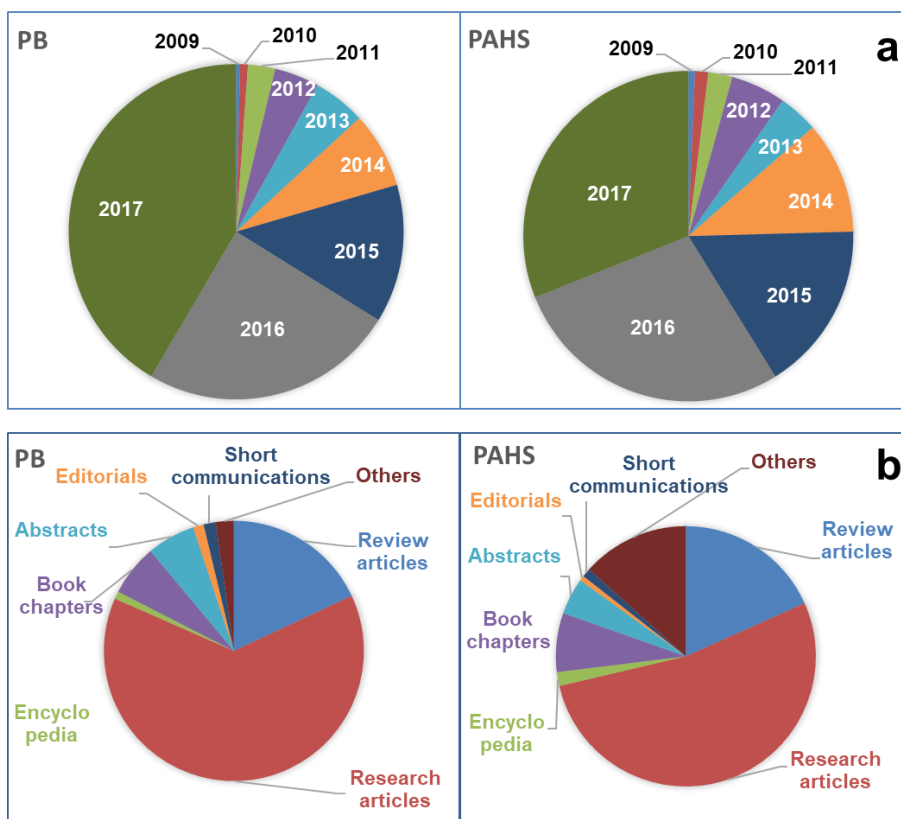
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**Fig. 1**



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**Fig. 2**



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**Fig. 3**

