ABSTRACT

A batch experiment was conducted to examine the effects of biochar on the behaviour of soil-borne arsenic and metals that were mobilized by three low-molecular-weight organic acids. In the presence of citric acid, oxalic acid and malic acid at a molar concentration of 0.01 M, the surface of biochar was protonated, which disfavours adsorption of the cationic metals released from the soil by organic acid-driven mobilization. In contrast, the oxyanionic As species were re-immobilized by the protonated biochar effectively. Biochar could also immobilize oxyanionic Cr species but not cationic Cr species. The addition of biochar increased the level of metals in the solution due to the release of the biochar-borne metals under attack by LMWOAs via cation exchange. Biochar could also have the potential to enhance reductive dissolution of iron and manganese oxides in the soil, leading to enhanced release of trace elements bound to these oxides. The findings obtained from this study have implications for evaluating the role of biochar in immobilizing trace elements in rhizosphere. Adsorption of cationic heavy metals on biochar in the presence of LMWOAs is unlikely to be a mechanism responsible for the impeded uptake of heavy metals by plants growing in heavy metal-contaminated soils.

Key words: Biochar, organic acid, metal, arsenic, soil.

1   Introduction

Low-molecular-weight organic acids (LMWOAs) released from plant roots play an important role in mobilization of soil-borne nutrients and trace elements in rhizosphere (Jones and Darrah, 1994). In contaminated soils where elevated level of trace elements is encountered, this enhanced bioavailability of trace elements may cause microbial toxicity and phytotoxicity (Mossa et al., 2017; Visioli et al., 2013). It is also possible that plants growing in the contaminated soils take up excessive amounts of trace elements and accumulate in the edible portion to a level that could result in health problems for human or animals that consume the plant products (Brekken and Steinnes, 2004; Fu et al., 2008; Hao et al., 2011).

Biochar produced from biomass via pyrolysis is thought to be an excellent sorbent due to its large specific surface area (Li et al., 2017; Xu et al., 2016). Non-activated biochar materials tend to be alkaline and therefore have negatively charged surfaces (Wang and Liu, 2017). In theory, this favours adsorption of cationic metals but disfavours adsorption of anions. Mechanisms responsible for removal of cationic metals from aqueous solution by biochar are likely to include: (a) physical sorption that involves electrostatic interaction between the biochar surfaces and solution-borne metals, (b) replacement of H^+ in functional groups on biochar surfaces by solution-borne metals through complexation or cation exchange, and (c) formation of precipitates through reactions between solution-borne metals and biochar-borne phosphate, carbonate or hydroxyl ions. These proposed mechanisms are valid when the alkaline nature of biochar remains unchanged such as when a biochar material is in contact with aqueous solutions having a pH value similar to the biochar. For example, in an aqueous system involving Ca^{2+} and biochar, the Ca^{2+} may be removed from the solution by electrostatic attraction, adsorption to negatively charged biochar surfaces, replacing H^+ or other cations in a functional group, or formation of practically insoluble $CaCO_3$, $CaPO_4$ or $Ca(OH)_2$ under alkaline conditions.

The above mechanisms have also been proposed to take place for cationic heavy metals such as Cd^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+} and Zn^{2+} (Aran et al., 2016; Cui et al., 2016; Li et al., 2017). However, environmental media containing elevated concentration of dissolved heavy metals always have acidic pH, which could markedly modify the surface conditions of biochar. This needs to be taken into account when proposing the mechanisms for heavy metal immobilization in these systems. So far, there has been no systematic research done to investigate the effects of biochar on behaviour of heavy metals and metalloids in the presence of LMWOAs. This information is important for evaluation of biochar functions in terms of heavy metal and metalloid immobilization in rhizospheric environments. The objectives of this study was to (a) characterise the softwood biochar; (b) examine the effects of the biochar on the behaviour of soil-borne cationic and anionic metals and metalloids in the presence of three common LMWOAs; and (c) observe the temporal variation in these metals and metalloids under the set reaction systems.

2   Materials and Methods

2.1   The Contaminated Soil Used in the Experiment

A multi-contaminated soil was selected for this study. The soil material used for the experiments was a composite soil sample formulated by mixing subsamples collected from the surface soil layer (0-10 cm) at various locations within a closed landfill site in the Greater Manchester, United Kingdom that was previously investigated (Mukwaturi and Lin, 2015; Qin et al., 2016). After collection, the soil samples were oven-dried at 40 °C and then ground using a mortar and pestle to pass a 2 mm sieve. Samples were stored in an airtight resealable bag, prior to use in the experiments. The composite sample was then formulated and characterized. The pH, electrical conductivity (EC) and total concentration of major metals and arsenic are given in Table 1.

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89 **Table 1 Some major physical and chemical characteristics of the soil and biochar material**
90 **used in the experiments**

Parameter	Soil	Biochar
pH	4.63	8.44
EC (dS/m)	0.019	0.160
Organic C content (%)	1.11	
Soil particle fraction <0.002 mm (%)	1	
Soil particle fraction 0.002-0.063 mm (%)	7	
Soil particle fraction 0.063-0.125 mm (%)	17	
Soil particle fraction 0.125-0.25 mm (%)	29	
Soil particle fraction 0.25-2 mm (%)	46	
Total surface area (m^2/g)		162
Total polycyclic aromatic hydrocarbon (mg/kg)		0.18
Moisture content (%)		1.00
Total carbon (%)		90.2
Hydrogen (%)		1.83
Oxygen (%)		6.02
Total ash (%)		1.89
Total nitrogen (%)		<0.1
As (mg/kg)	1202	nd
Ca (mg/kg)	1311	20642
Cr (mg/kg)	111	94.4
Cu (mg/kg)	44.8	39.7
Fe (mg/kg)	21035	1113
Mn (mg/kg)	34.3	869
Zn (mg/kg)	13.4	54.4
Pb (mg/kg)	672	5.60

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92 **2.2   The Biochar Material Used in the Experiment**

93 The biochar (labelled as SWP 700) used for the treatment of the contaminated soils was purchased

94 from the United Kingdom Biochar Research Centre (UKBRC). The biochar was made from

95 softwood pellets at a pyrolysis temperature of $700^{o}C$. The major physical and chemical

96 characteristics, as provided by the manufacturer, are given in Table 1. Prior to its use in the

97 experiment, the biochar sample was oven-dried at $40^{o}C$ for 48 hours and then ground using a mortar

98 and a pestle to pass through a 2 mm sieve. The thoroughly homogenised sample was put in an

99 airtight grip seal nylon bag prior to experiments.

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2.3   Design of Batch Experiment

A batch experiment was conducted using a biochar dose of 1 g for 10 g of the soil. Three common low-molecular-weight organic acids (citric acid, oxalic acid and malic acid) were selected for the experiment. Details on the experimental design are given in Table 2. 125 mL plastic bottles were used as batch reactors. After adding all the ingredients into a bottle, the reactor was shaken in a rotary shaker for 1 h and then pH and EC in the solution were measured. An aliquot of 15 mL supernatant was taken and stored in a centrifuge tube after filtration using a 0.22 μm nylon syringe filter. The solution samples were frozen prior to analysis of various elements. After the completion of sample collection, the bottles were placed in a cardboard box with appropriate cover to keep them in the dark at room temperature (ranging from 1 to 11 $^{\circ}$C during the period of the experiment). Following 1-week incubation, another 15 mL of supernatant was taken after measurements of pH and EC.

Table 2   Details on the design of the batch experiments

Treatment	Soil (g)	Biochar (g)	Water (mL)	0.01 M citric acid (mL)	0.01 M oxalic acid (mL)	0.01 M malic acid (mL)
SBSB	10	1	50			
S-CS-C	10	0		50		
S-OS-O	10	0			50	
S-MS-M	10	0				50
SB-CSB-C	10	1		50		
SB-OSB-O	10	1			50	
SB-MSB-M	10	1				50
SB-COSB-CO	10	1		25	25	
SB-CMSB-CM	10	1		25		25
SB-OMSB-OM	10	1			25	25

2.4   Analytical Methods

The functional groups of biochar sample used for the study were determined using a Thermo Scientific Nicolet iS10 FTIR spectrometer. Prior to analysis, the biochar was mixed with KBr (1:100 ratio) and then pressed into a KBr/biochar pellet. The spectra were performed within a 4,000 cm^{-1} to

119 400 cm^{-1} scan range at resolution of 4 cm^{-1}. A total of 100 scans were averaged, as this gives a better

120 signal-to-noise ratio (SNR). Smith (2011) explained that adding many scans together improves the

121 SNR, thus 100 scans should give a better result than fewer scans. The significant peaks were then

122 identified and the compositions of functional groups were determined by identifying the functional

123 groups that exists at different wavelengths.

124 The pH, EC and DO in the solution samples were measured using a Jenway-3510 pH meter, a

125 Mettler Toledo EC meter and an Oxyguard Handy MK1 DO meter, respectively. Various trace

126 elements were measured by inductively coupled plasma optical emission spectrometry (Varian

127 720ES ICP-OES).

128 **2.5   QA/QC and Statistical Analysis**

129 The experiment was performed in triplicates. All chemical reagents used in the experiment were of

130 analytical reagent grade. Ultrapure water (18.2 MΩ/cm) was used throughout the entire course of the

131 experiment. Repeatability analysis shows that the mean relative standard deviation (RSD) was 0.9%

132 for pH, 3.9% for EC, 5.0% for As, 13% for Co, 24% for Cr, 5.9% for Cu, 3.3% for Fe, 2.8% for Mn

133 and 9.7% for Pb.

134 One-way analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine

135 the statistical significance between the treatments.

136 **3   Results**

137 **3.1   FTIR Analysis of the Biochar**

138 The spectra of biochar used for the study is shown in Fig. 1. A broad O-H stretch could be observed

139 at ~3400 cm^{-1} (Brewer, Schmidt-Rohr, Satrio and Brown, 2009). The strong peak observed at ~1640

140 cm^{-1} was assigned to aromatic C=C and C=O functional groups (Gai et al., 2014; Jindo et al., 2014)

141 whilst the weaker peak at ~1380 cm^{-1} was assigned aliphatic CH$_3$ (Özçimen and Ersoy-Meriçboyu,

142 2010). The stretch observed at ~1130 cm^{-1} is associated with aliphatic C-O-C which is related to the

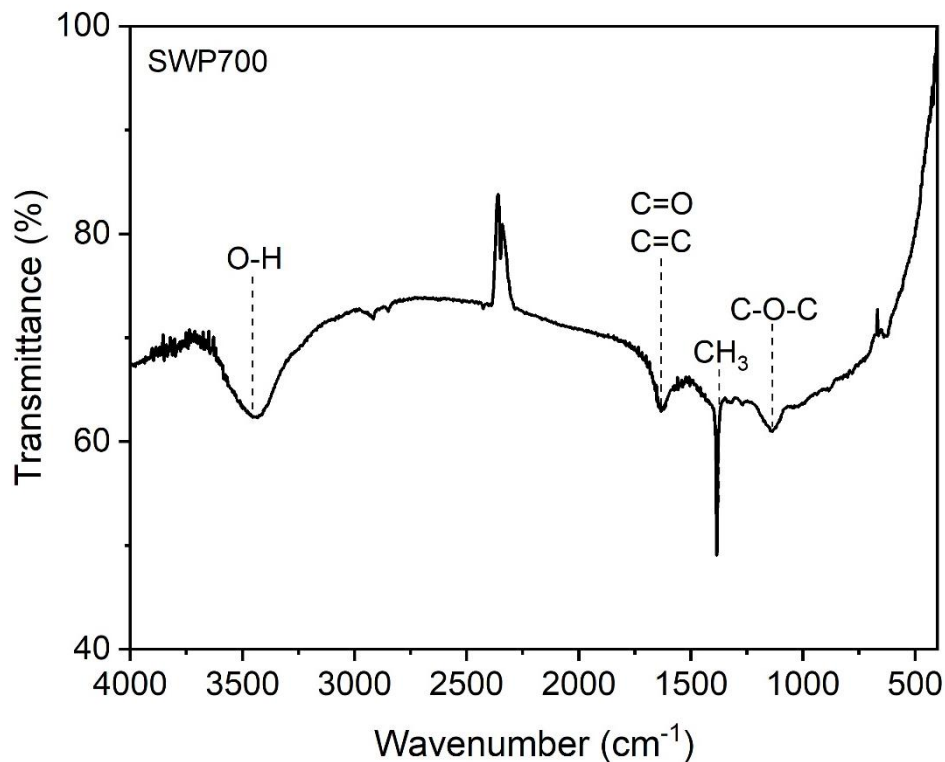143 cellulose content of the char material (Melo, Coscione, Abreu, Puga and Camargo, 2013).

144

153 **Figure 1 The Fourier-transform infrared (FTIR) spectra of Biochar SWP700 used in the**

154 **experiment**

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156 **3.2   pH and EC in the Solutions**

157 As expected, addition of the LMWOAs resulted in a decrease in pH. For each LMWOA, the pH

158 tended to be lower in the treatment without added biochar than in the treatment with added biochar.

159 There was a significant (P <0.05) difference between S-C and SB-C (the pair of citric acid

160 treatments), and between S-M and SB-M (the pair of malic acid treatments). The combined acid-

161 treatments (SB-CO, SB-CM and SB-OM) showed a value somewhere in between. There was a trend

162 to show that pH increased after 7 days of incubation for the SB and the treatments except for SB-C

163 and SB-CM (Table 3).

Table 3 pH and EC in the solutions after 1-h shaking and 7-day incubation for the SB and various treatments

| Treatment	pH		EC (μS/cm)	
	1 hour	7 days	1 hour	7 days
SB	4.99±0.03g	5.70±0.03h	52.0±2.65a	76.3±10.3a
S-C	3.62±0.05a	3.69±0.01a	812±4.84d	857±8.45f
S-O	3.71±0.05b	3.99±0.01e	1138±10.1f	571±21.7d
S-M	3.90±0.07de	4.01±0.01e	572±3.21b	516±4.67c
SB-C	3.89±0.01de	3.80±0.00b	814±6.67d	853±11.1f
SB-O	3.78±0.01bc	4.17±0.02fg	921±15.0e	502±7.51bc
SB-M	4.10±0.01f	4.15±0.01f	571±6.66b	503±5.51bc
SB-CO	3.82±0.03cd	3.92±0.02d	819±25.3d	707±8.95e
SB-CM	3.91±0.01de	3.86±0.01c	707±10.3c	728±12.9e
SB-OM	4.00±0.01ef	4.21±0.01g	577±20.9b	471±0.33b

*All values are presented as mean ± standard error (n= 3). Means with different letters in the same column are significantly different at p < 0.05.

Electrical conductivity (EC) also increased after addition of LMWOAs. There was no significant (P >0.05) difference between S-C and SB-C, and between S-M and SB-M. But EC was significantly (P <0.05) higher in S-O than in SB-O. The EC in each of the combined acid treatments tended to be smaller than the mean value of the two relevant single acid treatments. The EC in the treatments involving oxalic acid tended to markedly decrease after 7 days of incubation (Table 3).

3.3 Fe and Mn in the Solutions

Figure 2 shows the concentration of Fe and Mn in the solutions after 1-h shaking and 7-day incubation for SB and various treatments. As expected, addition of LMWOAs increased the concentration of all the three metals in the solutions. For each of these two metals, the concentration in the solution was significantly lower in the treatment without added biochar than in the treatment with added biochar except for S-O vs SB-O for Fe, which shows no significant (P >0.05) difference. There was a drop in the concentration of both metals after 7 days of incubation for the single oxalic acid treatments regardless of whether the biochar was added or not. This was particularly evident for Fe, showing approximately 40% reduction in soluble Fe in the solution.

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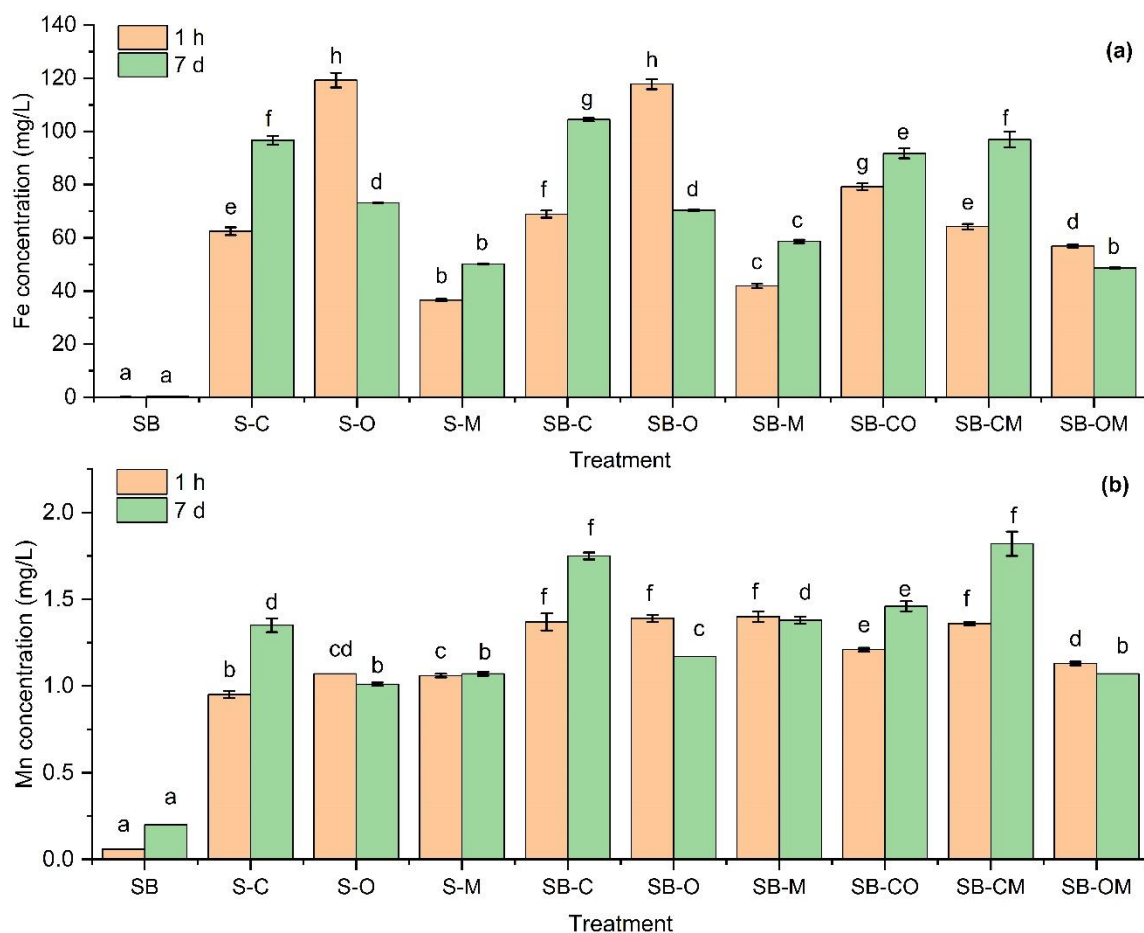
Figure 2 Graphs showing (a) iron and (b) manganese in various solutions after 1-h shaking and 7-day incubation for SB and various treatments (at a biochar dose of 1g). Means with different letters above the bars for the same sampling occasion differ significantly at P <0.05.
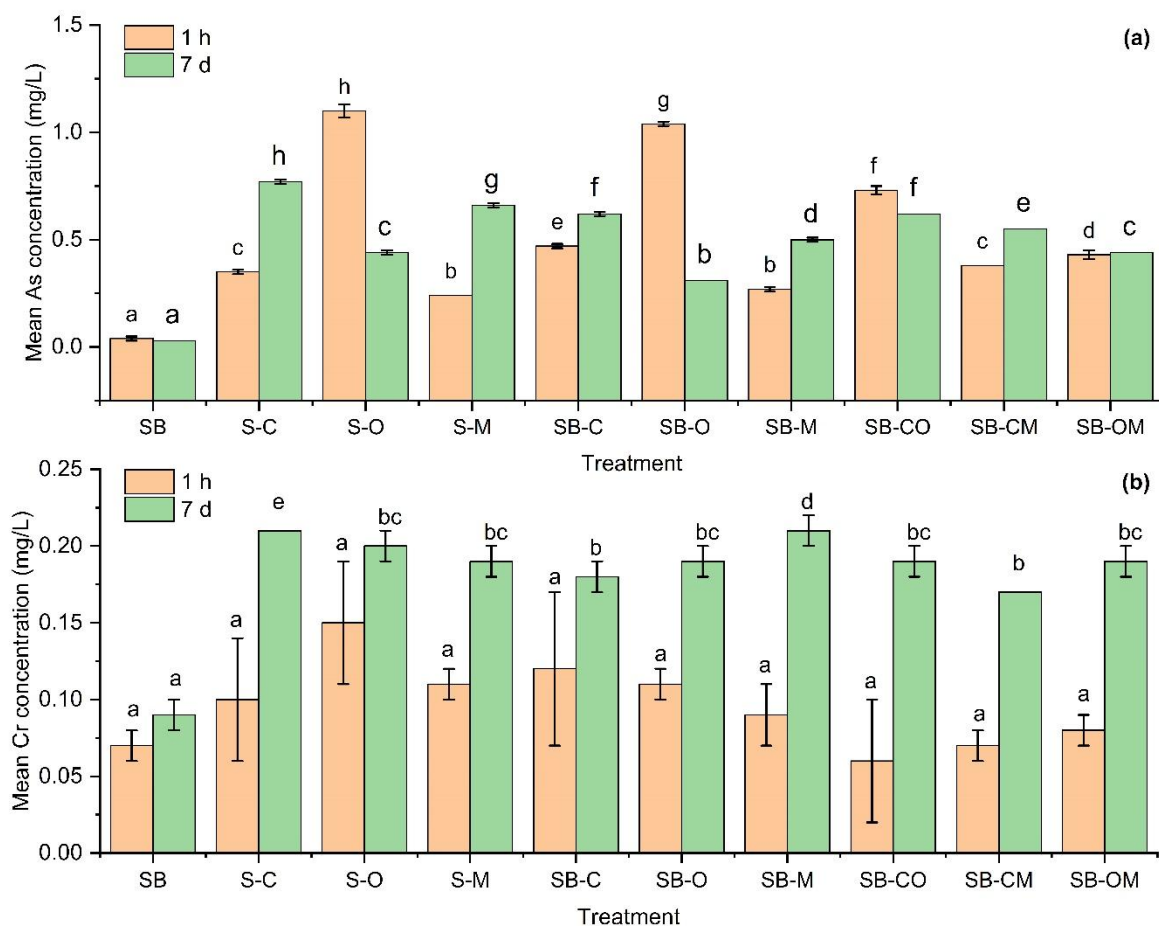
3.4   Arsenic and Chromium

After 1 h of shaking, As in the solution was significantly lower in the treatment without added biochar than in the treatment with added biochar except for the malic acid treatments, which show no significant (P >0.05) difference between S-M and SB-M. After 7 days of incubation, solution-borne As increased for the citric and malic acid treatments regardless of biochar addition. However, the oxalic acid treatments consistently showed the opposite. It is interesting to note that after 7 days of

incubation, the As in the solution was higher in the treatment without added biochar than that in the treatment with added biochar for all the three organic acids (Fig. 3a).

Figure 3 Graphs showing (a) arsenic and (b) chromium in various solutions after 1-h shaking and 7-day incubation for SB and various treatments (at a biochar dose of 1g). Means with different letters above the bars for the same sampling occasion differ significantly at P <0.05.

For Cr, there was no significant (P >0.05) difference between SB and the treatments after 1 h of shaking. After 7 days of incubation, all the treatments had higher Cr in the solutions, as compared to SB. Mixed results were observed for different organic acid treatments; for citric acid treatment, Cr was higher in S-C than in SB-C; for oxalic acid treatments, there was no significant difference in

208 solution Cr between S-O and SB-O; and for malic acid treatments, solution Cr was lower in S-M

209 than in SB-M (Fig. 3b).

210 **3.5   Copper, Lead and Zinc in the Solutions**

211 The concentration of these three heavy metals in the solution was significantly ($P < 0.05$) lower in the

212 SB than in the treatments. For Cu, there was no significant ($P > 0.05$) difference in solution-borne Cu

213 between S-C and SB-C, and between S-M and SB-M. Although statistical analysis shows that

214 solution-borne Cu was significantly ($P < 0.05$) lower in S-O than in SB-O, the difference between

215 both treatments was very small. The "no significant difference" status remained after 7 days of

216 incubation for S-C vs SB-C and S-M vs SB-M. But, for the oxalic acid treatments, the solution-borne

217 Cu was significantly higher in S-O than in SB-O. For Pb, there was no significant difference in the

218 solution-borne Pb between S-C and SB-C, and between S-M and SB-M. For the oxalic acid

219 treatments, solution-borne Pb was significantly ($P < 0.05$) higher in S-O than in SB-O. After 7 days

220 of incubation, there was no significant ($P > 0.05$) difference in the solution-borne Pb for any of the

221 same organic acid treatment pairs. The solution-borne Zn was always significantly ($P < 0.05$) higher

222 in the added biochar treatments than in their no-biochar counterparts after 1 h of shaking. However,

223 after 7 days of incubation, no significant ($P > 0.05$) difference was observed for C-AO vs T-AO

224 (Table 4).

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Table 4 **Copper, lead and zinc in the solutions after 1-h shaking and 7-day incubation for SB**
and various treatments with a dosage level of biochar at 1 g of biochar:10 g of soil

Element	Treatment	1 hour	7 days
Copper (mg/L)	SB	0.03±0.01a	0.15±0.00a
	S-C	0.23±0.00bc	0.33±0.00d
	S-O	0.72±0.00f	0.49±0.00g
	S-M	0.18±0.00b	0.26±0.00b
	SB-C	0.29±0.06c	0.32±0.00d
	SB-O	0.73±0.02g	0.45±0.01f
	SB-M	0.18±0.01b	0.24±0.00b
	SB-CO	0.52±0.01e	0.44±0.01f
	SB-CM	0.19±0.00b	0.30±0.01c
	SB-OM	0.43±0.01d	0.37±0.00e
Lead (mg/L)	SB	0.03±0.03a	0.11±0.02a
	S-C	0.18±0.01c	0.32±0.01d
	S-O	0.44±0.03g	0.18±0.00b
	S-M	0.09±0.00b	0.16±0.01b
	SB-C	0.23±0.03cd	0.32±0.01d
	SB-O	0.37±0.01f	0.19±0.00b
	SB-M	0.10±0.01b	0.17±0.01b
	SB-CO	0.29±0.02e	0.24±0.01c
	SB-CM	0.25±0.01de	0.40±0.03e
	SB-OM	0.11±0.00b	0.15±0.01b
Zinc (mg/L)	SB	0.02±0.00a	0.05±0.00a
	S-C	0.75±0.02c	0.56±0.01e
	S-O	0.92±0.00f	0.44±0.00c
	S-M	0.66±0.01b	0.45±0.00c
	SB-C	0.91±0.03f	0.64±0.00f
	SB-O	1.06±0.01g	0.44±0.00c
	SB-M	0.78±0.02cd	0.50±0.01d
	SB-CO	0.91±0.01f	0.56±0.01e
	SB-CM	0.87±0.01e	0.66±0.03f
	SB-OM	0.82±0.01d	0.40±0.00b

*All values are presented as mean ± standard error (n= 3). Means with different letters in the same column for the same metal are significantly different at $p < 0.05$.

3.6 Barium, Cobalt, Nickel, Strontium

Like most of other elements, solution-borne Ba, Co, Ni and Sr were all lower in SB than in the treatments. While solution-borne Ba tended to be higher in the biochar treatments than in their counterparts, no significant (P >0.05) difference was observed except that Ba was significantly (P <0.05) lower in S-C than in SB-C, and significantly (P <0.05) higher in S-O than in SB-O after 7 days of incubation (Supplementary Table S1).

240   For Co, there was not significant (P >0.05) difference between any pair of the biochar vs no-biochar

241   treatments. After 7 days of incubation, there was no significant (P >0.05) difference in solution Co

242   for any of biochar vs no-biochar treatment pairs (*i.e.* S-C vs SB-C, S-O vs SB-O, and S-M vs SB-M).

243   There was literally no significant (P >0.05) difference in solution-borne Ni between biochar and no-

244   biochar treatments for any LMWOA types. Solution-borne Sr was significantly lower in the no-

245   biochar treatments than in their biochar treatment counterparts except for S-O vs SB-O. For Ba and

246   Co in the oxalic acid treatments, there was an increase in the concentration after 7 days of incubation

247   while the opposite was observed for Ni and Sr (Supplementary Table S1).

248   **3.7   Potassium, Calcium and Magnesium**

249   The solution-borne K was also significantly (P <0.05) lower in the no-biochar treatments than their

250   biochar treatment counterparts except for S-O vs SB-O. There is a clear trend that the solution-borne

251   Ca was consistently lower (significant at P <0.05) in the no-biochar treatments than their biochar

252   treatment counterparts for all the LMWOA types (Supplementary Table S2).

253   Like Ca, solution-borne Mg was also consistently lower (significant at P <0.05) in the no-biochar

254   treatments than their biochar treatment counterparts for all the LMWOA types (Supplementary Table

255   S2).

256   Unlike most of other elements in the oxalic acid treatments which showed marked decrease from the

257   1st h to the 7th day, there was only a very slight decrease in Ca and Mg, and for K, there was even a

258   marked increase from the 1st h to the 7th day (Supplementary Table S2).

259   **4   Discussion**

260   The pH of the soil used in the experiment had a pH of 4.63, which is sufficiently high to keep the

261   iron and manganese oxides and the trace elements bound to them practically insoluble. This is

262 confirmed by the previous work showing that water-extractable Fe, Mn, As, Cr, Co, Cu and Pb were

263 under detection limits (Mukwaturi and Lin, 2015; Qin et al., 2016). Addition of LMWOAs

264 significantly solubilized oxides of iron and manganese in the soil (Fig. 2). This was accompanied by

265 the release of trace elements (As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sr and Zn) that were likely to be bound

266 to these oxides, as shown in previous work (Onireti and Lin, 2016; Onireti et al., 2017).

267 The pH of 0.01 M citric acid, oxalic acid and malic acid solution was 2.5, 2.1 and 2.6, respectively.

268 After getting in contact with the soil during the 1-h shaking operation, the pH in the solutions rose to

269 >3.5, indicating consumption of H^+ by reactions with soil components, including protonation of

270 variably charged soil colloids such as clays and humic substances. Biochar materials have large

271 surface area with variably charged sites (Mukherjee et al., 2011). Therefore, protonation of the

272 variably charged sites could also take place on the biochar surfaces. The higher pH in each organic

273 acid treatment with added biochar, relative to that in its no-added biochar counterpart, may be

274 attributed to this effect though acid neutralization by the alkaline materials contained in the biochar

275 might also be important. The protonation of biochar surfaces was likely to drive the change of the

276 biochar surfaces from a negatively charged-dominated status to a neutral- or positively charged-

277 dominated status (Qian et al., 2016; Shi et al., 2017; Mia et al., 2018). As such, the biochar surfaces

278 were no longer attractive to the cationic heavy metals and this explains why the heavy metals

279 mobilized by LMWOAs were not removed from the solution in the presence of the biochar. The

280 different behaviour of arsenic after 7 days of incubation is attributable to its oxyanion nature. The

281 negatively charged arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) can be adsorbed by the positively charged

282 site on the biochar surfaces. For example:

283 $[Biochar]^{3+} + AsO_4^{3-} \rightarrow [Biochar]^{3+}\text{-}AsO_4^{3-}$ (1)
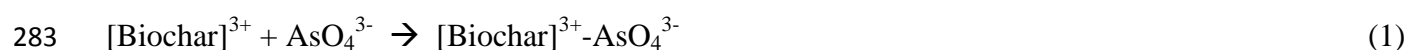
284   The reason that the effect of biochar to immobilize As was not observed at the time after 1 h of

285   shaking is that, probably at this point, the protonation of biochar surfaces was still incomplete. This

286   can be supported by the fact that the solution pH continued to increase after the 1-h shaking.

287   Solution-borne Cr may be in either a cation (Cr^{3+}) or part of an oxyanion ($Cr_2O_7^{2-}$ or CrO_4^{2-}). Under

288   the investigated systems, immobilization of chromium by the protonated biochar could only take

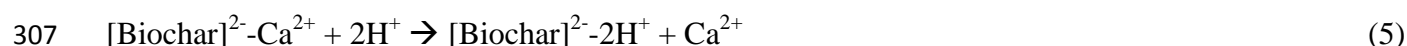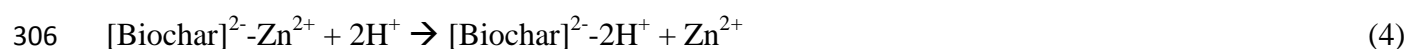289   place when the chromium was in anionic forms. For example

290    $[Biochar]^{2+} + CrO_4^{2-} \rightarrow [Biochar]^{2+}\text{-} CrO_4^{2-}$ (2)
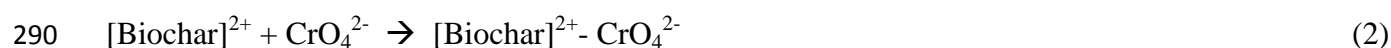
291   Following interaction with the added LMWOAs, soil-borne Cr(III) might be released due to

292   acidification. For example:

293    $Cr(OH)_3 + 3H^+ \rightarrow Cr^{3+} + 3H_2O$ (3)

294   Cr(VI) in chromate or dichromate adsorbed on iron oxides could also be liberated due to reductive

295   iron dissolution. However, part of the soluble Cr(VI) could then be reduced to form Cr^{3+} in the

296   presence of LMWOAs (Sun et al., 2009; Wrobel et al., 2015), depending on the reducing capacity of

297   the organic acid. The relatively higher Cr in no-added biochar system than in the biochar-treated

298   system for citric acid treatments indicates that part of the Cr was adsorbed by the biochar. In

299   contrast, no Cr was removed by the biochar in the presence of oxalic acid and malic acid. This

300   suggests that citric acid had a weaker capacity to reduce Cr(VI), as compared to oxalic and malic

301   acids under the set experimental conditions in this study. Chen et al. (2013) also observed a weaker

302   Cr(VI)-reducing capacity of citric acid, as compared to malic acid and tartaric acid.

303   The consistent trend that the concentration of solution-borne metals was higher in the treatment with

304   added biochar than in its no-added biochar counterpart suggests release of these metals from the

305   biochar surfaces under attack by LMWOAs via cation exchange. For example:

306      $[\text{Biochar}]^{2-}\text{-}Zn^{2+} + 2H^+ \rightarrow [\text{Biochar}]^{2-}\text{-}2H^+ + Zn^{2+}$ (4)

307      $[\text{Biochar}]^{2-}\text{-}Ca^{2+} + 2H^+ \rightarrow [\text{Biochar}]^{2-}\text{-}2H^+ + Ca^{2+}$ (5)

308 For redox-sensitive metals such as iron and manganese, it is also likely that the added biochar

309 materials promoted the reductive dissolution of these metals (Xu et al., 2016). This can also have

310 effects on enhancing the release of metals and metalloids bound to the oxides of iron and manganese.

311 The findings obtained from this study have implications for evaluating the role of biochar in

312 immobilizing trace elements in rhizosphere. Several reports suggested that biochar could reduce

313 bioavailability and uptake of heavy metals by plants (e.g. Al-Wabel et al., 2015; Almaroai et al.,

314 2014; Bian et al., 2014; Herath et al., 2015; Kim et al., 2015). This work suggests that adsorption of

315 cationic heavy metals on biochar in the presence of LMWOAs is unlikely to be a mechanism

316 responsible for the impeded uptake of heavy metals by plants growing in heavy metal-contaminated

317 soils. To support this hypothesis, further work including plant growth experiment is required to

318 obtain insights into the biochemical processes for explaining the observed phenomena.

319 This work was conducted to provide first-hand information for evaluating the technical and

320 economic feasibility of using biochar as a remediating agent. It is realized that the application rate of

321 biochar was relatively high. However, for highly valued, heavily contaminated urban soils such as

322 those encountered in Manchester that pose a significant health risk to the residents in the

323 contaminated areas, it may be acceptable for remedial actions at relatively high costs.

324 **5   Conclusion**

325 In the presence of citric acid, oxalic acid and malic acid at a molar concentration of 0.01 M, the

326 surface of biochar was protonated, which disfavours adsorption of the cationic metals released from

327 the soil by organic acid-driven mobilization. In contrast, the oxyanionic As species were re-

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immobilized by the protonated biochar effectively. Biochar could also immobilize oxyanionic Cr species but not cationic Cr species. The addition of biochar increased the level of metals in the solution due to the release of the biochar-borne metals under attack by LMWOAs via cation exchange. Biochar could also have the potential to enhance reductive dissolution of iron and manganese oxides in the soil, leading to enhanced release of trace elements bound to these oxides.

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