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Vause, Danielle, Heaney, Natalie and Lin, Chuxia

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1 **Differential Release of Sewage Sludge Biochar-borne Elements by Common Low-molecular-**

2 **weight Organic Acids**

3 Danielle Vause, Natalie Heaney and Chuxia Lin*

4 School of Environment and Life Science, University of Salford, Greater Manchester M5 4WT

5 United Kingdom

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9 *Corresponding Author: Email: C.Lin@salford.ac.uk

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20 **ABSTRACT**

21 Biochar materials originated from sewage sludge mat contain elevated levels of potentially toxic

22 elements. There was a lack of information on the mobility of biochar-borne elements, as driven by

23 low-molecular-weight organic acids (LMWOAs) contained in plant root exudates. A batch

24 experiment was conducted to examine the effects of three common LMWOAs on the release of

25 major elements and trace elements with a focus on various potentially toxic trace elements. The

26 results showed that substantial amounts of Al, Mn, Fe, K, Na and Mg were extracted from two

27 sewage sludge-derived biochar materials by the LMWOAs. A much higher release rate of potentially

28 toxic trace elements was observed in the presence of LMWOAs, as compared to reported data using

29 extractants not encountered in root exudates. The LMWOA-driven releasibility of various potentially

30 toxic trace elements was in the following decreasing order: Zn > Ni > Pb > Cu > Cr > Co = Cd.

31 Other trace elements that are subject to mobilization in the presence of LMWOAs included B, Ba, In,

32 Li and Sr except Ba under oxalic acid extraction. Among the three LMWOAs, oxalic acid showed a

33 generally stronger capacity to mobilize these metals. The findings obtained from this study provides

34 new information that can be used for better evaluating the phyto-availability of trace elements bound

35 to sewage sludge-originated biochar materials.

36 **Keywords:** Sewage sludge, trace elements, biochar, low-molecular-weight organic acids, phyto-

37 availability

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1   Introduction

Pyrolysis is viewed as an effective approach for the treatment of sewage sludge while simultaneously generating bio-energy (Hossain et al., 2011; Agrafioti et al., 2013). The residue of sewage sludge pyrolysis could also be used as biochar for various environmental applications (Yuan et al., 2015). However, owing to generally elevated concentration of trace elements in the feedstock (van Wesenbeeck et al., 2014), biochar materials originated from sewage sludge may be a source of trace elements to the environments (Hossain et al., 2010), which may limit its beneficial utilization given the potential environmental impacts from the release of the biochar-borne trace elements of potential toxicity. Therefore, it is important to understand the releasability of sewage sludge biochar-borne trace elements in order to evaluate the environmental risk associated with a given beneficial application. The mobility of sewage sludge biochar-borne trace elements was tested by various researchers using different extractants e.g. distilled water (Gondek et al., 2014; Gondek and Mierzwa-Hersztek, 2017), NH_4NO_3 (Mierzwa-Hersztek et al., 2018), dilute H_2SO_4 and HNO_3 (Zhou et al., 2017), DTPA-$CaCl_2$-TEA (Liu et al., 2014; Lu et al., 2016; Huang et al., 2017). Liu et al (2014) found sewage sludge biochar had an elevated level of total Cd, Cr, Cu, Pb and Zn but only a small fraction of these metals was available for plant uptake and their bioavailability was in the following decreasing order: Zn > Cr > Cu > Pb > Cd. Similarly, Gondek and Mierzwa-Hersztek (2017) reported low bioavailable forms of trace elements to the order of Zn > Pb > Cd > Cu. A TCLP study by Agrafiotiet al. (2013) revealed that leachate from sewage sludge biochar contained < 0.74 mg/kg of heavy metals.

Soil application represents a major avenue for biochar utilization (Ahmad et al., 2014). In the rhizosphere, various low-molecular-weight organic acids (LMWOAs) are present due to root exudation (Jones and Darrah, 1994). Therefore, the added biochar materials are likely to be exposed to these naturally occurring LMWOAs, which may cause liberation of the biochar-borne elements

through acidification, reduction or/and complexation (Onireti and Lin, 2016; Alozie et al., 2018). While mobilization of trace elements from sewage sludge biochar materials has been investigated using chemical reagents that are not encountered in rhizosphere as mentioned above, there is currently no information on the chemical behaviour of sewage sludge biochar-borne elements in the presence of LMWOAs that are frequently encountered in rhizospheric soils. This represents a knowledge gap for understanding the phyto-availability of sewage sludge biochar-borne elements in the soils amended with sewage sludge biochar materials. In this short communication, we report the observed release of various elements from two selected sewage sludge-originated biochar materials produced using the same feedstock but at different pyrolysis temperatures in the presence of three common root-released LMWOAs (citric acid, oxalic acid and malic acid). The objective was to gain a preliminary understanding of the role of these three common LMWOAs in mobilizing various elements from the two selected sewage sludge biochar materials, which will provide a basis for guiding further investigations to obtain insights into the biochemical mechanisms responsible for plant uptake of sewage sludge biochar-borne elements.

2   Materials and Methods

The two sewage sludge biochar materials (labelled as SS550 and SS700 for that produced under low-oxygen conditions at a pyrolysis temperature of 550 ^{o}C and 700 ^{o}C, respectively) used in the experiment were purchased from the United Kingdom Biochar Research Centre (UKBRC). The basic physical and chemical characteristics of the biochar materials provided by the manufacturer are given in Table S1 in the Supplementary Materials. The functional groups on the biochar surfaces were identified using a Fourier transform infrared spectrometer (FTIR).

A batch experiment was conducted with one control and three treatments being set for each biochar material. For the controls, 2 g of the respective biochar was extracted by 20 mL of deionized water. For the treatments, 20 mL of 0.02 M citric, malic or oxalic acid solution was used, respectively. The

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concentration of LMWOAs set for this study is within the concentration range encountered in rhizosphere (Jones and Darrah, 1994). Details on the experimental set-up are provided in Table S2 in the Supplementary Materials.

After adding all the ingredients, the batch reactors were shaken in a rotary shaker at 150 rpm for 1 hour. After shaking, the pH and electrical conductivity (EC) in the solution were measured using a calibrated pH meter and an EC meter, respectively. The solution was then filtered for determination of various elements using an inductively coupled plasma atomic emission spectrometer (Varian 720ES ICP-OES).

The experiment was performed in triplicate. All chemical reagents used in the experiment were of analytical reagent grade. Ultrapure water (18.2 MΩ/cm) was used throughout the entire course of the experiment. One-way analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine the statistically significant difference between the means of the controls/treatments. Values were reported as the mean ± standard error of the mean. Different letters indicate statistical significance ($p < 0.05$) and where no statistical significance between treatments were identified ($p > 0.05$), no letters were reported.

The release rate of a biochar-borne element by each of the LMWOAs is calculated using the following formula:

Release rate (%) = ELMWOA/Etotal x 100

Where ELMWOA stands for the concentration of an extracted element by an LMWOA and Etotal denotes the total concentration of that biochar-borne element.

3   Results and Discussion

The spectra of the two-biochar materials used for the study are shown in Fig. 1. No major changes in surface functionality for the biochar materials produced under different pyrolysis temperature were observed. This suggests that the biochar materials were relatively stable at these production temperatures in terms of functionality (Song et al., 2014). The broad stretch observed between 3200-3500 cm^{-1} can be assigned to –OH stretching (Keiluweit et al., 2010) and a slight decrease in intensity can be observed with increased pyrolysis temperature which is indicative of increased dehydration of the biochar material (Kim et al., 2012). At around 2921 cm^{-1} a small vibration can be observed for SS700 which is attributable to a CH aliphatic stretch (de Jesus et al., 2017). Another stretch, which indicates the presence of a C=O bond of amide I at ~1617 cm-1 (Lu et al., 2013; Fan et al., 2016). The strong peak observed for both biochar at ~1385 cm^{-1} is most likely aliphatic CH$_3$ deformation (Özçimen and Ersoy-Meriçboyu, 2010). A broad stretch present between 1000-1200 cm^{-1} can be assigned as aliphatic ether C–O and alcohol C–O stretching (Özçimen and Ersoy-Meriçboyu, 2010), which becomes more pronounced with increased pyrolysis temperature. There was only a slight difference in absorbance between the pre-extraction and post-extraction FTIR spectra (data not shown), indicating that no removal or formation of new functional groups on the reacted biochar materials. Scanning electron micrographs revealed a porous structure with substantial amounts of the precipitates for both biochar materials (Fig. S1).

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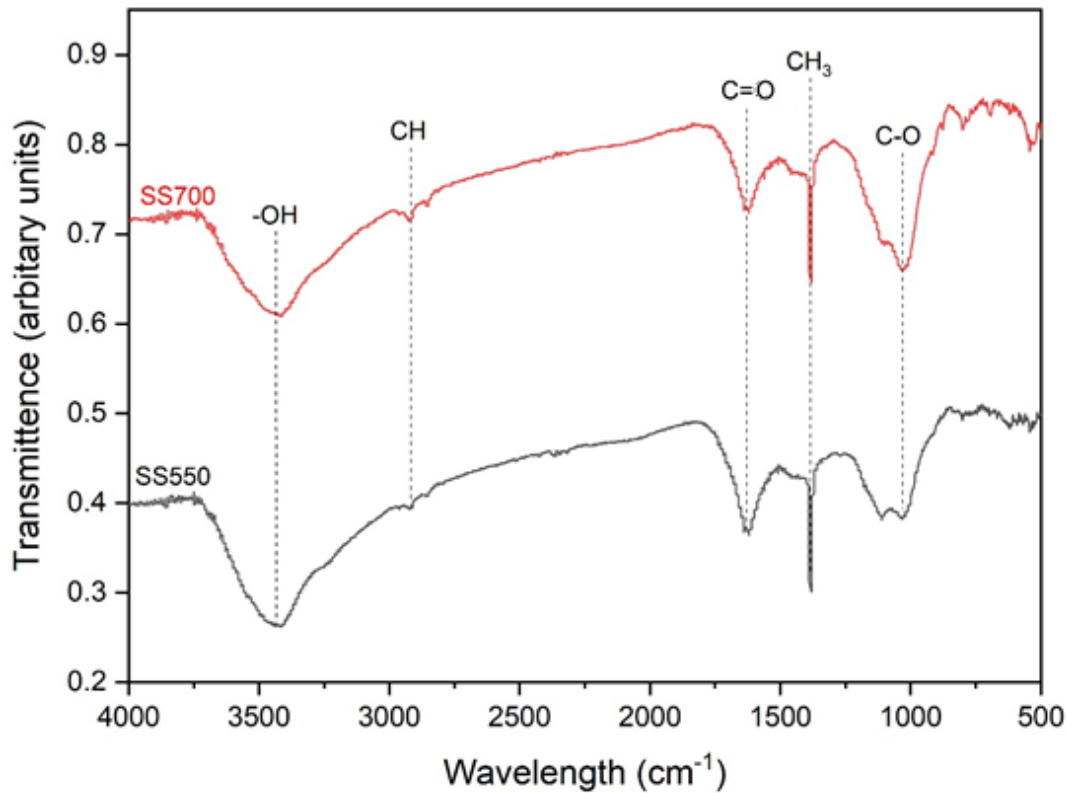
Figure 1 FTIR spectra of the two biochar materials (SS550 and SS700) used in the experiment.

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133   After the reaction, the mean pH in the control for SS550 was 7.20, which was significantly ($P <0.05$)

134   lower than that (pH 8.87) in the control for SS700 (Table 1). This was expected because the former

135   was less alkaline, as compared to the latter (Table S1 in the Supplementary Materials). For each

136   biochar material, the mean pH in any LMWOA treatment was always lower than that in the

137   respective control. This was due to acidification by the added organic acids. EC in the solutions also

138   generally increased after addition of citric and malic acids (Table 1), reflecting the dissolution of the

139   biochar-borne compounds.

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Table 1 pH and electrical conductivity in the solution

Treatment	pH	EC (µS/m)
SS550	7.20±0.01b	259±1.67ab
SS700	8.87±0.06a	185±6.84b
SS550-C	6.44±0.12f	411±69.55a
SS550-M	6.43±0.04f	385±116.43a
SS550-O	6.57±0.02ef	258±6.00ab
SS700-C	6.66±0.02de	254±0.67ab
SS700-M	6.77±0.03d	258±9.60ab
SS700-O	7.02±0.02c	144±1.76b

Values are means ± standard error of the mean (n=3). Means in each column with different letters indicate statistical significance (P<0.05)

In both controls (SS550 and SS700), no Al was detected. For Fe, only a trace amount was detected for SS700 and none was detected for SS550. These are expected since the solubility of aluminium and iron oxides is low at neutral and slightly alkaline pH. Significantly more (P <0.05) K was released from SS550, as compared to SS700. For both biochar materials, oxalic acid tended to extract more Al, as compared to either citric acid or malic acid. More Al tended to be extracted from SS550, as compared to SS700 (Table 2). It is likely that the biochar-borne Al was mainly in hydrolysed form. Given that the solution pH was above 6, the mobilization of biochar-borne Al was likely to be driven by complexation rather than acidification. Under the set experimental conditions, oxalic acid is more effective in terms of solubilizing aluminium hydroxides. The same trend (oxalic acid treatment > citric acid and malic acid treatments) for Fe was observed only for SS700. For SS550, citric acid tended to extract more Fe, as compared to malic acid and oxalic acid despite that there was no statistically significant difference being observed (P >0.05). The concentration of K, Na and Mg was all lower in the controls than in the treatments (Table 2), suggesting a release of exchangeable K, Na and Mg by H^+ from the organic acid. At the same molar concentration, oxalic acid has a stronger pK_a value as compared to the other two LMWOAs (citric acid pK_a= 3.13, malic acid pK_a= 3.46 and oxalic acid pK_a= 1.25, respectively) (Strobel, 2001). This may partially explain why significantly more K and Na (P<0.05) were extracted in the oxalic acid treatment than in the other

organic acid treatments for SS550. Unlike other basic cations, Ca showed no significant difference between the control and the treatments (Table 2), suggesting that Ca in the solution was from the dissolution of water-soluble calcium compounds and no exchangeable Ca was released from the biochar materials. The high level of water-extractable Mn in the controls indicated the presence of water-soluble Mn^{2+}, which is relatively stable in a pH less 8 (McBride, 1994). In general, the added LMWOAs significantly enhanced the release of Mn from the biochar materials, especially for SS550 (Table 2). This may be attributed to cation exchange (replacement of exchangeable Mn by H^+ from the added organic acids), and dissolution of manganese compounds via complexation to form soluble manganese-citrate/malate/oxalate complexes and reduction to form soluble Mn^{2+} (Onireti and Lin, 2016; Alozie et al., 2018).

Table 2 Comparison of extractable major elements (mg/kg) in the biochar materials among the controls and treatments

Treatment	Al (mg/kg)	Ca (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Na (mg/kg)
SS550	0.00±0.00d	859±3.77a	0.00±0.00d	1216±63.4d	533±17.2e	5.91±0.00cd	1122±138c
SS700	0.00±0.00d	797±2.33a	3.55±3.55d	310±41.4e	1623±128c	0.35±0.65e	276±13.1e
SS550-C	5098±1252bc	707±90.9a	18165±4413a	2317±601ac	4043±988b	504±0.26b	1421±367bc
SS550-M	4524±396bc	806±8.00a	11245±3516ac	2634±14.4ab	5163±703b	419±120bc	1749±111b
SS550-O	9032±2491a	823±23.8a	11132±5452ac	2725±227a	4769±51.7b	772±45.4a	2384±26.8a
SS700-C	3641±134bc	824±1.81a	6636±249bcd	1952±21.3bcd	7483±6.33a	272±71.2cd	827±24.9d
SS700-M	2440±49.1cd	823±2.55a	3603±54.9cd	1669±45.2cd	7217±92.6a	200±2.85d	914±6.01d
SS700-O	6561±304ab	823±7.35a	13420±761ab	1877±80.6cd	7397±138a	467±4.41b	1006±43.7cd

Values are means ± standard error of the mean (n=3). Means in each column with different letters indicate statistical significance (P<0.05)

For common heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) of environmental importance, none was detected in the controls for all these heavy metals. Due to the alkaline conditions, the surfaces of biochar and oxides tended to be negatively charged, which favoured the binding of cationic heavy metals but or anionic heavy metals. Therefore, it was unlikely that the biochar-borne Cr was in anionic forms such as CrO_4^{2-} and $Cr_2O_7^{2-}$. Cd and Co were not detected in the treatments either (data not shown). Different patterns were observed for Cr, Cu, Ni, Pb and Zn (Fig. 2). Addition of

185 LMWOAs tended to result in the release of Cr from the biochar materials though the citric acid

186 treatment was more effective, especially for SS550. Gabriel and Salifoglou (2005) found that Cr

187 could favourably form a soluble complex with citrate. For Cu, nothing was detected for any of

188 LMWOA treatments for SS550. For SS700, the amount of Cu released from the biochar was in the

189 following decreasing order: citric acid > malic acid > oxalic acid (significant at P <0.05). Biochar

190 contains dissolved organic compounds, which increase with decreasing pyrolysis temperature (Smith

191 et al., 2016). Perhaps, the relatively abundant presence of biochar-borne dissolved organic

192 compounds in SS550 was responsible for the immobilization of Cu, which has a strong affinity to

193 organic matter.   The amount of Ni released was greater for SS700 than for SS550, which had no

194 detected Ni for the oxalic acid treatment and only a trace amount of extracted Ni for the malic and

195 citric acid treatments. The amount of extracted Ni from SS700 was smaller (significant at P <0.05)

196 in the malic acid treatment than in the other two treatments. The extracted Pb tended to decrease

197 from citric acid treatment to malic acid treatment to oxalic acid treatment for both biochar materials

198 though not all of them are statistically significant. Zn was the most abundant heavy metal released

199 from the biochar materials in this experiment. The amount of extracted Zn was significantly (P

200 <0.05) greater in the oxalic acid treatment than the other two organic acid treatments for both biochar

201 materials (Fig. 2b).

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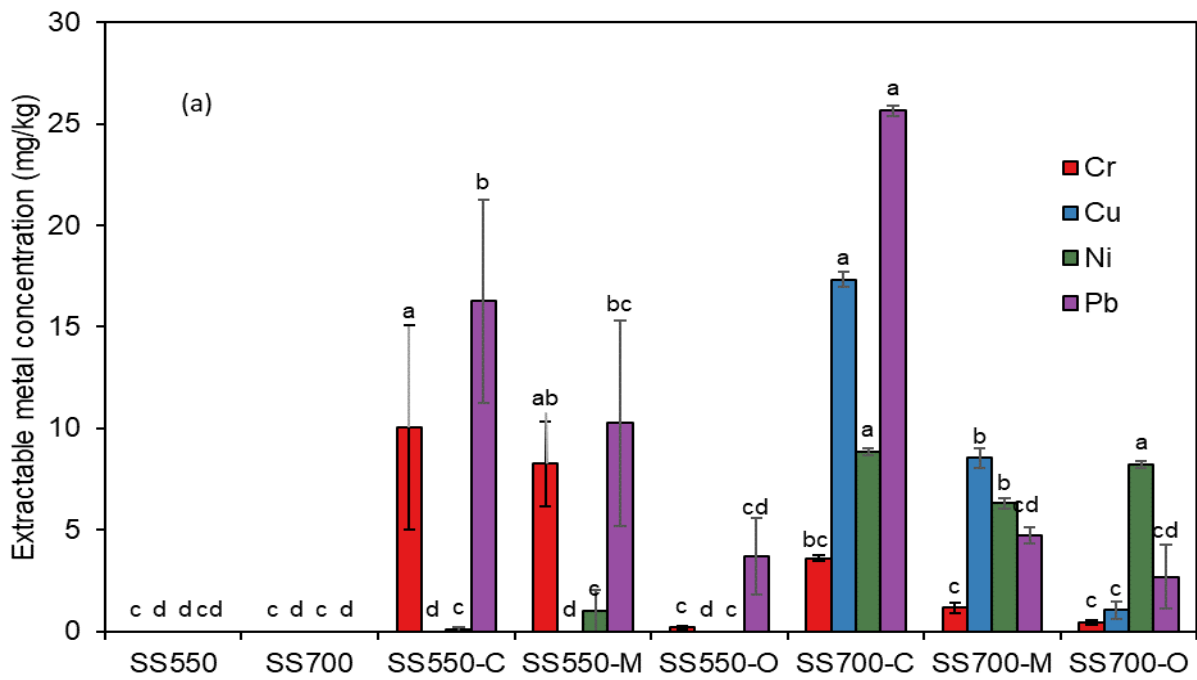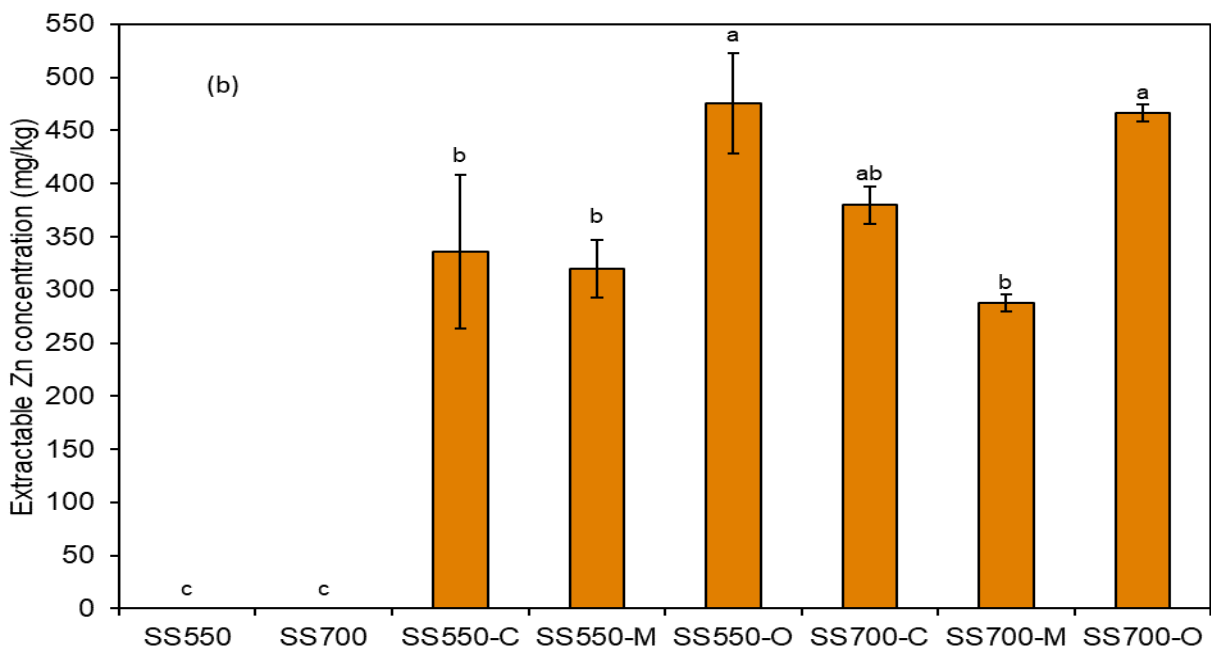
Figure 2 Comparison of extractable (a) Cr, Cu, Ni, Pb and (b) Zn in the biochar materials among the controls and treatments. Different letters above the bars indicate statistically significant difference (P <0.05) for each metal.

Liberation of several other trace elements from the biochar materials was also observed (Table 3). The water- and LMWOA-extractable B tended to be higher in SS700 than in SS550. There was a significant (P <0.05) difference in the released B for the SS550 citric acid treatment but no

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significant difference (P>0.05) for malic or oxalic acid treatments. Significantly (P <0.05) more B was released from SS700 compared to SS550 and the SS700 control to the order of citric acid > malic acid > oxalic acid. More Ba was released by citric acid and malic acid than by oxalic acid and for SS700, oxalic acid even caused immobilization of soluble Ba. This may be attributed to the formation of relatively insoluble Ba-oxalate complexes (Kravchenko et al., 2014) following the release of biochar-borne Ba by H^+ through cation exchange. Such complexes can precipitate, leading to the rapid removal of the extracted Ba from the solution (Strathmann and Myneni, 2004). Although no water-extractable In was presence for both biochar materials, relatively large amount of In was extracted by the LMWOAs for SS550 and SS700 with oxalic acid showing significantly stronger (P <0.05) capacity to extract In, as compared to the other two organic acids. Water extractable Li was present in both controls (SS550 > SS700) and a significant increase in concentration existed for oxalic acid treatments only (P>0.05). However, for SS700 nearly ten times more Li was extracted by oxalic acid (significant at P <0.05). Similarly, high amounts of Li were also extracted for the remaining LMWOA treatments. The presence of LMWOAs led to a further release of Li, probably through cation exchange. Extractable Sr was detected in the control for both biochar materials. The presence of LMWOAs led to significant (P <0.05) release of Sr from the biochar materials with more Sr being released from SS500 than from SS700.

Table 3 Comparison of extractable boron, barium, indium, lithium and strontium in the biochar materials among the controls and treatments

Treatment	B	Ba	In	Li	Sr
SS550	0.07±0.07d	2.56±0.05d	0.00±0.00e	4.16±0.15c	14.1±0.17c
SS700	5.11±0.89cd	0.27±0.06cd	0.00±0.00de	1.92±0.07e	4.11±0.19d
SS550-C	6.40±3.20c	170±40.9c	15.7±5.33b	6.55±1.58c	87.3±20.5a
SS500-M	2.73±0.32cd	152±16.8cd	12.2±1.87bc	7.34±0.18bc	88.9±1.60a
SS550-O	5.15±1.00cd	0.00±0.00cd	26.2±2.52a	11.0±0.05a	51.5±23.1b
SS700-C	29.5±0.97a	88.1±1.39a	7.00±0.18cd	8.58±0.11b	54.2±0.24b
SS700-M	24.64±1.66ab	66.62±2.42ab	3.07±0.15de	7.39±0.16bc	45.17±0.96bc
SS700-O	22.51±3.11b	0.00±0.00b	14.67±0.80b	10.50±0.55a	25.08±2.86bd

Values are means ± standard error of the mean (n=3). Means in each column with different letters indicate statistical significance (P<0.05)

The release rate (%) of Cd, Co, Cr, Cu, Ni, Pb and Zn for the two biochar materials tested in this study can be seen from Fig. 3. The releasibility of Zn was evident with over 30% of the biochar-borne Zn being liberated and oxalic acid tending to mobilize more Zn. The release rate of the biochar-borne elements by the LMWOAs generally followed the order Zn > Ni > Pb > Cu > Cr > Co = Cd. While the high mobility of Zn observed in this study was comparable to what were reported by other authors using other extracting agents, the LMWOA-driven release rate of trace elements was much higher and the order of mobility for various trace elements was also different, as compared to their reported rate (Liu et al., 2014; Gondek and Mierzwa-Hersztek, 2017).
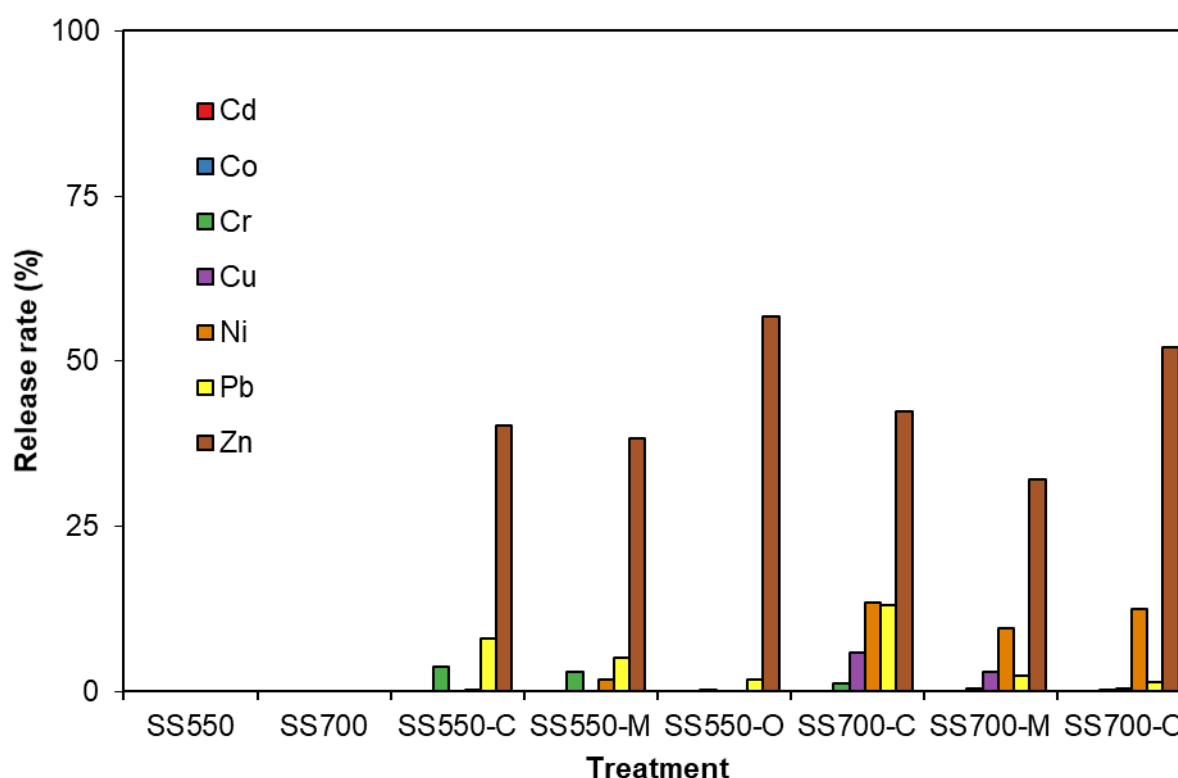
Figure 3 Release rate (%) of biochar-borne Cd, Co, Cr, Cu, Ni, Pb and Zn among the controls and treatments

Since extraction of biochar-borne trace elements by LMWOAs better simulates the soil conditions in the rhizosphere, the findings from this study provide new information that can be used for better evaluating the phyto-availability of trace elements bound to sewage sludge biochar materials.

4   Conclusion

Substantial amounts of Al, Mn, Fe, K, Na and Mg could be released from the sewage sludge biochar materials in the presence of LMWOAs through dissolution and cation exchange with oxalic acid showing a generally stronger capacity to mobilize these metals. There was a much higher release rate of potentially toxic trace elements in the presence of LMWOAs, as compared to that mobilized by chemical substances not encountered in root exudates. The LMWOA-driven releasibility of various potentially toxic trace elements was in the following decreasing order: Zn > Ni > Pb > Cu > Cr > Co = Cd. Other trace elements that are subject to mobilization in the presence of LMWOAs included B, Ba, In, Li and Sr except for Ba under oxalic acid extraction.

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337 Yuan, H., Lu, T., Huang, H., Zhao, D., Kobayashi, N., & Chen, Y. (2015). Influence of pyrolysis
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341   heavy metal adsorption and immobilization in soils. *International Journal of Environmental
342   Research and Public Health*, *14*(7), 681.

343

Supplementary Materials

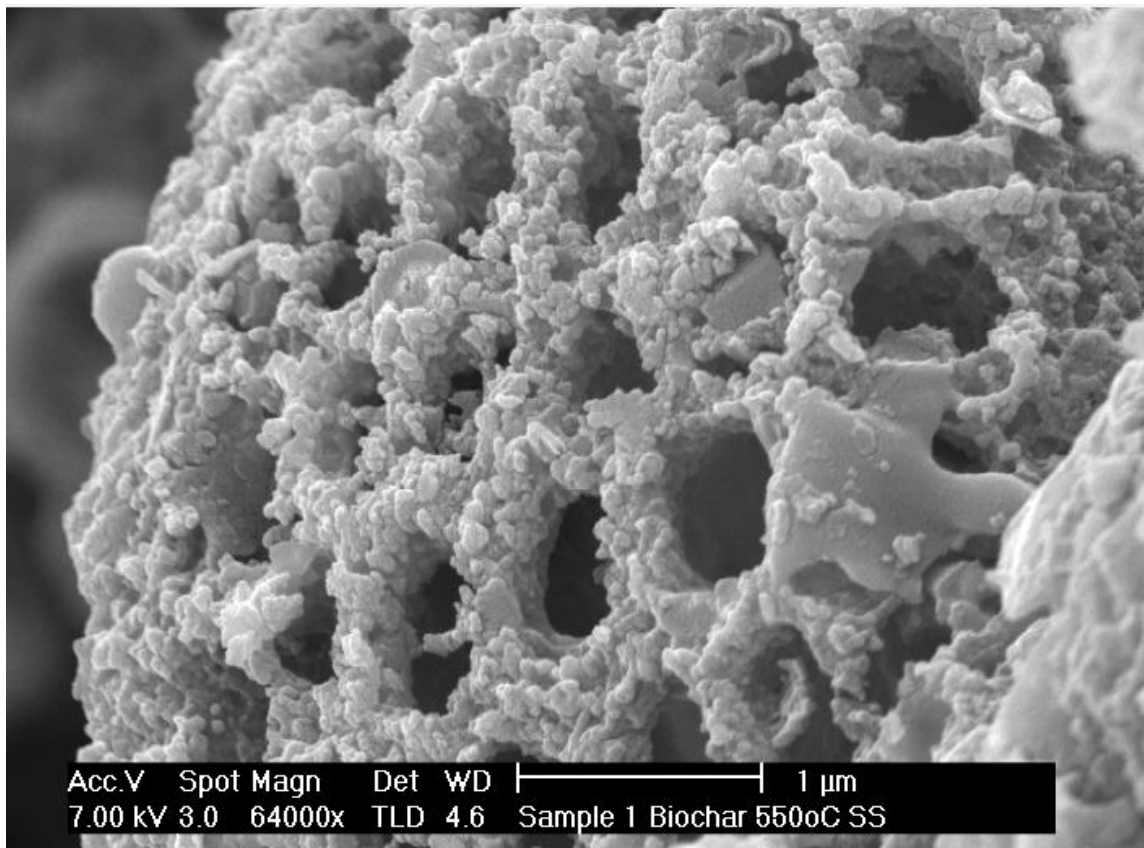**Table S1 Basic characteristics of the two biochar materials used in the experiment**

Property	SS550	SS5700
Moisture (%)	2.48	1.69
Ctot (%)	29.53	29.55
H (%)	1.33	0.83
O (%)	6.5	2.75
H:C	0.54	0.34
O:C	0.17	0.07
Total Ash (%)	58.89	63.91
Total N (%)	3.75	3.79
pH	8.29	9.12
Electrical Conductivity (dS/m)	0.280	0.113
PAH (mg/kg)	3.76	1.4
As (mg/kg)	<0.72	<0.72
Cd (mg/kg)	11.69	12.36
Cr (mg/kg)	275.69	292.72
Co (mg/kg)	11.58	12.68
Cu (mg/kg)	255.22	296.63
Pb (mg/kg)	201.19	195.97
Hg (mg/kg)	<0.23	<0.23
Mo (mg/kg)	5.59	4.67
Ni (mg/kg)	57.19	66.25
Se (mg/kg)	<1.40	<1.4
Zn (mg/kg)	835.69	896.21
Polarity Index (O+N)/C	0.35	0.22

Table S2 Details on experimental set-up

Treatment	Biochar (g)	0.02 M citric acid (mL)	0.02 M malic acid (mL)	0.02 M oxalic acid (mL)	Deionized Water (mL)
SS550-C	2	0	0	0	20
SS700-C	2	0	0	0	20
SS550-CA	2	20	0	0	0
SS550-MA	2	0	20	0	0
SS550-OX	2	0	0	20	0
SS700-CA	2	20	0	0	0
SS700-MA	2	0	20	0	0
SS700-OX	2	0	0	20	0

Figure S1 Scanning Electron Micrograph of (a) SS550 and (b) SS700

(a)

Acc.V Spot Magn Det WD ⊢————————⊣ 1 µm
7.00 kV 3.0 64000x TLD 4.6 Sample 1 Biochar 550oC SS

(b)

Acc.V Spot Magn Det WD ⊢————————⊣ 10 µm
7.00 kV 3.0 5000x SE 4.1 Sample 2 Biochar 700oC SS