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3 **The removal of lead, copper, zinc and cadmium from aqueous solution by biochar**

4 **and amended biochars**

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16 **Abstract**

17 The exponential growth in the use of motor vehicles is a key contributor to freshwater

18 degradation. Current remediation techniques require prohibitively expensive

19 contaminant treatment and extraction. Biochar represents an inexpensive option to

20 ameliorate contaminants from motorway runoff. Biochar from Norway spruce (Picea

21 abies (L.) Karst.) was produced under fast pyrolysis-gasification (450–500 °C for 90 s)

22 and amended with wood ash and basaltic rock dust to evaluate sorption of Pb, Cu, Zn

23 and Cd. The column study, designed to mimic field conditions, confirmed that

24 unamended biochar can bind contaminants for short periods, but that the addition of

25 amendments, particularly wood ash, significantly improves contaminant removal.

26   Wood ash-amended biochar removed 98–100% of all contaminants during the study,

27   driven by pH ($r = 0.73$–0.74; $p < 0.01$ dependent on metal species) and phosphorus

28   levels causing precipitation ($r = 0.47$–0.59; $p < 0.01$, dependent on metal species). The

29   contaminants' progression through the biochar subsections in the column indicated that

30   increasing the thickness of the biochar layer increased contaminant residence time and

31   removal.

32   **Keywords – Biochar, Heavy metal, Highway runoff, Contaminant removal**

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Introduction

40

41 Motor vehicles are recognised as a growing source of pollution in modern society. As

42 of April 2018, there were c.38M licensed vehicles on Britain's roads, a number that has

43 been growing by c.640 thousand vehicles per year since 2012 (Gov.uk 2018). Traffic

44 density is intrinsically linked to heavy metal contaminants (Hares and Ward 1999;

45 Ewen et al. 2009; Du et al. 2018) and as such the exponential growth of motor vehicles

46 and resultant increases in traffic density has led to escalating amounts of pollution.

47 The growth in the number of motor vehicles naturally increases in conjunction with

48 highway development, increasing pollution and runoff volume. Development has

49 replaced significant areas of natural permeable land with artificial impermeable

50 surfaces (Ladislas et al. 2015). These surfaces obstruct infiltration of precipitation into

51 the ground, increasing surface runoff, which washes away the polluted dust particles

52 resultant from anthropogenic activity (Ladislas et al. 2015; Charters et al. 2016;

53 Mohanty et al. 2018).

54 Heavy metal motorway pollution is seen as a key contributor to freshwater degradation,

55 contaminating the food chain and enabling direct human exposure to toxins through

56 freshwater leisure activities. Numerous studies indicate that the impact of increased

57 metal concentrations on aquatic life is significant and can increase vulnerability to

58 disease, mortality and a reduction in fecundity (Burrows and Whitton 1983; Mayer-

59 Pinto et al. 2010; Yi et al. 2011; Wu et al. 2016). Metal pollutants, such as Pb, Cu, Zn

60 and Cd, accrue in the aquatic environment, increasing their impact on aquatic species

61 and entering the food chain, causing increased concern globally (Cooper et al. 2009;

62 Wik et al. 2009; Kayhanian 2012). Human exposure to these heavy metals can have

63 significant detrimental health consequences including the impairment of neurological

64 functions, kidney damage, liver function, fragile bones, lung damage and mortality

65 (Järup 2003; Ewen et al. 2009).

66 Three key processes are currently used to remove pollutants: sedimentation, separation

67 and vegetated treatment processes. Current remediation techniques to remove heavy

68 metals from motorway runoff predominantly revolve around sedimentation, the

69 accumulation of which requires expensive treatment and extraction. For heavy metals,

70 capturing polluted sediment is the dominant method used through techniques such as

71 sedimentation tanks, balancing ponds (both wet and dry) and full retention oil traps.

72 Studies have shown heavy metal removal rates of these methods to be up to 70%

73 (Crabtree et al. 2006). Whilst these methods reduce aqueous heavy metal

74 concentrations, over time polluted sediment builds up in the relevant tanks, traps and

75 ponds creating a toxic waste product that is difficult and costly to remove.

76 The dredging of toxic sediment in order to extract it from ponds is exceptionally

77 expensive (Rulkens 2005). Depths of balancing ponds can be as shallow as 800 mm

78 with sediment accrual of up to 50 mm year−1 such build up reduces the removal

79 efficiency of ponds, putting nearby waterbodies at risk whilst exposing wildlife to

80 toxins within the ponds (Farm 2002; Karlsson et al. 2010; Weinstein et al. 2010).

81 Biochar deployment is a potential alternative to current processes commonly used to

82 remove pollutants. Biochar is the carbon rich porous product produced by pyrolysis

83 from plant- and animal-based biomass under oxygen limited conditions, with an

84 appearance similar to charcoal (Lehmann and Joseph 2009). It can be produced using a

85 multitude of feedstocks and a variety of pyrolysis conditions, both of which are key to

86 controlling its properties (Xiao et al. 2018).

87 Biochar can be used to remove heavy metal contaminants from polluted water

88 principally as a result of its sorption properties (Kilic et al. 2013). Immobilisation of

89 heavy metals takes place through several mechanisms including ionic bonding, cation

90   exchange, physical adsorption and co-precipitation (Zhang et al. 2013; Wang et al.

91   2018).

92   The efficacy of the immobilisation is influenced by the characteristics of three key

93   factors:

94   **The biochar**

95   Biochar characteristics differ with feedstock and pyrolysis conditions. These

96   differences influence bulk physical properties such as surface area and porosity (Mohan

97   et al. 2007; Ifthikar et al. 2017) and chemical properties such as functional groups,

98   mineral ash and pH which are instrumental in the binding of heavy metals to biochar

99   (Uchimiya et al. 2010; Xu et al. 2013a; Lehmann and Joseph 2015). Surface area and

100 total pore volume are intrinsically linked as highly porous structures, particularly

101 micropore structures, have a high surface area (Chen et al. 2011; Mohan et al. 2014). It

102 has been noted that surface area and porosity facilitate the adsorption of heavy metals

103 as a result of the volume of potential adsorption sites and that these physical properties

104 are controlled partly by pyrolysis conditions but to a greater extent by feedstock (Chen

105 et al. 2011). Oxygenated functional groups are a critical chemical property which act as

106 a key factor contributing to heavy metal adsorption as a result of electrostatic attraction

107 (Wang et al. 2018) with relevant groups such as carboxyl being present in biochar at

108 high pH values (Bogusz et al. 2015). pH also impacts precipitation with higher biochar

109 pH values enabling precipitation of Pb, Cu, Zn and Cd by carbonate and phosphate

110 minerals (Inyang et al. 2012). Elemental composition, for instance alkali metal and

111 alkaline earth concentrations, can also be changed via feedstock and pyrolysis

112 conditions, affecting biochar pH and cation exchange capacity (CEC) (Zhang et al.

113 2013). Additionally, carbon structure, a key driver of complex bonding, can be

114 manipulated through pyrolysis conditions such as temperature (Schreiter et al. 2018).

The medium

The characteristics of the containing medium such as soil, sediment or aqueous solution (for example motorway runoff) also impact immobilisation. Relevant characteristics here include the pH and temperature of the medium, concentrations and quantities of the contaminant and organic matter abundancy. The pH of the medium is key to the surface charge of the biochar and therefore electrostatic interactions; with increasing pH, there is an increasing negative charge due to deprotonation of acidic functional groups (Wang et al. 2018). The pH of the medium can also influence heavy metal speciation, which is instrumental in immobilisation (Kilic et al. 2013; Trakal et al. 2014). Increasing the temperature of the medium increases adsorption, as heavy metal ions are provided with enough energy to reach and adsorb onto biochar's interior structure (Liu and Zhang 2009).

The contaminant

Finally, the characteristics of the contaminant also play a role in immobilisation. The efficacy of biochar's remediation of heavy metals shows strong dependency on contaminant type (Inyang et al. 2012). Due to the importance of ionic bonding in the adsorption process, the stronger the positive valence on the metal ions, the greater the potential for adsorption (Kilic et al. 2013). The ionic radius is also of importance, with smaller radii being more easily adsorbed (Ko et al. 2004). The role that the contaminant plays in adsorption is indicated by the fact that different contaminants are more readily adsorbed by different types of biochar (Lehmann and Joseph 2009).

These well-understood sorption mechanisms are often explored in batch or continuous flow column studies which provide results unlikely to be reproduced in the field. Batch studies produce a laboratory-based maximum sorption capacity to quantify contaminant removal where potential removal is recorded. Although a closer approximation to field

conditions than batch studies, continuous flow column studies are also still specifically

designed to preclude issues encountered in the field such as channelling effects and

clogging, again resulting in removal values difficult to achieve in the field (Ramírez-

Pérez et al. 2013; Callery et al. 2016; Arán et al. 2017).

This pulse column study moves further away from maximum sorption capacity and

towards complex field approximation where issues such as preferential flow and

sporadic precipitation are recreated. The primary aim of this study is to ascertain the

efficacy of biochar and amended biochars as an affordable remediator for heavy metals

from motorway runoff, specifically Pb, Cu, Zn and Cd. The study focused on heavy

metal pollutants due to their toxicity, non-biodegradable nature and bioavailability in

receiving waterbodies. The depth of immobilisation and retention times of biochar and

amended biochars were investigated to assess the potential for the approach to be

scaled-up and used in the field.

Methods and materials

Pilot study

Preliminary work was undertaken to determine the residency time of a solution within a

biochar water column; residency being intrinsically linked with the potential for

sorption (Mohanty et al. 2018). Four water columns were established containing 50 g,

80 g, 90 g and 100 g of biochar, respectively, to determine the appropriate volume of

biochar to be used during the main study. Each volume was held in a clear, acrylic,

open-ended tube, with a column height of 600 mm, an interior diameter of 44 mm and a

3-mm thick wall (Fig. 1). Each acrylic tube was held in place at 300 mm above bench

level with a clamp stand, enabling a 1-L bottle with a funnel lined with a Whatman 11-

μm qualitative filter paper to be situated underneath to capture the eluate. A 25-μm

165   nylon mesh (150 mm × 100 mm) was attached to the base of each water column to

166   prevent the loss of biochar. Between the base of the biochar and the nylon mesh,

167   120 mm of cotton wool was inserted to allow any eluate to drain away whilst reducing

168   re-contact with the study material. Water columns were kept at room temperature and

169   covered with filter paper to reduce evaporation. The quantity (mL) and retention time

170   (min) of the solution were all measured for each volume of biochar.

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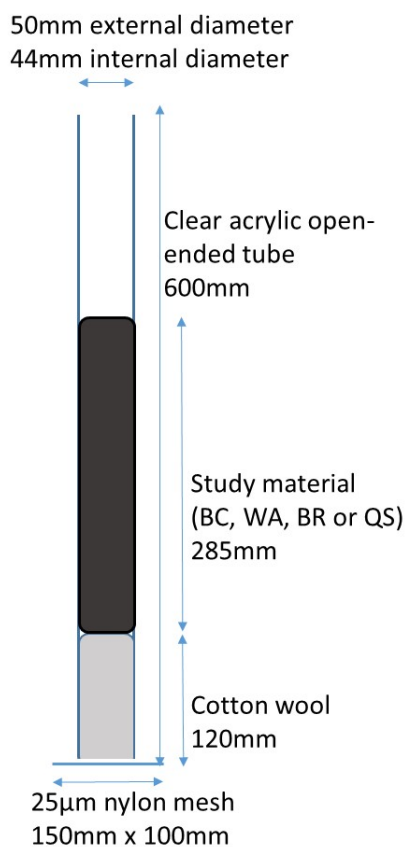
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173   **Fig 1**. Water columns into which the aqueous solution was administered for biochar (BC), biochar

174   amended with wood ash (WA), biochar amended with basaltic rock dust (BR) and quartz sand (QS).

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176   **Selection and preparation of biochar, amendments and control**

177   The biochar used in this study consisted of Norway spruce (*Picea abies* (L.) Karst.)

178   wood chips pyrolyzed in a Pyrocal BigChar-1000 pyrolysis-gasification kiln at a

179   temperature of 450–500 °C, with a retention time of ~ 90 s and was granulated

180   (< 3 mm). Norway spruce, as a softwood, was chosen because of its greater number of

181   pores and surface area for sorption to take place in comparison with hardwood

182   (Mohanty et al. 2018). Amendments to the biochar were mixed dry at room

183   temperature, at a ratio of 1:1, with a plasterer's whisk. Mixed wood ash was selected as

184   an amendment due to its high pH, phosphorus (P) and alkaline earth content (Mg and

185   Ca). Basaltic rock dust was used because of its high pH and alkaline earth content (Mg

186   and Ca). Quartz sand was employed as a control due to its neutral pH, low levels of

187   alkaline earth and low levels of heavy metal pollutants.

188

189   **Pre-study analysis**

190   pH measurements were carried out by soaking biochars with deionised water at a 1:5

191   solid/water ratio for 24 h in a 150-mL Sterilin plastic screw top container, which was

192   agitated on a Unitwist 400 Orbital Shaker. The pH of the resultant slurry was measured

193   using a previously calibrated Voltcraft pH Meter that was rinsed with deionised water

194   between samples. The pH for the quartz sand control was determined by adding 50 g of

195   sand to 100 mL of deionised water in a 150-mL Sterilin plastic screw top container

196   which was agitated for 1 h before measuring the pH. The elemental composition of the

197   biochar, amended biochars and quartz sand was determined using a benchtop Rigaku

198   NEX CG Energy-Dispersive XRF spectrometer, which was calibrated with internal

199   standards. He, rather than air, was used in the XRF chamber to ascertain heavy metal

200   (Pb, Cu, Zn and Cd), alkali metal (K), alkaline earth (Mg and Ca) and P concentrations.

201   Samples of each of the study materials were dried at 50 °C for 24 h and ground using a

202   pestle and mortar to minimise gaps between sample particles within XRF sample

203   containers, reducing air pockets and giving more precise analytical results. These

samples were transferred, in triplicate, into Scimed polyethylene sample cups of 32-mm diameter using 4-μm Prolene films for support. The containers were filled between 5 and 10 mm with the samples which were then pressed manually further reducing air pockets, the sample mass determined and placed in the XRF spectrometer. Samples were analysed in batches of 15 and results were calculated as concentration values (in mg L−1) before conversion to percentage change from solution. Each sample was analysed in triplicate to determine XRF precision and the mean value used in further calculations.

Water column experiment

To evaluate the efficacy of biochar's immobilisation of Pb, Cu, Zn and Cd, a study using aqueous solutions was undertaken. The study consisted of four sets of four replicate water columns with set 1 containing biochar (BC), set 2 containing biochar amended with wood ash (WA), set 3 containing biochar amended with basaltic rock dust (BR) and set 4 containing the quartz sand control (QS). The water column set up used in the pilot study was repeated for the full study (Fig. 1). As a result of the pre-trial residence test, 90 g of biochar was added to each of the first set of four replicate water columns and compressed with an aluminium rod to a height of 285 mm with a volume of ~ 450 mL. This volume was then used as a template for the sets of water columns holding WA, BR and QS.

Heavy metal solution

Liu and Zhang (2009) studied biochar's sorption of Pb in aqueous solution up to a concentration of up to 40 mg L−1. Hence, a solution containing 40 mg L−1 of each contaminant (Pb, Cu, Cd and Zn) was used in this study to stress the biochars beyond

229   what would be encountered in field conditions (Crabtree et al. 2009; Zhao et al. 2010;

230   MacKay et al. 2011). The stock solution was mixed in a grade A volumetric flask

231   (5000 ± 1.2 mL) within a fume cabinet. Deionised water was added to half fill the

232   volumetric flask. Two hundred millilitres of each of the four single element Fisher

233   1000 mg kg−1 heavy metals of AAS standard grade was added using a 50-mL glass

234   pipette. The metal standards were held in 5% HNO3 and as such the study eluent

235   constituted an acidic solution whereby all four metals were dissolved. Forty-two

236   millilitres of this solution was added to each column at 24-h intervals via a syringe.

237   This volume was calculated from an average of the highest 30 daily precipitation values

238   in South East England during the period 2000 to 2018, to mimic both severe first

239   flushing after an antecedent dry period and the sporadic nature of precipitation in the

240   field (Metoffice.gov.uk 2018). Eluate samples were collected every 6 days, allowing

241   24 h after the day six solution was added, for the duration of the study.

242

243   **Eluate analysis**

244   Analysis of the eluate was conducted by XRF to determine heavy metal (Pb, Cu, Cd

245   and Zn), alkali metal (K), alkaline earth (Mg and Ca) and P concentrations. Fifty

246   millilitres of 6-day eluate from each water column and from the solution batch was

247   stored in 50-mL centrifuge tubes at room temperature. XRF cannot directly measure

248   liquids as they would evaporate in the vacuum chamber (P. Brouwer, pers. comm.,

249   2010). As a result, Rigaku Ultra Carry Light disks were used for the analysis of the

250   eluate, which enabled the concentrations (in mg L−1) to be determined for Pb, Cu, Zn,

251   Cd, Mg, Ca, K and P. Two hundred microlitres of eluate was pipetted onto the filter

252   paper portion of the Ultra Carry Light disk for each sample. Each disk was left to dry

253   for 8 h at room temperature prior to analysis. The XRF chamber was evacuated and the

254   eluate on the disks was analysed in batches of 15 samples in triplicate.

255

256   **Subsection analysis**

257   Post-day 36, each water column was frozen at $-20\ °C$ for 24 h to enable each column

258   to be cut into five equal subsections. Whilst freezing has been found to change metal

259   speciation, it does not change total metal concentration (Florence 1977; Batley 1990).

260   Analysis of each subsection was undertaken by XRF, using He in the chamber to

261   determine heavy metal concentrations (Pb, Cu, Zn and Cd). As detection of elements

262   by XRF is affected by water content (Roberts 2015), solid samples were dried for 24 h

263   at 50 °C before XRF analysis. The proportion of contaminant held in each subsection

264   was then determined to understand the movement of contaminant through the study

265   material in each water column.

266

267   **Statistical analysis**

268   Comparisons between the different biochars' contaminant removal values were

269   performed using the Kruskal-Wallis test using a probability threshold of $p = 0.01$.

270   Correlation analysis using Pearson's R was undertaken to test relationships between

271   heavy metal remediation and biochar characteristics.

272

273   **Results**

274   **Pre-study contaminant concentrations**

275   For the biochar and amended biochars the levels of intrinsic contaminant metals were

276   low (Table 1).

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	Pre-study contaminant concentration			
Study Materials	Cd (mg.kg^{-1})	Cu (mg.kg^{-1})	Pb (mg.kg^{-1})	Zn (mg.kg^{-1})
Biochar (BC) average	0 ± 0	12 ± 0	7 ± 0	48 ± 1
Biochar amended with wood ash (WA) average	0 ± 0	134 ± 2	79 ± 1	371 ± 8
Biochar with basaltic rock dust (BR) average	0 ± 0	24 ± 1	18 ± 0	81 ± 2
Quartz sand (QS) average	0 ± 0	8 ± 0	0 ± 0	4 ± 0

284 **Table 1.** Pre study concentration of heavy metal contaminants in biochar, amended biochar and quartz

285 sand (mg.kg^{-1})

286

Pre-study P, pH, Mg, K and Ca measurements

288 P, pH, Mg, K and Ca were quantified for each study material in pre-study analysis

289 (Table 2). For each of these five categories, WA displayed the highest pre-study levels.

290 BR had the second highest levels in terms of pH, Mg, Ca and K. BC was third in most

291 categories with the exception of P where it displayed low concentrations in comparison

292 with WA rather than the undetectable amounts of P in BR and QS. QS, as the control,

293 displayed the lowest values of all of the properties measured.

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	Pre-study levels of pH and alkali and alkaline earth				
Study materials	pH	P (mg.kg^{-1})	Mg (mg.kg^{-1})	K (mg.kg^{-1})	Ca (mg.kg^{-1})
Biochar (BC) average	8.7 ± 0.0	35 ± 11	0 ± 0	4040 ± 139	8080 ± 197
Biochar amended with wood ash (WA) average	11.5 ± 0.0	4770 ± 108	16700 ± 578	35700 ± 788	208000 ± 5030
Biochar with basaltic rock dust (BR) average	10.2 ± 0.0	0 ± 0	13900 ± 521	9850 ± 38	35200 ± 38
Quartz sand (QS) average	7.5 ± 0.0	0 ± 0	0 ± 0	542 ± 18	112 ± 8

301

302 **Table 2.** Pre study levels of pH, P, alkali and alkaline earth in biochar, amended biochar and quartz sand

303

304 **Eluate and subsection analysis:**

305 *Pb eluate*

306 Pb was the contaminant most successfully remediated by the biochar and amended

307 biochars. Elimination rates for BC, WA and BR started at 99–100% (Fig. 2). By days

308 13–18, BC started to show reduced removal of contaminants and by days 19–24, it had

309 started to desorb, adding Pb to the eluate. Desorption decreased until days 31–36 when

310 remediation levels matched QS control levels. WA and BR maintained elimination

311   rates of 99–100% for the remainder of the study. QS, as the control, did not decrease

312   Pb concentration. Over the duration of the study, WA and BR removed 100% of Pb

313   showing no significant difference in efficacy between them, whereas BC only removed

314   4%, significantly less than both WA and BR, with QS at − 19%.

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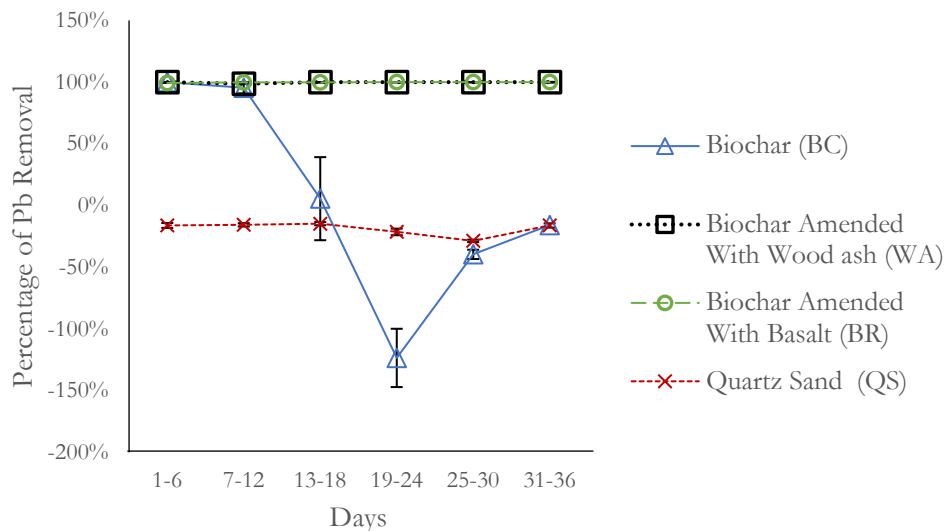
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317   **Fig 2**. The removal and desorption of lead in percentage terms for each of the study materials over the

318   duration of the study. Values below quartz sand control levels represent desorption.

319

320   *Pb distribution in the column subsections*

321   The proportions of Pb at each 57-mm subsection varied between the study materials

322   (Fig. 3). BC, which desorbed Pb and returned to control levels of remediation by the

323   end of the study (Fig. 2), showed no significant difference between the concentrations

324   of Pb in each subsection and showed no significant differences from the subsections of

325   the QS control. WA, which immobilised 100% of Pb (Fig. 2), held 83% of the

326   contaminant in the first subsection with only 3% in the final subsection (Fig. 3). BR,

327   which also removed 100% of Pb (Fig. 2), showed a far smaller percentage than WA in

328   the first subsection (5%), with 87% of Pb held in subsections 2, 3 and 4, with only 7%

15

329   held in subsection 5 (Fig. 3). These proportions indicate that as the study material

330   reached maximum removal capacity, Pb moved through the subsections until, post-

331   desorption, proportions of the contaminant were lessened and became equal throughout

332   the layers.

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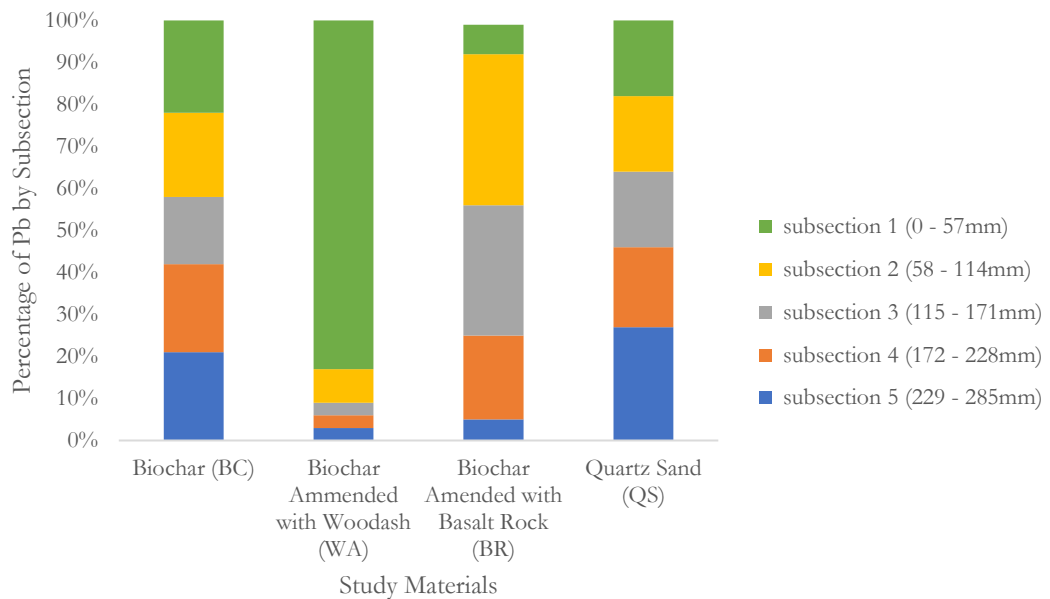
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335   **Figure 3.** The relative proportion of lead in each 57mm subsection for each study material post study.

336

337   *Cu eluate*

338   Cu elimination rates for BC, WA and BR were found to be 99–100% during days 1–6

339   (Fig. 4). BC elimination rates declined on days 7–12 and continued to drop until

340   desorption reached its maximum on days 19–24. Removal by BC had returned to

341   control levels by days 31–36. BR maintained its initial Cu removal percentage until

342   days 31–36 when capacity was reached and desorption began (Fig. 4). WA maintained

343   elimination rates of 98–100% for the entirety of the study. In contrast, QS, as the

344   control, did not decrease the Cu concentration. Over the duration of the study, WA

345   removed 99% of Cu, significantly more than the other three materials; in contrast, BR

346   removed 74%, significantly higher than BC, which removed 1% with QS at − 19%.

347   at -19%.

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349

Figure 4. The removal and desorption of copper in percentage terms for each of the study materials over
the duration of the study. Values below quartz sand control levels represent desorption.

Cu distribution in the column subsections

BC desorbed Cu (Fig. 4) and displayed no significant difference in Cu concentrations

between subsections. Similarly, QS which did not remediate Cu showed no significant

difference in proportions of Cu between each subsection. WA removed Cu at 99%,

(Fig. 4) holding 80% in subsection 1 (Fig. 5) with only 4% in the final subsection. BR

showed signs of desorbing Cu on days 31–36, reflected by 30% of Cu being held in the

final subsection. These proportions suggested that the contaminant was in the process

of draining out of the water column due to desorption.
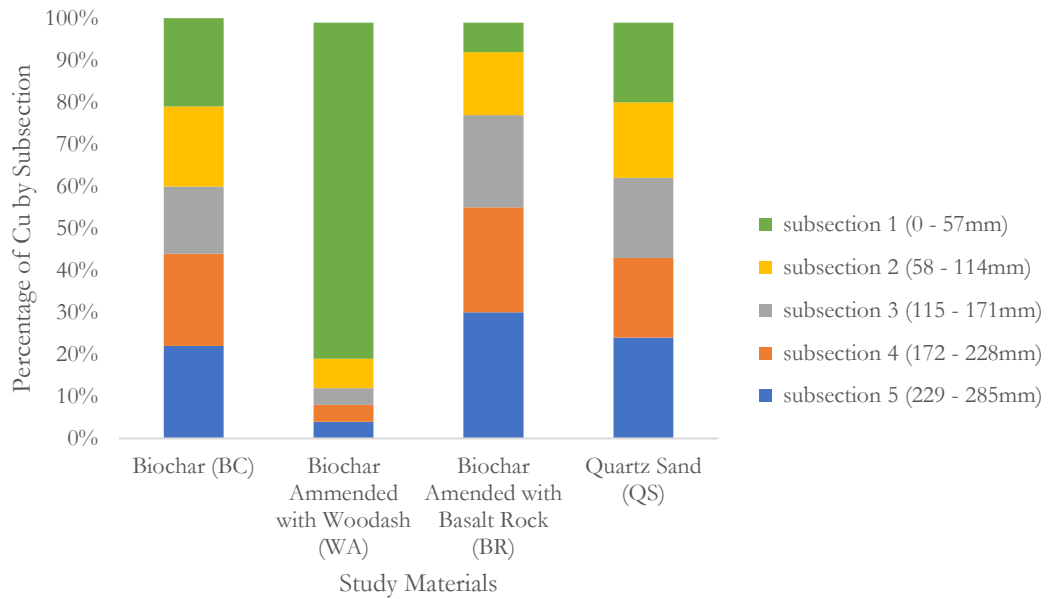
Figure 5. The relative proportion of copper in each 57mm subsection for each study material post study.

Zn eluate

Zn elimination rates for BC, WA and BR started at 98–100%. BC removal rates started to decline by days 7–12 with a drop to 84% (Fig. 6). By days 13–18, it had begun to desorb and continued to do so during days 19–24. Remediation returned to near control levels by days 25–30 and was at control levels by days 31–36. BR maintained 98% Zn removal until days 19–24 when elimination rates dropped to 67% where they stayed for days 25–30. However, desorption took place by days 31–36. WA removal of Zn remained between 97 and 100% for the period of the study. Again, QS, as the control, did not decrease the Zn concentration. Over the duration of the study, WA removed 98% of Zn, again demonstrating significantly higher removal than all other study materials, BR removed 52%, which was significantly higher than BC, which removed − 11% with QS at − 21%.
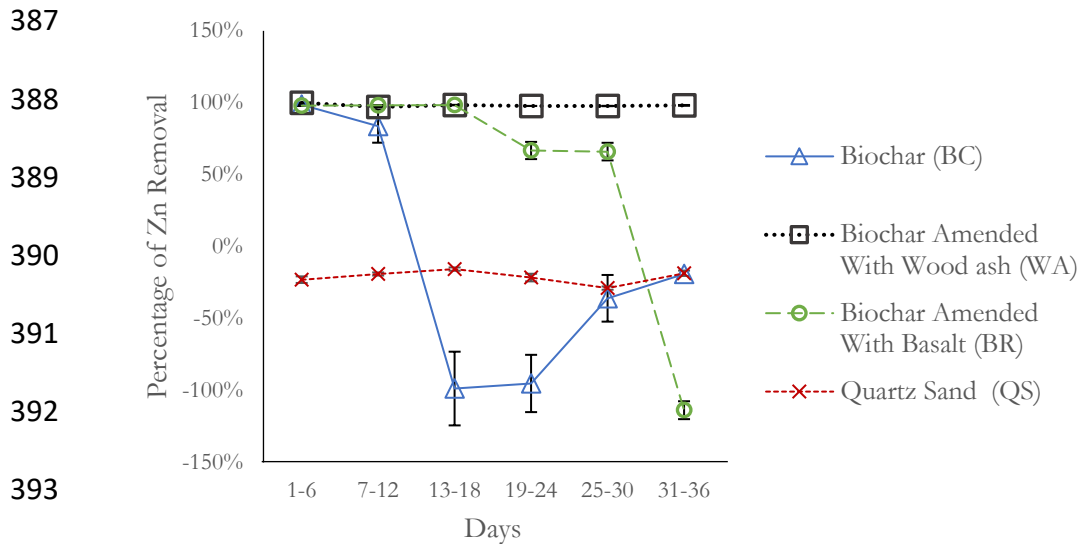
Figure 6. The removal and desorption of zinc in percentage terms for each of the study materials over the 36 day duration of the study. Values below quartz sand control levels represent desorption.

Zn distribution in the column subsections

Again, BC and the QS control showed no total net removal for Zn (Fig. 6) and as such Zn proportions showed no significant difference between the 57-mm subsections (Fig. 7). BR showed only 9% of Zn held in subsection 1, with the largest proportion seen in subsection 5 (25%). This signified that Zn was leaving the study material, as demonstrated by BR's desorption of Zn on days 31–36. Although WA did not desorb Zn during the trials, there is evidence that the contaminant was moving down the subsections with only 55% retained in subsection 1 and 19% in subsection 2 (Fig. 7).
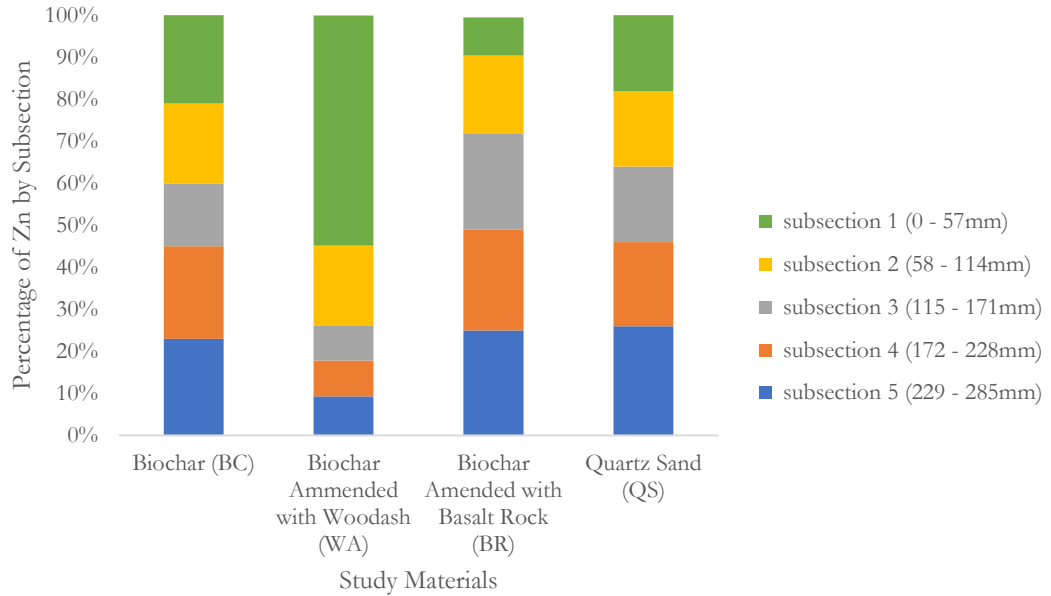
Figure 7. The relative proportion of zinc in each 57mm subsection for each study material post study.

Cd eluate

Overall Cd was the contaminant that was least successfully removed. Removal by BC, WA and BR was at 100% for days 1–6 (Fig. 8). However, BC elimination rates of Cd started to decline by days 7–12. Desorption was seen by days 13–18 and continued into days 19–24 before returning to control levels by days 25–30 where it remained for days 31–36. BR maintained 100% of Cd removal until days 19–24 when a marked drop occurred to just above control levels (Fig. 8). Control levels were reached pre-desorption during days 25–30 but desorption occurred on days 31–36. However, WA maintained Cd elimination rates of 100% throughout the study. Again QS, as the control, did not decrease the Cd concentration of the eluate. Whilst Cd proved to be the contaminant that was least successfully immobilised amongst biochar and amended biochars overall (Fig. 8), WA still removed 100% of Cd, significantly more than BR, at 29%, which in turn was significantly higher than BC, at 5% removal, with QS at −20%.
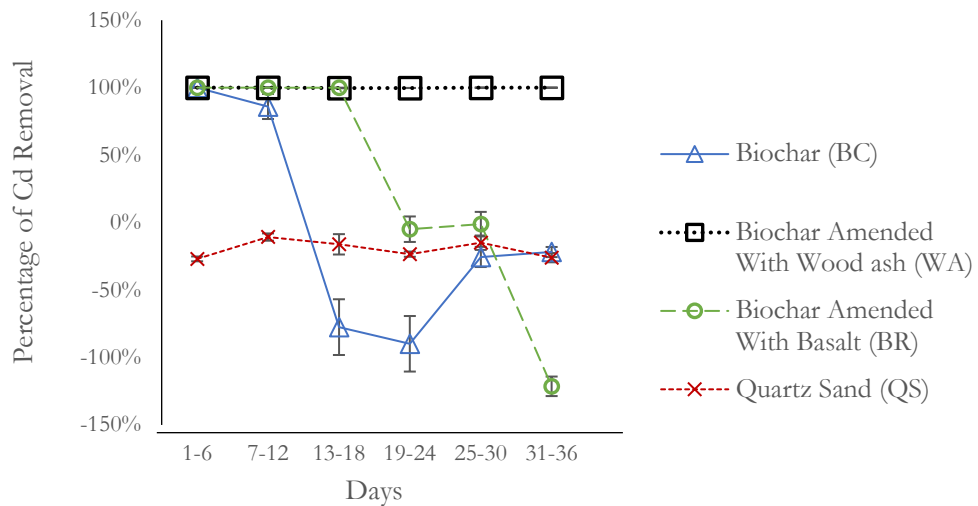
Figure 8. The removal and desorption of zinc in percentage terms for each of the study materials over the 36 day duration of the study Values below quartz sand control levels represent desorption.

Cd distribution in the column subsections

BC and QS both showed a relatively even distribution of Cd between the 57-mm subsections (Fig. 9), indicative of their lack of total net Cd removal (Fig. 8). Although BR removed more Cd than BC and QS over the first 30 days, it had started to desorb all three contaminants by days 31–36, a process reflected in the proportions of contaminant held in the subsections. Cd proportions in each WA subsection (Fig. 9) were concentrated in subsection 1, as removal was still taking place.
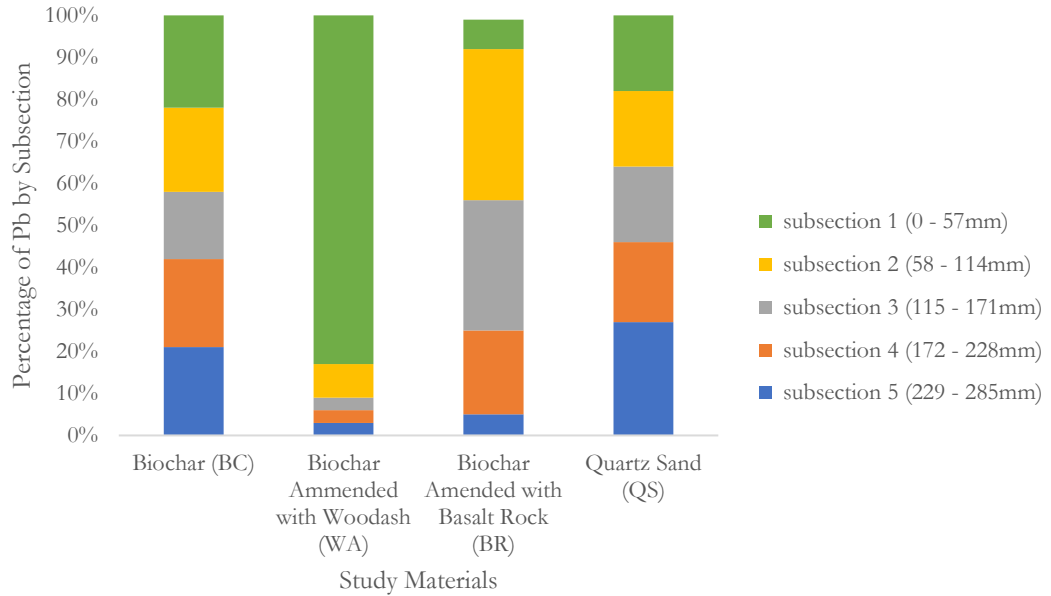
Figure 9. The relative proportion of cadmium in each 57mm subsection for each study material post study.

Eluate pH

The pH increase from eluent to eluate showed significant differences between study materials (Fig. 10). WA caused the highest eluate pH change, BR the second and BC the lowest. BC, WA and BR neutralised the acid eluent to varying degrees during the study, in line with the concentrations of alkali and alkaline earths seen in each study material (Table 2). Correlations between contaminant removal and eluate pH were $r = 0.73–0.74$; $p < 0.01$ (dependent on metal).
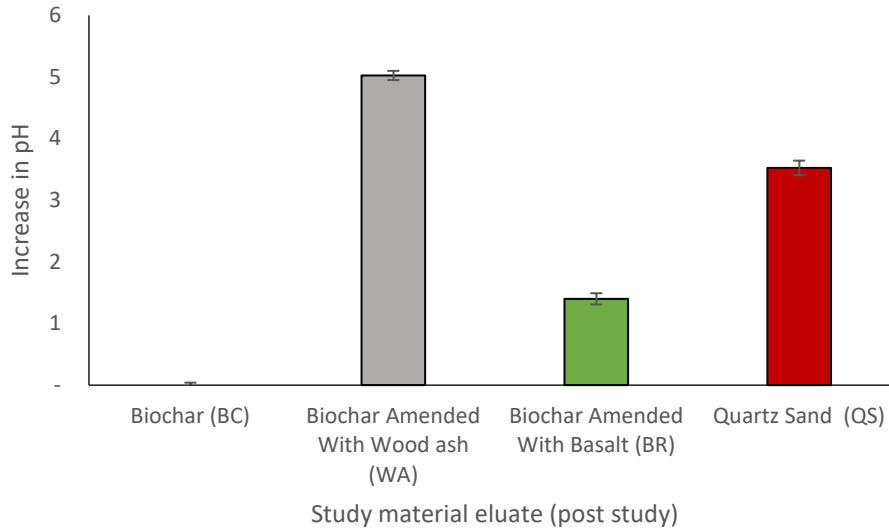
Figure 10. The change in pH levels from eluent to eluate by study material

Discussion

In this study, we investigated the ability of biochar to remove heavy metal pollutants,

specifically Pb, Cu, Zn and Cd, from motorway runoff. This remediation takes place

due to the physical and chemical properties of the (amended)-biochar enabling the

removal of these contaminants (Lu et al. 2012). It was also hypothesised that biochar's

removal efficacy of polluted motorway runoff can be improved through amendments,

such as the addition of wood ash or basaltic rock dust. The study confirmed that

biochar can immobilise contaminants for a short period but that the addition of

amendments, particularly wood ash, significantly improves the ability to immobilise all

contaminants examined in this study for an extended time period (Figs. 2, 4, 6 and 8).

The principal factors affecting removal have been examined in relation to each metal

for biochar (BC), biochar amended with wood ash (WA) and biochar amended with

basaltic rock dust (BR), to ascertain their respective importance in the removal process

for each contaminant studied. WA displayed the highest pre-study levels of pH, P, Mg,

K and Ca, which were hypothesised to increase contaminant removal. WA also showed

23

476   the largest increase in pH from eluent to eluate partly as a result of the release of oxides

477   and carbonates in the ash causing alkalinity to increase (Cerrato et al. 2016). Such

478   deprotonation likely increased the negative surface charge of the biochar increasing the

479   electrical attraction of the metal cations and changed the dissociation of surface

480   functional groups (Xiao et al. 2018). Phosphorus minerals have also been seen to

481   contribute to the sorption of Pb, Cu, Cd and Zn through precipitation as insoluble

482   phosphate salts at higher pH (Lehmann and Joseph 2015). Furthermore, the increased

483   pH also decreased the solubility of heavy metals in solution leading to their

484   precipitation (Pourbaix 1966). The pre-study hypothesis that WA would be the most

485   successful remediator, with the greatest potential to be scaled up, was borne out during

486   the study (Figs. 2, 3, 4, 5, 6, 7, 8 and 9).

Pb sorption

488   Several key factors influenced the sorption of Pb during this study. The principal factor

489   of importance was pH, which showed a strong correlation with Pb removal ($r = 0.73$;

490     $p < 0.01$) supporting the results of previous studies (Xu et al. 2013b; Mohan et al. 2007)

491   and Wang et al. 2018). Mohan et al. (2007) asserted that the maximum absorption of Pb

492   occurred between pH 4 and 5, close to the post-study pH of the WA eluate, which

493   ranged from pH 5.4 to 5.8. pH changes Pb speciation at low pH, at which it is found in

494   soluble form (Pb2+) rather than the Pb precipitate Pb (OH)2 found at higher pH

495   (Pourbaix 1966). BC was not as successful in its removal of Pb (Fig. 2) and showed pH

496   levels well below the maximum sorption range outlined in Mohan et al.'s (2007) study.

497   The concentration of total P in the eluate showed a strong negative correlation with

498   sorption of Pb ($r = -0.59$; $p < 0.01$). The higher the amount of P lost from the study

499   materials to the eluate, the lower the amount of P that was available within the study

500   materials to cause precipitation. Uchimiya et al. (2010) observed that the remediation

501   of Pb was primarily as a result of phosphate-based ligands forming Pb phosphate

502   precipitates. Cation exchange capacity (CEC) was also of importance to Pb remediation

503   in this study, through the exchange of Mg ($r = 0.50$; $p < 0.01$) and Ca ($r = 0.58$;

504    $p < 0.01$), as reported by Lu et al. (2012). However, contrary to published research (Lu

505   et al. 2012), K ion exchange was not of strong importance in this study ($r = 0.30$;

506    $p < 0.01$).

507   **Cu sorption**

508   As for Pb, the eluate pH value showed the most significant correlation with Cu sorption

509   ($r = 0.74$; $p < 0.01$). This is in line with Chen et al. (2011) who noted how pH

510   significantly affected the removal of both Cu and Zn. Removal levels were reported to

511   rise with pH levels until a pH of 5 was reached, agreeing with this study's finding.

512   With a pH value of < 4, reduced available negative sorption sites due to competition

513   from H+ ions and a soluble metal speciation (Cu2+) will be found. This would go some

514   way towards explaining the significant differences between WA and BC in terms of

515   sorption of Cu (Figs. 4 and 5).

516   Eluate P levels (and therefore a reduction in study material P levels) showed a negative

517   correlation with Cu sorption ($r = -0.54$; $p < 0.01$). This is likely as a result of

518   precipitation with PO43− (Xu et al. 2013b). Xu et al. (2013b) asserted that metal

519   phosphate and metal carbonate precipitation 75–100% of Cu sorption. Whilst this study

520   indicated that precipitation as a result of pH and P is the dominant factor in Cu

521   removal, contrary to Xu et al. (2013b), CEC has some limited relevance through the

522   exchange of Ca (Ca: $r = 0.53$, $p < 0.01$, Mg: $r = 0.29$, $p < 0.01$ and K: $r = 0.35$, $p < 0.01$).

523   **Zn sorption**

524   As for Pb and Cu, eluate pH displayed the strongest correlation with Zn sorption

525   ($r = 0.74$, $p < 0.01$) further supporting the conclusions of Chen et al. (2011) regarding

526 the significance of pH for the remediation of both Zn and Cu. Zn displays very similar

527 removal drivers to Cu with pH and P being the primary drivers and CEC having a

528 moderate or weak impact on sorption. Of the four study contaminants, the similarities

529 between Cu and Zn are not unexpected due to their similar electron structure and size

530 of ionic radius (Park et al. 2015). Again, eluate P levels showed a strong negative

531 correlation with Zn sorption ($r = -0.54$; $p < 0.01$). As with Cu, Xu et al. (2013b)

532 attributed Zn sorption to precipitation, citing PO_4^{3-} as an important factor. CEC was a

533 minor factor in sorption of Zn with moderate sorption correlation with Ca ($r = 0.42$;

534 $p < 0.01$) and K ($r = 0.35$; $p < 0.01$) and a weak or no correlation with Mg ($r = 0.16$;

535 $p < 0.13$). The moderate sorption correlation with Ca contradicts Xu et al. (2013b) who

536 observed no link to CEC but rather saw removal as entirely the result of precipitation.

537 **Cd sorption**

538 Cd was the contaminant least susceptible to removal across the study materials (Figs. 8

539 and 9). Despite this overall trend, Cd elimination rates by WA were at 100% and

540 showed no indications of desorption, even from the progression of Cd through the WA

541 subsections (Fig. 9). Again, pH was the most influential factor in sorption ($r = 0.74$;

542 $p < 0.01$) with P also being of relevance, but less so than with other contaminants

543 ($r = -0.47$; $p < 0.01$). The ordering of correlation between the different metals and P

544 was also seen in Uchimiya et al.'s study (2010). The results from both studies showed

545 that P was most important in the precipitation of Pb ($r = -0.59$; $p < 0.01$), followed by

546 Cu ($r = -0.54$; $p < 0.01$) and finally Cd ($r = -0.47$; $p < 0.01$).

547 In contrast to Pb, Cd results indicated that CEC had, at best, a moderate influence on

548 sorption through Ca ($r = 0.34$; $p < 0.01$) and K ($r = 0.40$; $p < 0.01$) with Mg having no

549 discernible correlation with sorption ($r = -0.02$; $p < 0.83$). These findings are in line

550 with other studies where CEC is discounted as a major driver of Cd removal (Mohan et

551   al. 2007; Uchimiya et al. 2010; Xu et al. 2013b). Of all the contaminants studied, Cd is

552   the most toxic and therefore potentially the contaminant of most interest. Other studies

553   have commented on the difficulty of removing Cd and its desorption, in part, due to

554   displacement by Pb (Christophi and Axe 2000). Hence, the success of WA represents a

555   promising pathway to follow.

556   **Feasibility of scaling up**

557   Analysis of the eluate demonstrated the capability of biochar to immobilise heavy

558   metals; analysis of the water column subsections demonstrated the feasibility of scaling

559   this process up. Most prior studies have focused on sorption capacity through

560   laboratory studies, with little to no focus on retention timescales prior to desorption or

561   the consequences on the field management of biochar (Inyang et al. 2012; Zhang et al.

562   2017; Schreiter et al. 2018). When analysis of the eluate and the subsections of this

563   study are reviewed together, the potential to scale up deployment of amended biochars

564   as remediators of motorway runoff is apparent. When no desorption is evident through

565   the eluate, such as WA's remediation of Cu (Fig. 4) and there is no indication of

566   desorption, the majority of the contaminant is held in the uppermost subsection

567   (Fig. 11). As sorption capacity is reached, the contaminant travels through the

568   subsections, decreasing the proportions at the higher subsections and increasing

569   proportions in the lower subsections. This can be seen with BR's desorption of Zn (Fig.

570   6) leading to increasing Zn proportions in the lower subsections (Fig. 11). Post-

571   desorption, as shown by BC's desorption of Zn (Fig. 6), the contaminant has flowed

572   through each subsection leaving the study material and as a result the proportions of

573   contaminant in each subsection are equal in the same way as the control shows equal

574   proportions (Fig. 11). The progression of the contaminant through the study materials

575   indicates that as biochar thickness increases, residence time and the volume of

576   contaminant held increases, thus making scaling up feasible.

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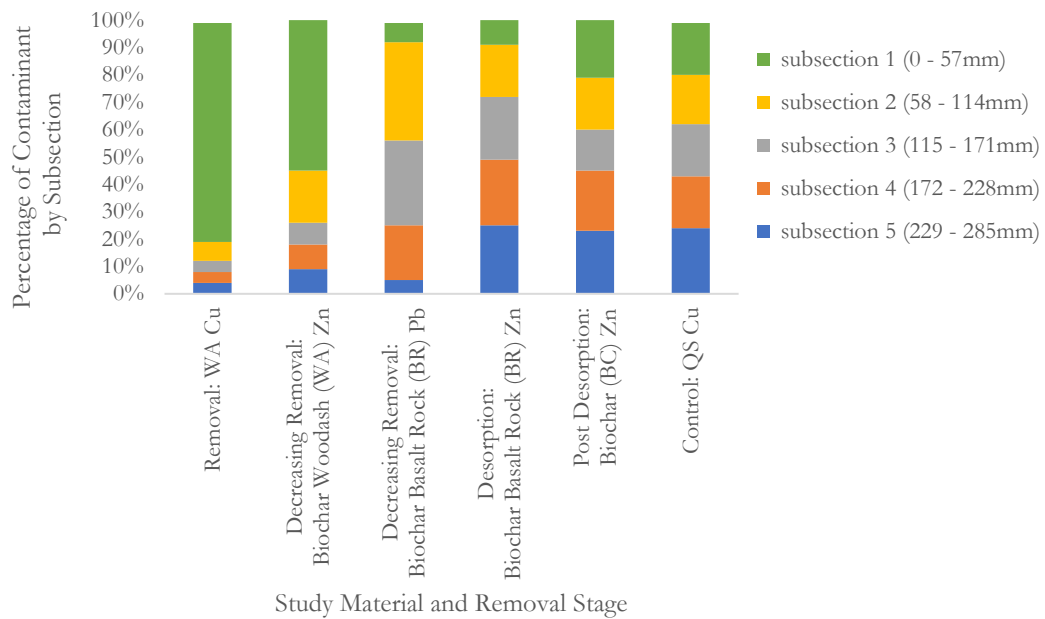
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579   **Figure 11.** The progression of heavy metals through biochar. Moving from removal to decreasing

580   removal to desorption then finally to post desorption / control status.

581

582   The retention time of contaminants is key to the viability of using amended biochar in

583   the field due to its intrinsic link with management time and resource. The feasibility of

584   scaling up the use of biochar, alongside its immobilisation properties, provides the

585   opportunity to deploy biochar as a filter for contaminated motorway runoff.

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588

589   **Conclusion**

590   This work shows that biochar amended with wood ash can be used as an effective

591   remediator of Pb, Cu, Zn and Cd in the field. Its use would combat freshwater

592   degradation contributed to by increased motor vehicle usage and the resultant polluted

593   runoff. In this study, the elimination rates of Pb, Cu, Zn and Cd were shown to differ

594   significantly between biochar (BC), biochar amended with wood ash (WA) and biochar

595   amended with basaltic rock dust (BR). Amended biochar showed significantly more

596   removal of all contaminants (WA > BR > BC). WA was the only study material that

597   did not show signs of desorption in the eluate for any of the contaminants during the

598   36-day study. Pb, Cu, Zn and Cd removal showed strong correlations with pH and total

599   P content indicating that metal speciation, surface charge and precipitation with P were

600   the primary influence on immobilisation. CEC was seen to be relevant in Pb removal,

601   of secondary importance in Cu and Zn removal and of weak or at best moderate

602   importance in Cd removal.

603   In this work, we explored a worst case scenario field situation with pulses and dried

604   columns to approximate issues such as preferential flow and bioavailable metals to

605   maximise toxicity. In these conditions, scaling up the use of biochar to be effective in

606   the field was found to be feasible. Subsection analysis showed that increased thickness

607   of biochar would increase the residence time of the contaminant. Lengthening the

608   efficacy period of the biochar increases the time between removal and replacement of

609   the biochar required in the field, decreasing management time and cost.

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