



The removal of lead, copper, zinc and cadmium from aqueous solution by biochar and amended biochars

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Abstract

The exponential growth in the use of motor vehicles is a key contributor to freshwater degradation. Current remediation techniques require prohibitively expensive contaminant treatment and extraction. Biochar represents an inexpensive option to ameliorate contaminants from motorway runoff. Biochar from Norway spruce (*Picea abies* (L.) Karst.) was produced under fast pyrolysis-gasification (450–500 °C for 90 s) and amended with wood ash and basaltic rock dust to evaluate sorption of Pb, Cu, Zn and Cd. The column study, designed to mimic field conditions, confirmed that unamended biochar can bind contaminants for short periods, but that the addition of amendments, particularly wood ash, significantly improves contaminant removal. Wood ash-amended biochar removed 98–100% of all contaminants during the study, driven by pH ($r = 0.73$ – 0.74 ; $p < 0.01$ dependent on metal species) and phosphorus levels causing precipitation ($r = 0.47$ – 0.59 ; $p < 0.01$, dependent on metal species). The contaminants' progression through the biochar subsections in the column indicated that increasing the thickness of the biochar layer increased contaminant residence time and removal.

Keywords Biochar · Heavy metal · Highway runoff · Contaminant removal

Introduction

Motor vehicles are recognised as a growing source of pollution in modern society. As of April 2018, there were c.38M licensed vehicles on Britain's roads, a number that has been

growing by c.640 thousand vehicles per year since 2012 (Gov.uk 2018). Traffic density is intrinsically linked to heavy metal contaminants (Hares and Ward 1999; Ewen et al. 2009; Du et al. 2018) and as such the exponential growth of motor vehicles and resultant increases in traffic density has led to escalating amounts of pollution.

The growth in the number of motor vehicles naturally increases in conjunction with highway development, increasing pollution and runoff volume. Development has replaced significant areas of natural permeable land with artificial impermeable surfaces (Ladislas et al. 2015). These surfaces obstruct infiltration of precipitation into the ground, increasing surface runoff, which washes away the polluted dust particles resultant from anthropogenic activity (Ladislas et al. 2015; Charters et al. 2016; Mohanty et al. 2018).

Heavy metal motorway pollution is seen as a key contributor to freshwater degradation, contaminating the food chain and enabling direct human exposure to toxins through freshwater leisure activities. Numerous studies indicate that the impact of increased metal concentrations on aquatic life is significant and can increase vulnerability to disease, mortality and a reduction in fecundity (Burrows and Whitton 1983; Mayer-Pinto et al. 2010; Yi et al. 2011; Wu et al. 2016). Metal pollutants, such

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as Pb, Cu, Zn and Cd, accrue in the aquatic environment, increasing their impact on aquatic species and entering the food chain, causing increased concern globally (Cooper et al. 2009; Wik et al. 2009; Kayhanian 2012). Human exposure to these heavy metals can have significant detrimental health consequences including the impairment of neurological functions, kidney damage, liver function, fragile bones, lung damage and mortality (Järup 2003; Ewen et al. 2009).

Three key processes are currently used to remove pollutants: sedimentation, separation and vegetated treatment processes. Current remediation techniques to remove heavy metals from motorway runoff predominantly revolve around sedimentation, the accumulation of which requires expensive treatment and extraction. For heavy metals, capturing polluted sediment is the dominant method used through techniques such as sedimentation tanks, balancing ponds (both wet and dry) and full retention oil traps. Studies have shown heavy metal removal rates of these methods to be up to 70% (Crabtree et al. 2006). Whilst these methods reduce aqueous heavy metal concentrations, over time polluted sediment builds up in the relevant tanks, traps and ponds creating a toxic waste product that is difficult and costly to remove.

The dredging of toxic sediment in order to extract it from ponds is exceptionally expensive (Rulkens 2005). Depths of balancing ponds can be as shallow as 800 mm with sediment accrual of up to 50 mm year⁻¹ such build up reduces the removal efficiency of ponds, putting nearby waterbodies at risk whilst exposing wildlife to toxins within the ponds (Farm 2002; Karlsson et al. 2010; Weinstein et al. 2010).

Biochar deployment is a potential alternative to current processes commonly used to remove pollutants. Biochar is the carbon rich porous product produced by pyrolysis from plant- and animal-based biomass under oxygen limited conditions, with an appearance similar to charcoal (Lehmann and Joseph 2009). It can be produced using a multitude of feedstocks and a variety of pyrolysis conditions, both of which are key to controlling its properties (Xiao et al. 2018).

Biochar can be used to remove heavy metal contaminants from polluted water principally as a result of its sorption properties (Kilic et al. 2013). Immobilisation of heavy metals takes place through several mechanisms including ionic bonding, cation exchange, physical adsorption and co-precipitation (Zhang et al. 2013; Wang et al. 2018).

The efficacy of the immobilisation is influenced by the characteristics of three key factors:

The biochar

Biochar characteristics differ with feedstock and pyrolysis conditions. These differences influence bulk physical properties such as surface area and porosity (Mohan et al. 2007; Iftthikar et al. 2017) and chemical properties such as functional groups, mineral ash and pH which are instrumental in the

binding of heavy metals to biochar (Uchimiya et al. 2010; Xu et al. 2013a; Lehmann and Joseph 2015). Surface area and total pore volume are intrinsically linked as highly porous structures, particularly micropore structures, have a high surface area (Chen et al. 2011; Mohan et al. 2014). It has been noted that surface area and porosity facilitate the adsorption of heavy metals as a result of the volume of potential adsorption sites and that these physical properties are controlled partly by pyrolysis conditions but to a greater extent by feedstock (Chen et al. 2011). Oxygenated functional groups are a critical chemical property which act as a key factor contributing to heavy metal adsorption as a result of electrostatic attraction (Wang et al. 2018) with relevant groups such as carboxyl being present in biochar at high pH values (Bogusz et al. 2015). pH also impacts precipitation with higher biochar pH values enabling precipitation of Pb, Cu, Zn and Cd by carbonate and phosphate minerals (Inyang et al. 2012). Elemental composition, for instance alkali metal and alkaline earth concentrations, can also be changed via feedstock and pyrolysis conditions, affecting biochar pH and cation exchange capacity (CEC) (Zhang et al. 2013). Additionally, carbon structure, a key driver of complex bonding, can be 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 abundance. 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- μ m qualitative filter paper to be situated underneath to capture the eluate. A 25- μ m nylon mesh (150 mm \times 100 mm) was attached to the base of each water column to prevent the loss of biochar. Between the base of the biochar and the nylon mesh, 120 mm of cotton wool was inserted to allow any eluate to drain away whilst reducing re-contact with the study material. Water columns were kept at room temperature and covered with filter paper to reduce evaporation. The quantity (mL) and retention time (min) of the solution were all measured for each volume of biochar.

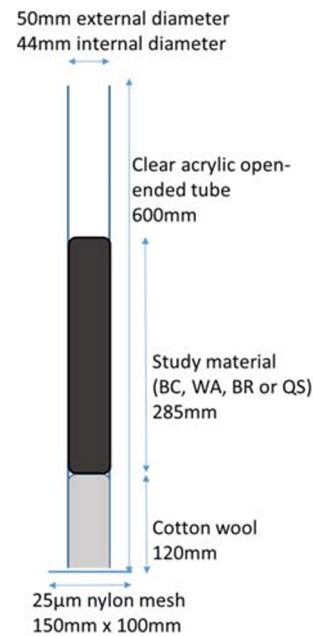


Fig. 1 Water columns into which the aqueous solution was administered for biochar (BC), biochar amended with wood ash (WA), biochar amended with basaltic rock dust (BR) and quartz sand (QS)

Selection and preparation of biochar, amendments and control

The biochar used in this study consisted of Norway spruce (*Picea abies* (L.) Karst.) wood chips pyrolyzed in a Pyrochar BigChar-1000 pyrolysis-gasification kiln at a temperature of 450–500 °C, with a retention time of \sim 90 s and was granulated ($<$ 3 mm). Norway spruce, as a softwood, was chosen because of its greater number of pores and surface area for sorption to take place in comparison with hardwood (Mohanty et al. 2018). Amendments to the biochar were mixed dry at room temperature, at a ratio of 1:1, with a plasterer's whisk. Mixed wood ash was selected as an amendment due to its high pH, phosphorus (P) and alkaline earth content (Mg and Ca). Basaltic rock dust was used because of its high pH and alkaline earth content (Mg and Ca). Quartz sand was employed as a control due to its neutral pH, low levels of alkaline earth and low levels of heavy metal pollutants.

Pre-study analysis

pH measurements were carried out by soaking biochars with deionised water at a 1:5 solid/water ratio for 24 h in a 150-mL Sterilin plastic screw top container, which was agitated on a Unitwist 400 Orbital Shaker. The pH of the resultant slurry was measured using a previously calibrated Voltcraft pH Meter that was rinsed with deionised water between samples. The pH for the quartz sand control was determined by adding 50 g of sand to 100 mL of deionised water in a 150-mL Sterilin plastic screw top container which was agitated for

1 h before measuring the pH. The elemental composition of the biochar, amended biochars and quartz sand was determined using a benchtop Rigaku NEX CG Energy-Dispersive XRF spectrometer, which was calibrated with internal standards. He, rather than air, was used in the XRF chamber to ascertain heavy metal (Pb, Cu, Zn and Cd), alkali metal (K), alkaline earth (Mg and Ca) and P concentrations. Samples of each of the study materials were dried at 50 °C for 24 h and ground using a pestle and mortar to minimise gaps between sample particles within XRF sample 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 what would be encountered in field conditions (Crabtree et al. 2009; Zhao et al. 2010; MacKay et al. 2011). The stock solution was mixed in a grade A volumetric flask (5000 ± 1.2 mL) within a fume cabinet. Deionised water was added to half fill the volumetric flask. Two hundred millilitres of each of the four single element Fisher 1000 mg kg^{-1} heavy metals of AAS standard grade was added using a 50-mL glass

pipette. The metal standards were held in 5% HNO_3 and as such the study eluent constituted an acidic solution whereby all four metals were dissolved. Forty-two millilitres of this solution was added to each column at 24-h intervals via a syringe. This volume was calculated from an average of the highest 30 daily precipitation values in South East England during the period 2000 to 2018, to mimic both severe first flushing after an antecedent dry period and the sporadic nature of precipitation in the field (Metoffice.gov.uk 2018). Eluate samples were collected every 6 days, allowing 24 h after the day six solution was added, for the duration of the study.

Eluate analysis

Analysis of the eluate was conducted by XRF to determine heavy metal (Pb, Cu, Cd and Zn), alkali metal (K), alkaline earth (Mg and Ca) and P concentrations. Fifty millilitres of 6-day eluate from each water column and from the solution batch was stored in 50-mL centrifuge tubes at room temperature. XRF cannot directly measure liquids as they would evaporate in the vacuum chamber (P. Brouwer, pers. comm., 2010). As a result, Rigaku Ultra Carry Light disks were used for the analysis of the eluate, which enabled the concentrations (in mg L^{-1}) to be determined for Pb, Cu, Zn, Cd, Mg, Ca, K and P. Two hundred microlitres of eluate was pipetted onto the filter paper portion of the Ultra Carry Light disk for each sample. Each disk was left to dry for 8 h at room temperature prior to analysis. The XRF chamber was evacuated and the eluate on the disks was analysed in batches of 15 samples in triplicate.

Subsection analysis

Post-day 36, each water column was frozen at -20 °C for 24 h to enable each column to be cut into five equal subsections. Whilst freezing has been found to change metal speciation, it does not change total metal concentration (Florence 1977; Batley 1990). Analysis of each subsection was undertaken by XRF, using He in the chamber to determine heavy metal concentrations (Pb, Cu, Zn and Cd). As detection of elements by XRF is affected by water content (Roberts 2015), solid samples were dried for 24 h at 50 °C before XRF analysis. The proportion of contaminant held in each subsection was then determined to understand the movement of contaminant through the study material in each water column.

Statistical analysis

Comparisons between the different biochars' contaminant removal values were performed using the Kruskal-Wallis test using a probability threshold of $p = 0.01$.

Correlation analysis using Pearson's *R* was undertaken to test relationships between heavy metal remediation and biochar characteristics.

Results

Pre-study contaminant concentrations

For the biochar and amended biochars, the levels of intrinsic contaminant metals were low (Table 1).

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

P, pH, Mg, K and Ca were quantified for each study material in pre-study analysis (Table 2). For each of these five categories, WA displayed the highest pre-study levels. BR had the second highest levels in terms of pH, Mg, Ca and K. BC was third in most categories with the exception of P where it displayed low concentrations in comparison with WA rather than the undetectable amounts of P in BR and QS. QS, as the control, displayed the lowest values of all of the properties measured.

Eluate and subsection analysis

Pb eluate

Pb was the contaminant most successfully remediated by the biochar and amended biochars. Elimination rates for BC, WA and BR started at 99–100% (Fig. 2). By days 13–18, BC started to show reduced removal of contaminants and by days 19–24, it had started to desorb, adding Pb to the eluate. Desorption decreased until days 31–36 when remediation levels matched QS control levels. WA and BR maintained elimination rates of 99–100% for the remainder of the study. QS, as the control, did not decrease Pb concentration. Over the duration of the study, WA and BR removed 100% of Pb showing no significant difference in efficacy between them, whereas BC only removed 4%, significantly less than both WA and BR, with QS at –19%.

Pb distribution in the column subsections

The proportions of Pb at each 57-mm subsection varied between the study materials (Fig. 3). BC, which desorbed Pb and returned to control levels of remediation by the end of the study (Fig. 2), showed no significant difference between the concentrations of Pb in each subsection and showed no significant differences from the subsections of the QS control. WA, which immobilised 100% of Pb (Fig. 2), held 83% of the contaminant in the first subsection with only 3% in the final subsection (Fig. 3). BR, which also removed 100% of Pb (Fig. 2), showed a far smaller percentage than WA in the first subsection (5%), with 87% of Pb held in subsections 2, 3 and 4, with only 7% held in subsection 5 (Fig. 3). These proportions indicate that as the study material reached maximum removal capacity, Pb moved through the subsections until, post-desorption, proportions of the contaminant were lessened and became equal throughout the layers.

Cu eluate

Cu elimination rates for BC, WA and BR were found to be 99–100% during days 1–6 (Fig. 4). BC elimination rates declined on days 7–12 and continued to drop until desorption reached its maximum on days 19–24. Removal by BC had returned to control levels by days 31–36. BR maintained its initial Cu removal percentage until days 31–36 when capacity was reached and desorption began (Fig. 4). WA maintained elimination rates of 98–100% for the entirety of the study. In contrast, QS, as the control, did not decrease the Cu concentration. Over the duration of the study, WA removed 99% of Cu, significantly more than the other three materials; in contrast, BR removed 74%, significantly higher than BC, which removed 1% with QS at –19%.

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

Table 1 Pre study concentration of heavy metal contaminants in biochar, amended biochar and quartz sand (mg kg^{-1})

Study materials	Pre-study contaminant concentration			
	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

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

Study materials	Pre-study levels of pH and alkali and alkaline earth				
	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	16,700 ± 578	35,700 ± 788	208,000 ± 5030
Biochar with basaltic rock dust (BR) average	10.2 ± 0.0	0 ± 0	13,900 ± 521	9850 ± 38	35,200 ± 38
Quartz sand (QS) average	7.5 ± 0.0	0 ± 0	0 ± 0	542 ± 18	112 ± 8

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.

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%.

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).

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,

Fig. 2 The removal and desorption of lead in percentage terms for each of the study materials over the duration of the study. Values below quartz sand control levels represent desorption

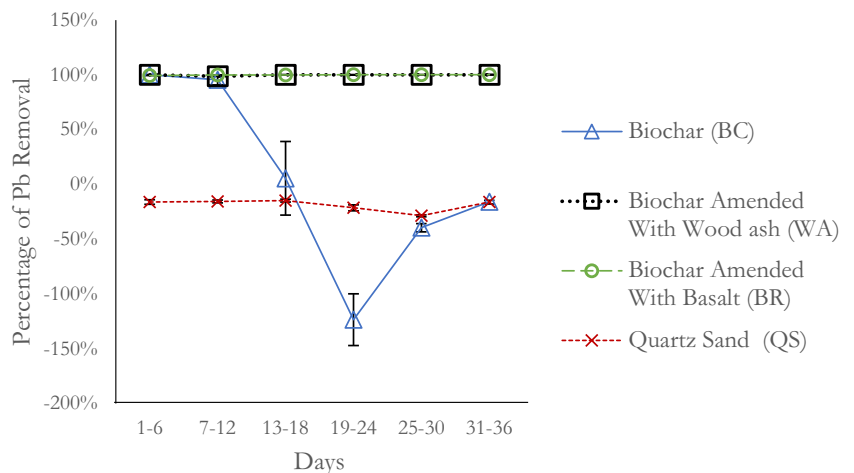
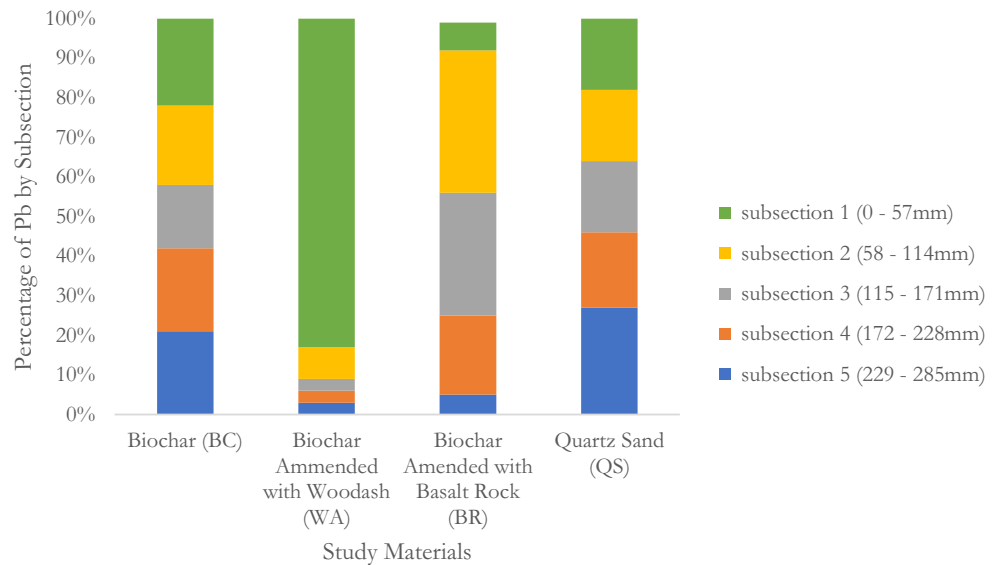


Fig. 3 The relative proportion of lead in each 57-mm subsection for each study material post-study



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%.

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.

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 $r = 0.73\text{--}0.74$; $p < 0.01$ (dependent on metal).

Fig. 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

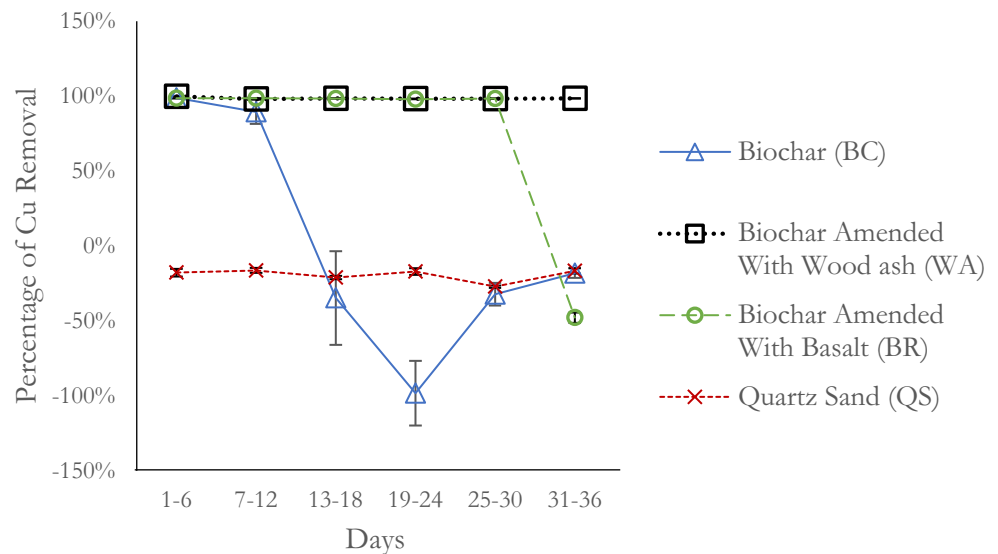
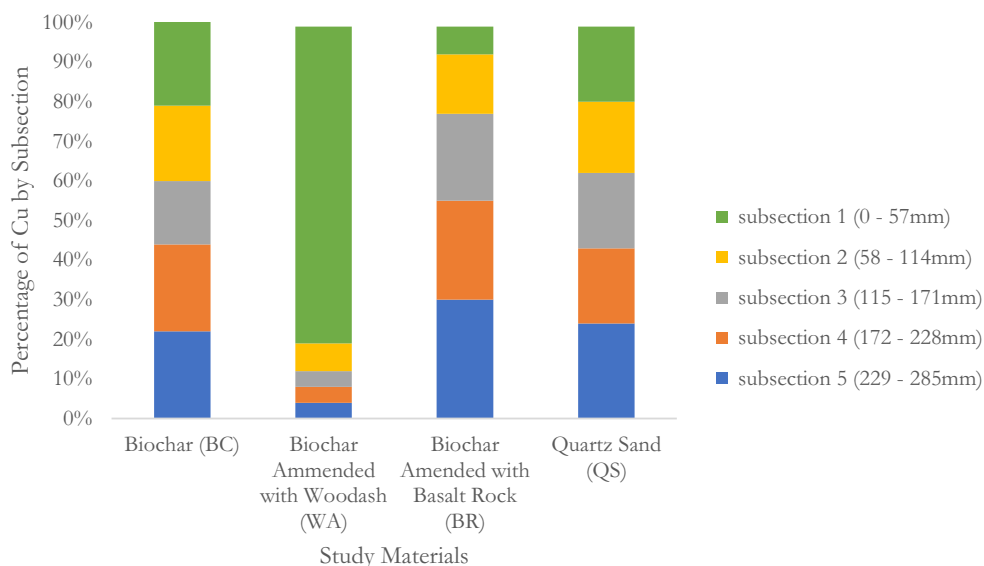


Fig. 5 The relative proportion of copper in each 57-mm subsection for each study material post-study



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 the largest increase in pH from eluent to eluate partly as a result of the release of oxides and carbonates in the ash causing alkalinity to increase (Cerrato et al. 2016). Such deprotonation likely increased the negative surface charge of the biochar increasing the electrical attraction of the metal cations and changed the dissociation of surface functional groups (Xiao et al. 2018). Phosphorus minerals have also been seen to contribute to the sorption of Pb, Cu, Cd and Zn through precipitation as insoluble phosphate salts at higher pH (Lehmann and Joseph 2015). Furthermore, the increased pH also decreased the

Fig. 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

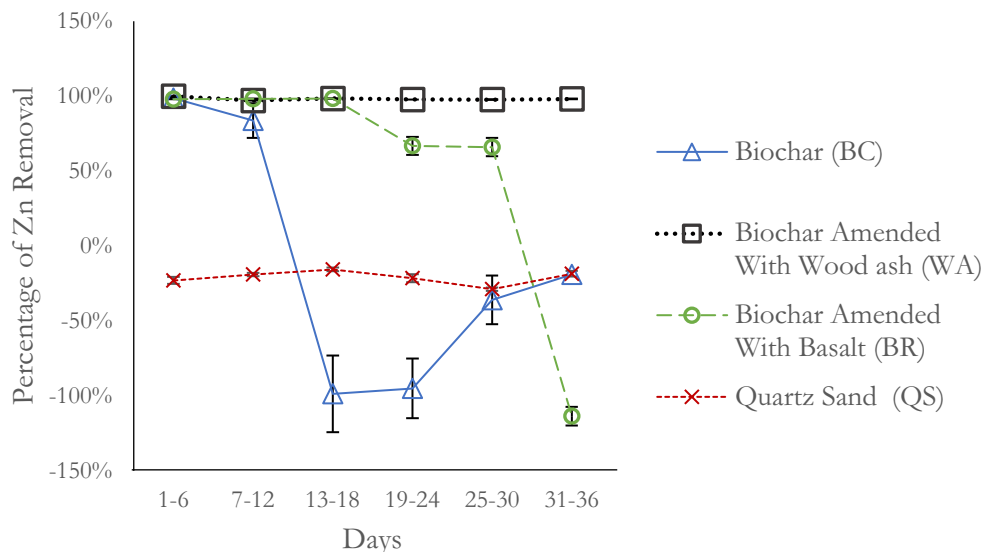
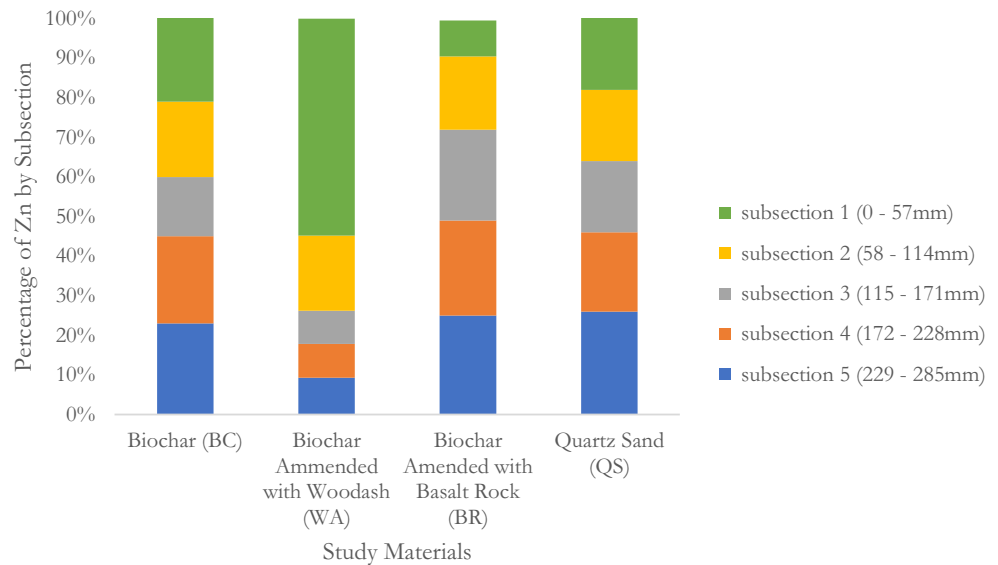


Fig. 7 The relative proportion of zinc in each 57-mm subsection for each study material post-study



solubility of heavy metals in solution leading to their precipitation (Pourbaix 1966). The pre-study hypothesis that WA would be the most successful remediator, with the greatest potential to be scaled up, was borne out during the study (Figs. 2, 3, 4, 5, 6, 7, 8 and 9).

Pb sorption

Several key factors influenced the sorption of Pb during this study. The principal factor of importance was pH, which showed a strong correlation with Pb removal ($r = 0.73$; $p < 0.01$) supporting the results of previous studies (Xu et al. 2013b; Mohan et al. 2007) and Wang et al. 2018). Mohan et al. (2007) asserted that the maximum absorption of Pb occurred between pH 4 and 5, close to the post-study pH of the WA eluate, which ranged from

pH 5.4 to 5.8. pH changes Pb speciation at low pH, at which it is found in soluble form (Pb^{2+}) rather than the Pb precipitate $Pb(OH)_2$ found at higher pH (Pourbaix 1966). BC was not as successful in its removal of Pb (Fig. 2) and showed pH levels well below the maximum sorption range outlined in Mohan et al.'s (2007) study.

The concentration of total P in the eluate showed a strong negative correlation with sorption of Pb ($r = -0.59$; $p < 0.01$). The higher the amount of P lost from the study materials to the eluate, the lower the amount of P that was available within the study materials to cause precipitation. Uchimiya et al. (2010) observed that the remediation of Pb was primarily as a result of phosphate-based ligands forming Pb phosphate precipitates. Cation exchange capacity (CEC) was also of importance to Pb remediation in this study, through the exchange of Mg ($r = 0.50$; $p < 0.01$) and Ca ($r = 0.58$; $p < 0.01$), as reported by

Fig. 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

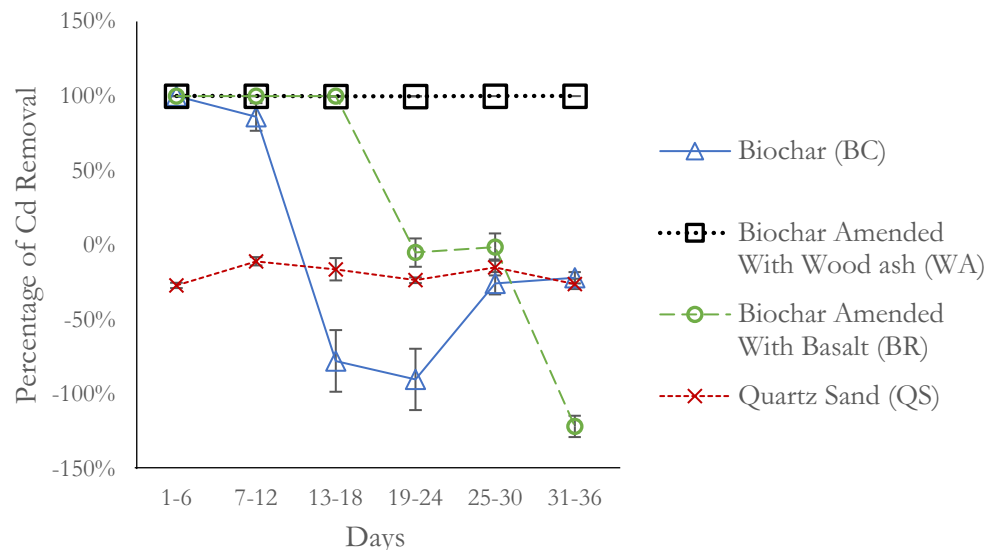
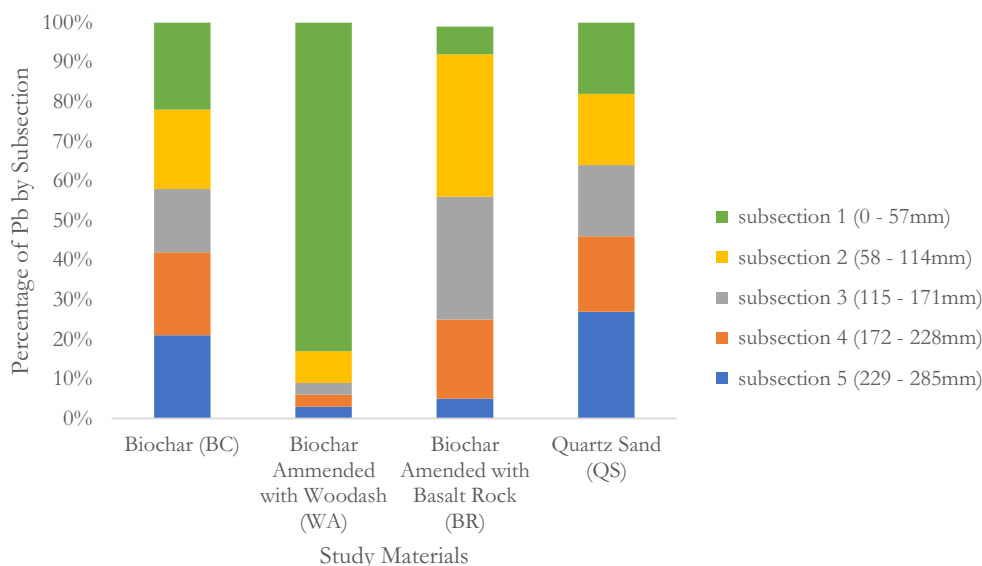


Fig. 9 The relative proportion of cadmium in each 57-mm subsection for each study material post-study

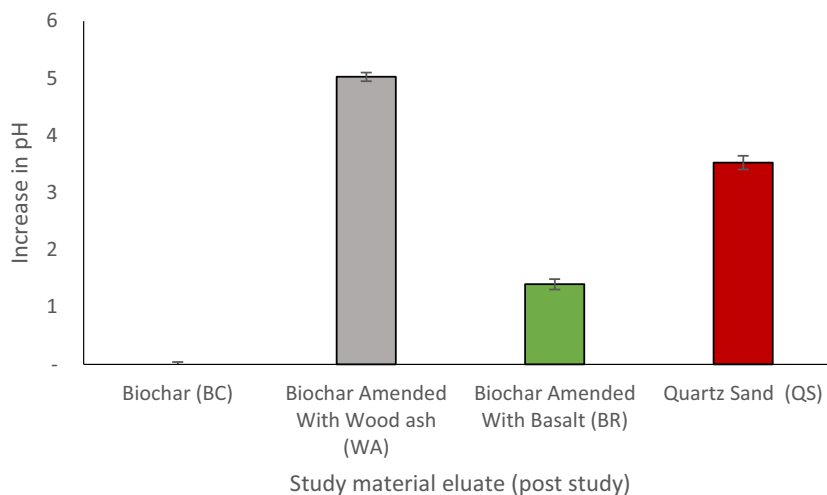


Lu et al. (2012). However, contrary to published research (Lu et al. 2012), K ion exchange was not of strong importance in this study ($r = 0.30$; $p < 0.01$).

Cu sorption

As for Pb, the eluate pH value showed the most significant correlation with Cu sorption ($r = 0.74$; $p < 0.01$). This is in line with Chen et al. (2011) who noted how pH significantly affected the removal of both Cu and Zn. Removal levels were reported to rise with pH levels until a pH of 5 was reached, agreeing with this study’s finding. With a pH value of < 4 , reduced available negative sorption sites due to competition from H^+ ions and a soluble metal speciation (Cu^{2+}) will be found. This would go some way towards explaining the significant differences between WA and BC in terms of sorption of Cu (Figs. 4 and 5).

Fig. 10 The change in pH levels from eluent to eluate by study material



Eluate P levels (and therefore a reduction in study material P levels) showed a negative correlation with Cu sorption ($r = -0.54$; $p < 0.01$). This is likely as a result of precipitation with PO_4^{3-} (Xu et al. 2013b). Xu et al. (2013b) asserted that metal phosphate and metal carbonate precipitation 75–100% of Cu sorption. Whilst this study indicated that precipitation as a result of pH and P is the dominant factor in Cu removal, contrary to Xu et al. (2013b), CEC has some limited relevance through the exchange of Ca (Ca: $r = 0.53$, $p < 0.01$, Mg: $r = 0.29$, $p < 0.01$ and K: $r = 0.35$, $p < 0.01$).

Zn sorption

As for Pb and Cu, eluate pH displayed the strongest correlation with Zn sorption ($r = 0.74$, $p < 0.01$) further supporting the conclusions of Chen et al. (2011) regarding the significance of pH for the remediation of both Zn and Cu. Zn displays very similar removal drivers to Cu with pH and P being

the primary drivers and CEC having a moderate or weak impact on sorption. Of the four study contaminants, the similarities between Cu and Zn are not unexpected due to their similar electron structure and size of ionic radius (Park et al. 2015). Again, eluate P levels showed a strong negative correlation with Zn sorption ($r = -0.54$; $p < 0.01$). As with Cu, Xu et al. (2013b) attributed Zn sorption to precipitation, citing PO_4^{3-} as an important factor. CEC was a minor factor in sorption of Zn with moderate sorption correlation with Ca ($r = 0.42$; $p < 0.01$) and K ($r = 0.35$; $p < 0.01$) and a weak or no correlation with Mg ($r = 0.16$; $p < 0.13$). The moderate sorption correlation with Ca contradicts Xu et al. (2013b) who observed no link to CEC but rather saw removal as entirely the result of precipitation.

Cd sorption

Cd was the contaminant least susceptible to removal across the study materials (Figs. 8 and 9). Despite this overall trend, Cd elimination rates by WA were at 100% and showed no indications of desorption, even from the progression of Cd through the WA subsections (Fig. 9). Again, pH was the most influential factor in sorption ($r = 0.74$; $p < 0.01$) with P also being of relevance, but less so than with other contaminants ($r = -0.47$; $p < 0.01$). The ordering of correlation between the different metals and P was also seen in Uchimiya et al.'s study (2010). The results from both studies showed that P was most important in the precipitation of Pb ($r = -0.59$; $p < 0.01$), followed by Cu ($r = -0.54$; $p < 0.01$) and finally Cd ($r = -0.47$; $p < 0.01$).

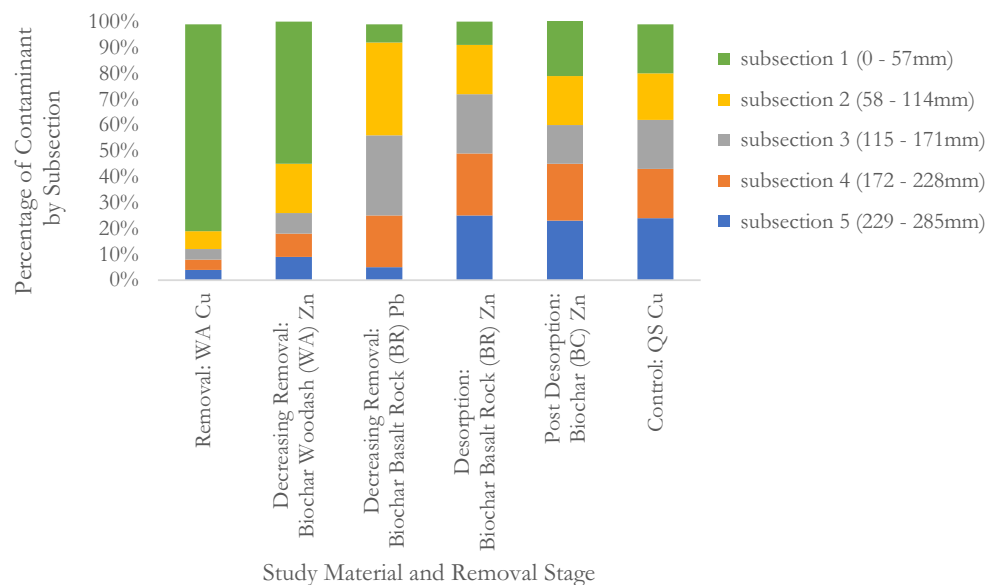
In contrast to Pb, Cd results indicated that CEC had, at best, a moderate influence on sorption through Ca ($r = 0.34$; $p < 0.01$) and K ($r = 0.40$; $p < 0.01$) with Mg having no discernible correlation with sorption ($r = -0.02$; $p < 0.83$). These

findings are in line with other studies where CEC is discounted as a major driver of Cd removal (Mohan et al. 2007; Uchimiya et al. 2010; Xu et al. 2013b). Of all the contaminants studied, Cd is the most toxic and therefore potentially the contaminant of most interest. Other studies have commented on the difficulty of removing Cd and its desorption, in part, due to displacement by Pb (Christophi and Axe 2000). Hence, the success of WA represents a promising pathway to follow.

Feasibility of scaling up

Analysis of the eluate demonstrated the capability of biochar to immobilise heavy metals; analysis of the water column subsections demonstrated the feasibility of scaling this process up. Most prior studies have focused on sorption capacity through laboratory studies, with little to no focus on retention timescales prior to desorption or the consequences on the field management of biochar (Inyang et al. 2012; Zhang et al. 2017; Schreiter et al. 2018). When analysis of the eluate and the subsections of this study are reviewed together, the potential to scale up deployment of amended biochars as remediators of motorway runoff is apparent. When no desorption is evident through the eluate, such as WA's remediation of Cu (Fig. 4) and there is no indication of desorption, the majority of the contaminant is held in the uppermost subsection (Fig. 11). As sorption capacity is reached, the contaminant travels through the subsections, decreasing the proportions at the higher subsections and increasing proportions in the lower subsections. This can be seen with BR's desorption of Zn (Fig. 6) leading to increasing Zn proportions in the post lower subsections (Fig. 11). Post-desorption, as shown by BC's desorption of Zn (Fig. 6),

Fig. 11 The progression of heavy metals through biochar. Moving from removal to decreasing removal to desorption then finally to post-desorption/control status



the contaminant has flowed through each subsection leaving the study material and as a result the proportions of contaminant in each subsection are equal in the same way as the control shows equal proportions (Fig. 11). The progression of the contaminant through the study materials indicates that as biochar thickness increases, residence time and the volume of contaminant held increases, thus making scaling up feasible.

The retention time of contaminants is key to the viability of using amended biochar in the field due to its intrinsic link with management time and resource. The feasibility of scaling up the use of biochar, alongside its immobilisation properties, provides the opportunity to deploy biochar as a filter for contaminated motorway runoff.

Conclusion

This work shows that biochar amended with wood ash can be used as an effective remediator of Pb, Cu, Zn and Cd in the field. Its use would combat freshwater degradation contributed to by increased motor vehicle usage and the resultant polluted runoff. In this study, the elimination rates of Pb, Cu, Zn and Cd were shown to differ significantly between biochar (BC), biochar amended with wood ash (WA) and biochar amended with basaltic rock dust (BR). Amended biochar showed significantly more removal of all contaminants (WA > BR > BC). WA was the only study material that did not show signs of desorption in the eluate for any of the contaminants during the 36-day study. Pb, Cu, Zn and Cd removal showed strong correlations with pH and total P content indicating that metal speciation, surface charge and precipitation with P were the primary influence on immobilisation. CEC was seen to be relevant in Pb removal, of secondary importance in Cu and Zn removal and of weak or at best moderate importance in Cd removal.

In this work, we explored a worst case scenario field situation with pulses and dried columns to approximate issues such as preferential flow and bioavailable metals to maximise toxicity. In these conditions, scaling up the use of biochar to be effective in the field was found to be feasible. Subsection analysis showed that increased thickness of biochar would increase the residence time of the contaminant. Lengthening the efficacy period of the biochar increases the time between removal and replacement of the biochar required in the field, decreasing management time and cost.

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