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Wood ash amended biochar for the removal of lead, copper, zinc and cadmium from aqueous solution

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1 **Wood ash amended biochar for the removal of lead, copper, zinc and cadmium**
2 **from aqueous solution**

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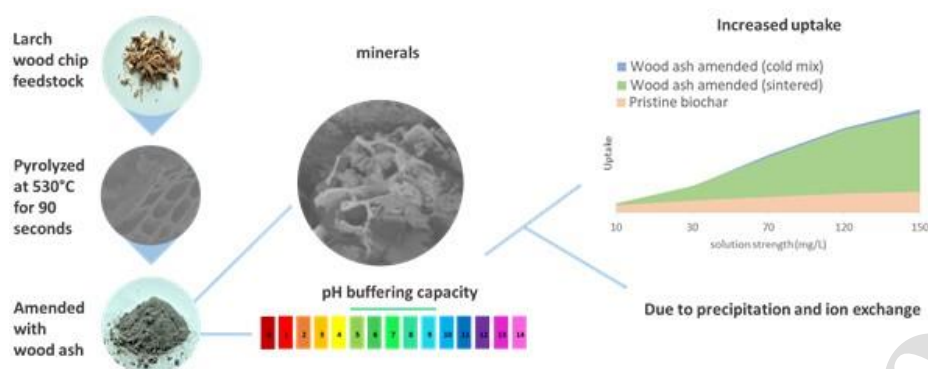
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18 **Abstract**

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3 19 Heavy metals in motorway adjoined aqueous environments have increased at an alarming
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5 20 rate over recent years. This increase has been primarily attributed to anthropogenic activities
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7 21 such as the increase of motor vehicle use. Current remediation techniques, such as balancing
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9 22 ponds have the potential to leave toxic residue with the associated removal costs often proving
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11 23 prohibitive. In this study biochar and wood ash amended biochar were evaluated as
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13 24 remediators of inorganic vehicular pollutants found in motorway runoff, specifically Pb, Cu, Zn
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15 25 and Cd. Biochar from European larch (*Larix decidua* (L.) Karst.) was produced via fast
16
17 26 pyrolysis-gasification (485–530 °C for 90 s) and amended with wood ash post pyrolysis.
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19 27 Pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar
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21 28 sintered with wood ash (WAS) were studied to evaluate metal immobilisation mechanisms and
22
23 29 maximum removal capacities. This study demonstrates that the amendment of biochar with
24
25 30 wood ash increases Pb, Cu, Zn, and Cd immobilisation by an order of magnitude compared
26
27 31 to BC. The addition of wood ash increases pH whilst adding minerals causing precipitation.
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29 32 Precipitation and ion exchange dominate metal immobilization and were not correlated to
30
31 33 surface area. Sustainability of feedstock, low feedstock / production costs and maximum
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33 34 measured contaminant removal (61.5 mg/g, 38.9 mg/g, 12.1 mg/g and 10.2 mg/g for Pb, Cu,
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35 35 Zn and Cd respectively) indicate that wood ash amended biochar is a viable option to
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37 36 immobilise Pb, Cu, Zn and Cd from motorway runoff.
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37 **Graphical Abstract**

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40 **Keywords**

41 Biochar, pH, precipitation, wood ash, heavy metals, runoff

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43 **1. Introduction**

44 Heavy metals in aqueous environments have increased at an alarming rate over recent years.

45 This increase has been primarily attributed to anthropogenic activities such as mining, waste

46 disposal, industrial activities, agriculture, and the increase of motor vehicles use. As of

47 September 2020 there are ~39 million vehicles registered in the UK, representing an increase

48 of ~5 million vehicles in 10 years (Gov.uk, 2018). This escalating increase in registered

49 vehicles and the resultant increase in annual average daily traffic has been seen to directly

50 correlate with an increase in pollutant input (Hwang *et al.*, 2016). Such an increase in vehicles

51 also naturally necessitates a growth in impermeable urban roads, pavements and motorways.

52 In highly developed areas these surfaces can account for up to 70% of the total surface

53 creating an increase in the volume and velocity of runoff (Budai and Clement, 2011; Ladislav

54 *et al.*, 2015; Hwang *et al.*, 2016). This runoff washes away contaminants from anthropogenic

55 sources, such as motor vehicles, carrying the pollutants into receiving waterbodies (Ladislav

56 *et al.*, 2015). The combination of the growth of motor vehicle numbers and the increase in1
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57 impermeable surfaces has led to rising amounts of pollution making traffic a major contributor
58 of contaminants into the UK's environment (Ladislas *et al.*, 2015).

59 The sources of vehicle runoff pollution are reasonably well understood and generally occur
60 through abrasive forces or leaks and include tyre wear, brake wear and motor oil. Tyre wear
61 is recognised primarily as a source for zinc (Zn), and to a lesser extent cadmium (Cd), lead
62 (Pb) and copper (Cu) (Legret and Pagotto, 1999; Budai and Clement, 2011). Pollutants
63 released through tyre wear, unlike exhaust emissions, are collected entirely on the road
64 surface, around 90% of which is captured by runoff, and subsequently may leach toxic
65 compounds (Budai and Clement, 2011; Markiewicz *et al.*, 2017). Each tyre releases ~1 kg of
66 mass during its lifespan of 50,000 km (Legret and Pagotto, 1999; Markiewicz *et al.*, 2017);
67 such wear leads to ~1,327,000 tonnes of rubber being released in Europe annually (Wagner
68 *et al.*, 2018). As a consequence Zn has been measured at levels as high as 240 ppm in road
69 dust and as high as 354 µg / L in road runoff (Legret and Pagotto, 1999; Apeagyei *et al.*, 2011).

70 Brake wear is recognised as a primary source of Cu; it has also been shown to contain
71 significant quantities of inorganic contaminants such as Cd, Pb, and Zn (Legret and Pagotto,
72 1999; Budai and Clement, 2011). Hwang *et al.* (2016) estimate that around 2400 tonnes of Cu
73 was released by brake wear in Europe during 2000. This has, in part, led to concentrations of
74 Cu and Pb being as high as 105 ppm and 73 ppm, respectively in road dust and Cu, Pb, and
75 Cd concentrations in runoff being as high as 45 µg / L, 58 µg / L, and 2.7 µg / L, respectively
76 (Legret and Pagotto, 1999; Farm, 2002). Motor oil is also recognised as a contributor to
77 inorganic pollution including Zn and to a lesser degree Pb and Cu (Budai and Clement, 2011).
78 Organic pollutants from sources such as tyre wear and motor oil are also of concern
79 (Markiewicz *et al.*, 2017). In addition to these sources exhaust emissions are a significant
80 source of organic particulate matter (PM) such as polycyclic aromatic hydrocarbons (PAHs)
81 and inorganic PM including metals (Agarwal, 2007).

82 The primary inorganic pollutants found in motorway runoff can also be found in other polluted
83 waters such as mine water, tailing ponds and industrial effluent in rivers. In these environments

84 concentrations of pollutants are often reported to be even higher than in road dust / runoff.
85 Abandoned metal mines are polluting waters with Pb, Cu and Zn at concentrations regularly
86 over 1000 µg / L (Todd et al., 2021); metal pollution in mine tailing ponds have been recorded
87 at levels of 150 ppm (Pb), 230 ppm (Cu) and 146 ppm (Zn) (Pagnanelli et al., 2004); and
88 extensive industrial Pb, Cu, Zn, and Cd river pollution has been measured with Zn as high as
89 167.8 µg / L (Saha et al., 2017).

90 Heavy metal pollutants entering waterways ~~as a result of motor vehicles~~ can lead to freshwater
91 degradation, threaten local plants and organisms, and negatively affect human health. Where
92 metal levels accumulate and increase beyond acceptable levels they become toxic and as a
93 result a significant environmental hazard for invertebrates and fish (Yi et al., 2011). Humans
94 are exposed to these heavy metals via the food chain and freshwater leisure activities. This
95 can lead to significant adverse health consequences such as reduced neurological function,
96 reduced liver function, reduced fertility, kidney damage, lung damage, osteoporosis and
97 mortality (Morais et al., 2012).

98 Although the impact of motorway runoff is recognised, current Sustainable Drainage Systems
99 (SuDS) that attempt to lessen the consequences of vehicle pollution have the unintended
100 consequence of filling with toxic residues with high removal costs. Presently attempts to
101 mitigate heavy metals primarily involve sedimentation, the subsequent accumulation of which
102 then require expensive treatment and extraction. SuDS such as balancing ponds (wet and
103 dry), sedimentation tanks, grassed surface water channels and constructed wetlands capture
104 sediment mitigating the flow of pollutants into water ways (Farm, 2002; Meland, 2016).
105 Although these methods initially reduce the influx of pollutants into freshwater systems, as
106 sediment levels increase with age, remediation effectiveness reduces (Farm, 2002). The
107 removal of this toxic sediment involves dredging which is prohibitively expensive (Meland,
108 2016).

109 The use of biochar is a potential remediation technique for motorway runoff, as well as for
110 mine waters and industrially polluted rivers, that could overcome the shortcomings and
111 expense of current runoff sedimentation techniques. This study sets out to explore biochar
112 and wood ash amended biochar in terms of the immobilisation of four key inorganic
113 contaminants found in motorway runoff: Pb, Cu, Zn and Cd. Engineered biochar is defined as
114 the carbon rich product obtained from the thermal decomposition of organic material under
115 oxygen limited conditions (pyrolysis) at temperatures generally under 900°C (Lehmann and
116 Joseph, 2009). The use of biochar in the immobilisation of metals in aqueous media has been
117 highlighted by a number of researchers with a view to remediate polluted waters (Bandara *et al.*,
118 2020; Cairns *et al.*, 2020). Its attractiveness is enhanced due to its relatively low cost,
119 availability and sustainability (Ahmad *et al.*, 2014; Wang *et al.*, 2018). Pristine biochar
120 immobilises inorganic contaminants via six key mechanisms: Cation exchange, change in
121 speciation with subsequent precipitation, cation- π interactions, functional group complexation,
122 electrostatic attraction, and reduction (Mohan *et al.*, 2011; Ahmad *et al.*, 2014; Bandara *et al.*,
123 2020).

124 Wood ash, a by-product of biomass power plants, can be used as an amendment to biochar
125 with the potential to improve biochar's immobilisation of inorganic contaminants due to its
126 mineral fraction and pH buffering capacity. The major components of wood ash have been
127 reported as Ca, K, Mg, S, P and Si (Cerrato *et al.*, 2016). Ca, K and Mg play an important role
128 in ion exchange. The presence of P and Si can induce the formation of phosphates, silicates
129 and siloxane which can be important in forming precipitates. The chemical constituents of
130 wood ash including alkali and alkaline earth metals, oxides and carbonates also have the
131 potential to cause the amended biochar to increase and buffer its environments pH inducing
132 changes in metal speciation that are favourable for the immobilisation of cationic metals such
133 as Pb, Cu, Zn and Cd (Cerrato *et al.*, 2016; Fidel *et al.*, 2017). Cairns *et al.* (2020) demonstrate
134 that the addition of wood ash as an amendment to pristine biochar can increase immobilisation

135 of Pb, Cu, Zn and Cd. The process was driven by pH and P content, but detailed understanding
136 of driving immobilisation mechanisms remained elusive.

137 The primary aim of this study is to ascertain if pristine larch biochar and / or wood ash amended
138 biochar is effective as an alternative green remediator of inorganic vehicular pollutants found
139 in motorway runoff specifically Pb, Cu, Zn and Cd. **Such remediation would also be relevant
140 for mine waters and industrially polluted rivers.** The effect of biochar amendments on
141 immobilisation capacities and mechanisms were investigated to understand if scaling up is
142 plausible.

143 **2. Methods:**

145 **2.1 Biochar production and wood ash amendment**

146 European larch (*Larix decidua* (L.) Karst.) wood chips were pyrolyzed in a Pyrocal BigChar-
147 1000 pyrolysis-gasification kiln at a temperature of 485-530°C, with a retention time of ~90s.
148 The biochar was granulated to <3mm with a Tria G1 granulator. Wood ash, originating from
149 a renewable energy plant in the UK, was added to the biochar post pyrolysis via two methods.
150 For the first method the wood ash was mixed at a ratio of 1:1 with biochar that had been
151 allowed to cool to ambient temperature in a cement mixer for 15 minutes. For the second
152 method, it was mixed with the freshly pyrolyzed, still hot biochar at a ratio of 1:1 for 15 minutes
153 in a cement mixer to sinter the materials. Wood ash was chosen as an amendment due to its
154 mineral fraction (including Ca, K, Mg, S, P and Si) and pH buffering capacity. The pristine larch
155 biochar, larch biochar cold mixed with wood ash and larch biochar sintered with wood ash are
156 referred to as BC, WA, and WAS throughout the study.

157 **2.2 Biochar Characterisation**

158 Sorbents were characterised via surface area and pore size analyser, Fourier transform
159 infrared spectroscopy (FTIR), x-ray powder diffraction (XRD) and scanning electron
160 microscopy with energy dispersive x-ray (SEM-EDX) analysis. FTIR was undertaken using a

161 Perkin Elmer Spectrum Two FTIR Spectrometer. Measurements are in the range of 400-4000
162 cm^{-1} to compare possible changes before and after sorbent loading. Pristine larch biochar
163 (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash
164 (WAS) were each mixed with KBr at a ratio of 1:100 (W/W) (Merino *et al.*, 2017). XRD was
165 used to identify possible crystalline precipitates formed on the surface of the sorbents. XRD
166 patterns were obtained using a Bruker D8 Discover with a Copper source (40kV, 40mA) and
167 a 1D detector. Powdered sorbents were pushed flat on a single signal silicate zero diffraction
168 plate to minimise background interference. Scans themselves had a 0.5 second time per step
169 and an increment of 0.02° over the range of 10-90 (Hasan Khan Tushar *et al.*, 2012; Li *et al.*,
170 2017). Specific surface area and pore volume distribution were determined from N_2
171 physisorption isotherms using the Brunauer–Emmett–Teller method and Barrett–Joyner–
172 Halenda method respectively. Vacuum dried samples were degassed at 105°C overnight and
173 initially measured with N_2 adsorption at the liquid nitrogen temperature of -196°C (77K) by a
174 NOVA 2000e surface area and pore size analyser (Cao and Harris, 2010). Due to the small
175 pore size of the pristine biochar, CO_2 was also used to determine pore size distribution
176 because of microporosity and kinetic limitations with N_2 physisorption (Sigmund *et al.*, 2017).
177 Surface morphologies were examined by scanning electron microscopy (Hitachi TM3000
178 desktop microscope). A working distance of 10mm and an acceleration voltage of 15kV were
179 used and images were obtained using the in-built Hitachi TM3000 software. Elemental
180 composition analysis was undertaken at the same surface locations by electron dispersive x-
181 ray spectroscopy (EDX) attached to the Hitachi TM3000 desktop microscope. An EDX
182 spectrum was produced after scanning the area of interest for ten minutes. Samples were
183 mounted to aluminium SEM stubs using conductive double-sided carbon tape to enable
184 examination of samples in an uncoated state (Eiblmeier *et al.*, 2014).

185 2.3 Sorption Experiments

186 Sorption batch experiments were carried out using Pb, Cu, Zn and Cd at five different
187 concentrations in the range of 10 mg/L to 150 mg/L applying different sorbent to solution ratio

188 to increase the range of measured sorbent loading. This range included scenarios to stress
189 the sorbents beyond what could be reasonably expected in road runoff and oversaturate them
190 (Crabtree *et al.*, 2009; Zhao *et al.*, 2010). All chemical reagents were of analytical grade and
191 the five concentrations were obtained by preparing a stock solution (1000 mg/L) of the metals,
192 using lead (II) nitrate ($\text{N}_2\text{O}_6\text{Pb}$) copper (II) nitrate hydrate ($\text{CuH}_2\text{N}_2\text{O}_7$), Zinc nitrate
193 hexahydrate ($\text{H}_{12}\text{N}_2\text{O}_{12}\text{Zn}$) and cadmium nitrate tetrahydrate ($\text{CdH}_8\text{N}_2\text{O}_{10}$) and diluting with
194 deionized water. The pH was adjusted to ~4.7 with the dropwise addition of HNO_3 to achieve
195 an equal pH between solutions that represented the closest to runoff conditions before
196 precipitation occurred for those metals. Two types of control experiments were included –
197 biochar without contaminants, as well as contaminants without biochar. All experiments were
198 performed in triplicates using a batch sorption equilibrium method (OECD, 2000)

199 All sorbents were oven dried at 105 °C for 24 h. A known amount of biochar (particle size of
200 < 3mm) was added to 25 mL of aqueous solution in 40 mL polyethylene Falcon tubes. Agitation
201 was achieved on a Unitwist 400 Orbital Shaker for 48 hrs at ~280 rpm to reach equilibrium.
202 Studies such as Uchimiya *et al.*, (2011) prescribe contact of 24 hours to reach equilibrium, but
203 longer contact times haven't shown significant changes in equilibrium concentration and
204 ensure that the adsorption phase had reached equilibrium (Wang *et al.*, 2018). The solution
205 was subsequently separated from the sorbent using an MSE Centaur 2 centrifuge at 3000 rpm
206 for 15 minutes (OECD, 2000). The supernatant was removed, pH measured using a calibrated
207 Voltcraft pH Meter and immediately acidified to < pH 2 with 1mL of 70% HNO_3 before being
208 filtered with a 0.45 μm PTFE syringe filter for analysis.

209 Pb, Cu, Zn and Cd concentrations of the acidified supernatants were measured using
210 Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES 5110, Agilent
211 Technologies Inc., USA). Sorbent loading (q) was calculated from the difference between
212 initial metal concentration and final metal concentrations in the aqueous phase:

$$213 \quad q = (C_i - C_{aq}) V / W$$

214 where c_i is the initial concentration of metals in solution, c_{aq} is the final equilibrium
215 concentration of metals in solution, V is the volume of solution and W is the weight of the
216 biochar. Equilibrium sorption coefficients (K_d) were calculated as:

$$217 \quad K_d = q/c_{aq}$$

218 where, K_d (L/kg) = amount of metal adsorbed onto biochar per L of water, q (mg/kg) = sorbent
219 loading (metals adsorbed by biochar) and C_{aq} (mg/L) = concentration in the aqueous phase.

220 K_d is commonly used in estimating the potential sorption of dissolved metals by a solid phase
221 with higher values indicating higher sorption potential (Pourret and Houben, 2018),

222 The contaminant loaded sorbents were further analysed via FTIR, XRD, SEM-EDX to detect
223 changes before and after sorption.

224 **2.4 Water chemistry and metal speciation**

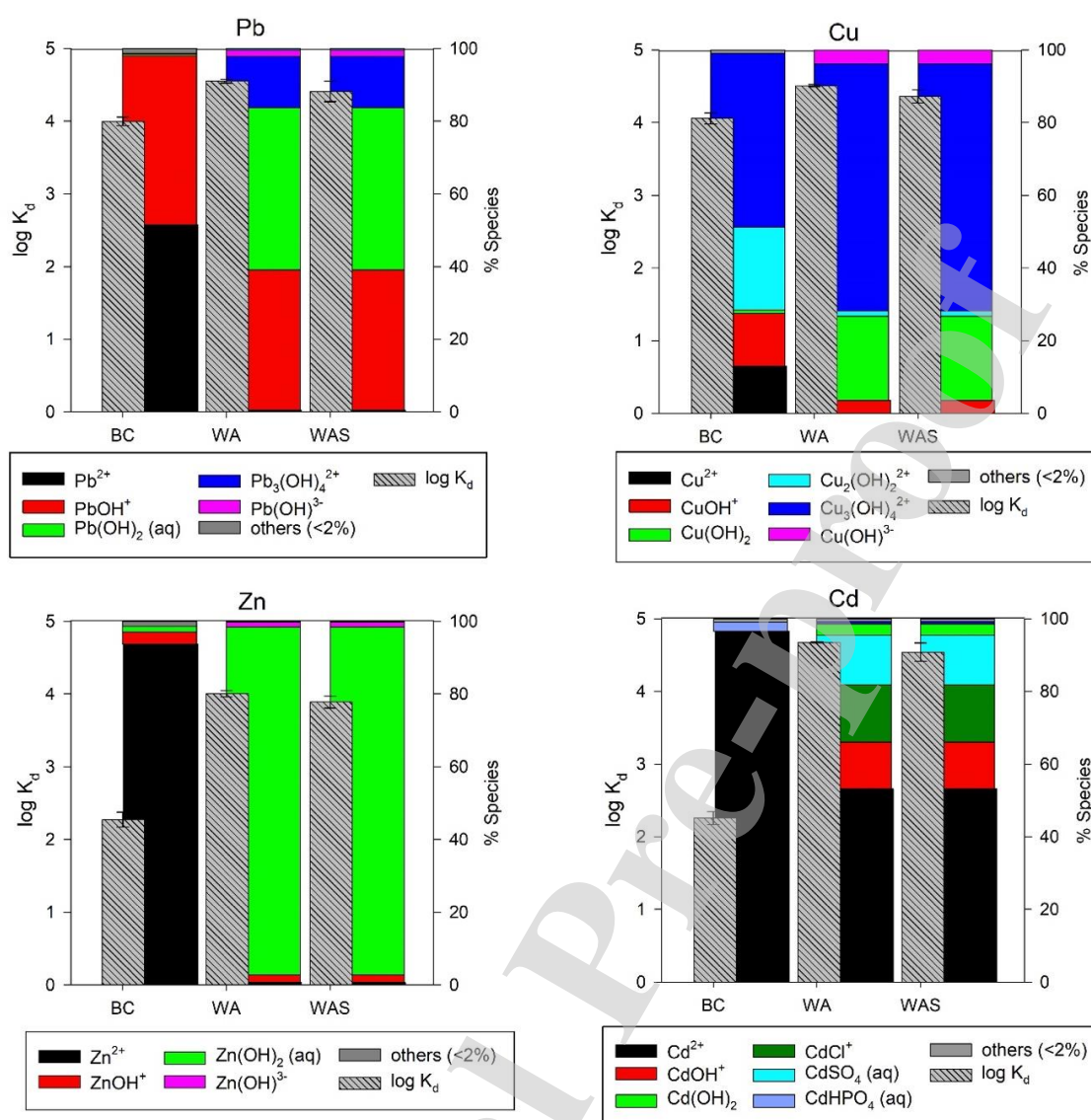
225 For speciation determination, samples with and without contaminants at a selected
226 concentration of 10 mg/L were analysed for other water chemistry parameters. These included
227 (i) base cation analysis (Ca, K, Na, and Mg) using ICP-OES, (ii) major anions (Cl^- , NO_3^{2-} , PO_4^{3-}
228 and SO_4^{2-}) using an ion exchange chromatograph (IC 930 Compact Flex, Metrohm,
229 Switzerland) and (iii) dissolved organic carbon using TOC analyser (Shimadzu, TOC-L series),
230 measuring non-purgeable organic carbon (NPOC). Speciation analysis of the solutions were
231 carried out using Visual MINTEQ version 3.1. Base cation analysis was also used to review
232 possible cation exchange. Total P and Si in the above solutions were measured via ICP-OES.
233 Together with PO_4^{3-} analysis, these parameters were used to check for their involvements in
234 the immobilization process. Speciation of C in the solid phase was measured using a
235 multiphase carbon analyzer RC-612 from LECO.

237 **3. Results and discussion**

238 **3.1 Contaminant removal by biochar and wood ash amended biochars**

239 Analysis of the aqueous phase shows that wood ash amended biochar, both cold mixed with
240 wood ash (WA) and sintered with wood ash (WAS), removed significantly more metals than
241 pristine larch biochar (BC) (SI 3A, B, C, D). Metals were removed in the order of
242 Pb>Cu>Zn>Cd by all three sorbents. The removal of Pb by BC was the lowest amongst the
243 sorbents with a maximum measured removal of 7.8 ± 0.1 mg/g (SI 5A). The maximum
244 measured removal of Pb by WA was 61.5 ± 3.1 mg/g and by WAS was 54.6 ± 3.3 mg/g (SI
245 5A). Maximum measured removal of Cu by BC was again the lowest amongst the materials
246 at 3.5 ± 0.1 mg/g (SI5 B). WA and WAS showed similar patterns and quantities of Cu removal
247 to each other, however WA showed a greater maximum measured removal at 38.9 ± 2.4 mg/g
248 with WAS at 33.8 ± 2.3 mg/g (SI5 B). The maximum measured removal of Zn by BC at $0.8 \pm$
249 0.1 mg/g was significantly lower than both WA and WAS (SI5 C). WA and WAS were very
250 similar to each other in terms of Zn removal but, again, the maximum measured removal by
251 WA was higher at 12.1 ± 0.2 mg/g than WAS at 11.2 ± 0.1 mg/g (SI5 C). Cd was the metal
252 that had the lowest measured removal by each of the materials. At 0.7 ± 0.1 mg/g the
253 maximum measured removal of Cd by BC was again significantly lower than both WA and
254 WAS (SI5 D). The removal of Cd and Zn show very similar removal behaviour in contrast with
255 Cu and Pb which both had a significantly higher maximum measured removal (SI5). WA and
256 WAS show very similar Cd removal; however, WA with a maximum measured removal of 10.2
257 ± 0.2 mg/g did outperform WAS with a maximum measured removal of 9.3 ± 0.1 mg/g (SI5 D).
258 Removal was measured within a multi metal solution where the presence of competing metal
259 ions in the solution for the same sorption sites can reduce the removal rate (Mantonanaki *et*
260 *al.*, 2016) which impacts Zn and Cd removal rates more than Pb and Cu (Xu and Zhao, 2013).

261



262

263 Figure 1: Bar graph showing the equilibrium distribution coefficients (K_d) of Pb, Cu, Zn and
 264 Cd with pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch
 265 biochar sintered with wood ash (WAS) at 10 mg/L, and stacked bars in the background
 266 showing metal aqueous species distributions. Error bars show \pm SD ($n = 3$).

267 3.2 Aqueous phase chemistry – immobilization via precipitation and ion exchange

268 Speciation plots across pH show that the distribution shifts from their divalent forms to hydroxyl
 269 forms as the pH increases (SI 1). As shown in Figure 1, the existence of these metal species
 270 in different hydroxyl forms is accompanied by increased sorption affinities (K_d values). Addition
 271 of anions such as PO_4^{3-} , Cl^- and SO_4^{2-} into solution can lead to the formation of mineral

272 precipitates. This combination of increased pH and presence of dissolved anions from wood
273 ash drives immobilization of the metals, due to oversaturation with certain mineral forms,
274 especially for Cd and Zn. Modeled saturation indices (SI 2A and 2B) indicate the possibility of
275 formation of precipitates such as $\text{Cd}_4(\text{OH})_6\text{SO}_4$, $\text{Zn}(\text{OH})_2$ and ZnO , being more prominent for
276 wood ash amended chars. Also, multiple phosphate containing phases, such as $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$,
277 $\text{Cd}_3(\text{PO}_4)_2$, $\text{Pb}_3(\text{PO}_4)_2$ are seen to be oversaturated. From MINTEQA modeling (SI 3) it was
278 determined that 99.5% and 99.9% of Pb and Cu, respectively, can be precipitated. Wood ash
279 amendments further allowed 99.4% Cd and 98.5% Zn to precipitate. Additionally, 99% and
280 73% of PO_4^{3-} can form precipitates in BC and WA/WAS systems, respectively.

281 In addition to modelling, differences in the total P, PO_4^{3-} and Si levels in the solutions with and
282 without the metals for the different materials (Figure 2) provide further evidence of
283 precipitation. For all three materials, total P in solution was significantly reduced and PO_4^{3-}
284 levels fall below the limit of quantification for all solutions with metals in contrast to solutions
285 without metals. This implies that some of the metal ions in solution are complexing with PO_4^{3-}
286 and precipitating onto the biochar surface, or co-precipitating with PO_4^{3-} . For WA and WAS,
287 Si levels were also reduced from 2.53 mg/L to 2.06 mg/L and from 2.44 mg/L to 2.01 mg/L in
288 the presence of the metals. From these results, it is implied that Si in the form of silicates on
289 the sorbent surfaces might be playing a role in the immobilization process for wood ash
290 amended biochars as seen in previous studies by Lu *et al.* (2012) and Gao *et al.* (2019).
291 Carbonate containing metal phases were not accounted and modelled for. However, C
292 speciation analysis of the solid phase using the carbon analyzer showed that WA and WAS
293 had 0.97% and 0.79% of inorganic C present, respectively. Thus, it is expected that the metals
294 can also be immobilized through formation of carbonates.

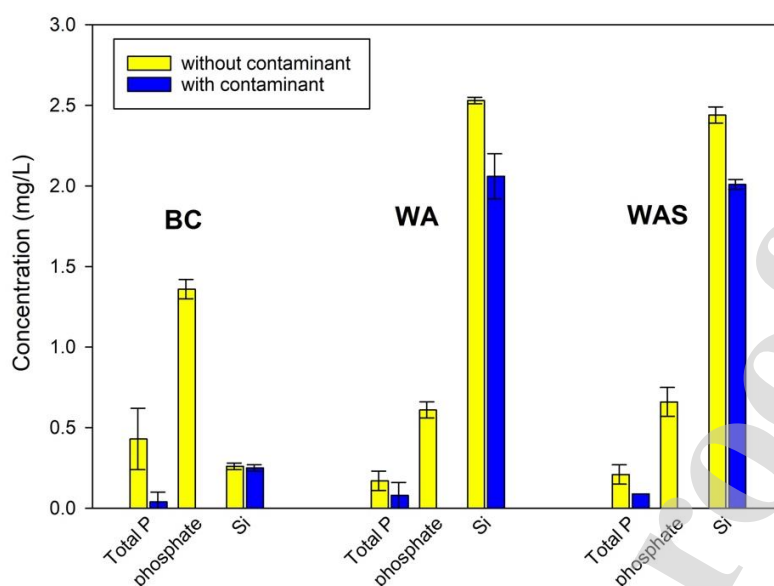
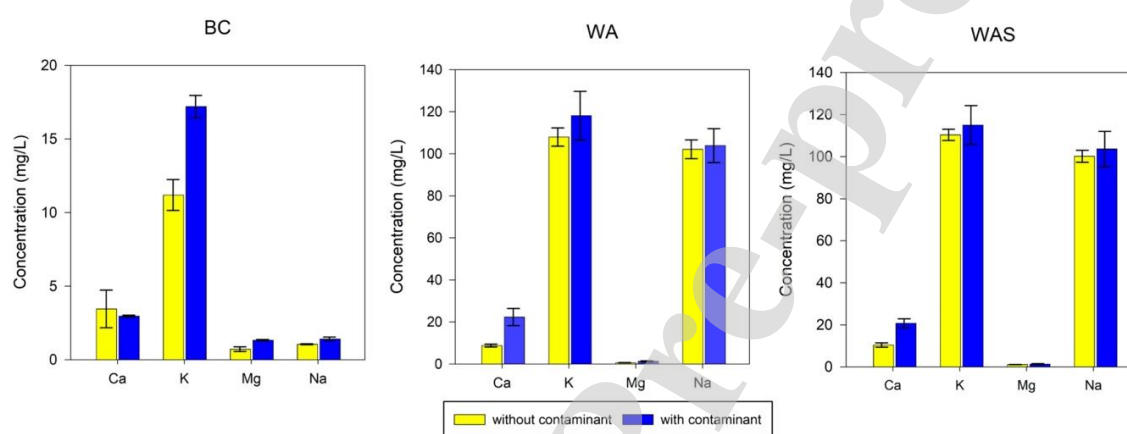


Figure 2: Concentration of Total P, phosphate (PO_4^{3-}) and Si in solution in the presence of different sorbents without and with metals ($n=3$)

All three sorbents also affect the water chemistry by adding base cations such as Ca^{2+} , Mg^{2+} , K^+ and Na^+ . Increased cation release in the presence of metals can indicate cation exchange processes occurring on the surface of biochar (Uchimiya *et al.*, 2010). If cation exchange is one of the driving mechanisms for immobilization, the target divalent metal contaminants will tend to replace divalent cations on the surface of the biochar, such as Ca^{2+} and Mg^{2+} rather than monovalent ones. For this purpose, we investigated base cations released from the sorbents, with and without 10 mg/L of metals present (Figure 3). For BC, small increases in concentration of the base cations Mg^{2+} , Na^+ and K^+ were observed from 0.72 ± 0.2 mg/L to 1.33 ± 0.1 mg/L, from 1.05 ± 0.0 mg/L to 1.41 ± 0.1 mg/L and from 11.19 ± 1.1 mg/L to 17.20 ± 0.8 mg/L, respectively. This indicates that cation exchange may be important in metal immobilisation by BC. For the wood ash amended biochars, a marked two-fold increase in Ca^{2+} concentration in the presence of metals was observed (Figure 2). For WA and WAS, Ca^{2+} increased from 8.7 ± 0.7 mg/L to 22.3 ± 4.1 mg/L and from 10.4 ± 1.0 mg/L to 20.7 ± 2.1 mg/L respectively. Increased levels of divalent Mg^{2+} were also observed for the wood ash amended chars. For WA Mg^{2+} increased from 0.63 ± 0.0 mg/L without metals to 1.23 ± 0.3 mg/L with

313 contaminants. For WAS, this was not as apparent with a concentration increase from $1.11 \pm$
 1
 2 314 0.1 mg/L to $1.32 \pm 0.2 \text{ mg/L}$. This increased release of base cations in the presence of the
 3
 4 315 metals with the wood ash treatments indicates that cation exchange plays a role in the
 5
 6 316 immobilization process. Such ion exchange is seen to be a key immobilisation mechanism for
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 8
 9 317 Pb, Cu, Zn and Cd by several studies but is secondary to precipitation (Lu *et al.*, 2012; Gao *et*
 10
 11 318 *al.*, 2019).

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320

321 Figure 3: Concentration of base cations in solution in the presence of the different sorbents
 322 without and with metals (n=3)

323 The pH of solution showed increases for each of the sorbents, with wood ash amended
 324 biochars increasing pH significantly more than BC (SI 4A). Rises in pH were greater at lower
 325 concentrations of Pb, Cu, Zn and Cd. There is strong correlation between rises in solution pH
 326 and immobilisation (SI 4B). For all of the sorbents such correlation is likely, at least in part, as
 327 a result of ion exchange increasing with pH driving the increase in negative charge of
 328 functional groups allowing alkali and alkaline earth metals to be exchanged more easily (Silber
 329 *et al.*, 2010). For wood ash amended biochars, but not for BC, the correlation of immobilisation
 330 and pH is also a result of the increase in pH driving precipitation. The pH buffering ability of
 331 the wood ash amended biochars raises the solution pH making it alkaline enough for (i) metal

332 hydroxide precipitation (SI 2A and 2B) (Chen *et al.*, 2015), and (ii) precipitation with
333 phosphates and silicates (Uchimiya *et al.*, 2010).

334 **3.3 Solid Phase Analysis - immobilisation via precipitation and ion exchange**

335 The following pre and post immobilisation solid phase analysis (FTIR, SEM-EDX, and XRD)
336 were implemented to further investigate the mechanisms of each sorbent in the immobilisation
337 of Pb, Cu, Zn and Cd alongside the measurement of surface area.

338 FTIR was used to identify functional groups to denote ion exchange, minerals capable of
339 precipitation and aromatic structures for BC, WA and WAS. WA and WAS follow very similar
340 pattern of peaks within the FTIR spectra pre-adsorption of the metal solution (Figure 4). Whilst
341 BC also shows similarities to WA and WAS in peaks above 1500 cm⁻¹ pre-adsorption, key
342 differences between wood ash amended biochar and BC are evident below 1500 cm⁻¹. Below
343 1500 cm⁻¹ peaks for both WA and WAS are seen which are attributed to phosphate (Uchimiya
344 *et al.*, 2010), siloxane (Gao *et al.*, 2019) as well as oxygenated functional groups (Iqbal *et al.*,
345 2009); phosphate and siloxane peaks, important for precipitation, are not evident in the FTIR
346 spectra of BC.

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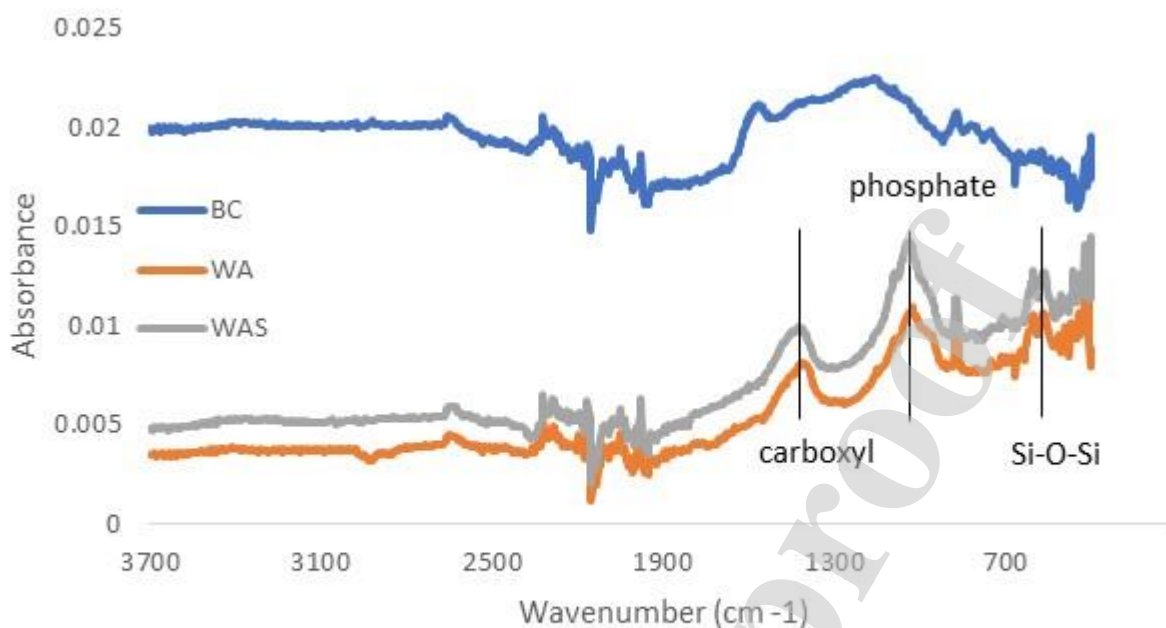


Figure 4 - FTIR spectra of pristine larch biochar (BC), larch biochar cold mixed with wood ash (WA) and larch biochar sintered with wood ash (WAS) before immobilisation of Pb, Cu, Zn and Cd.

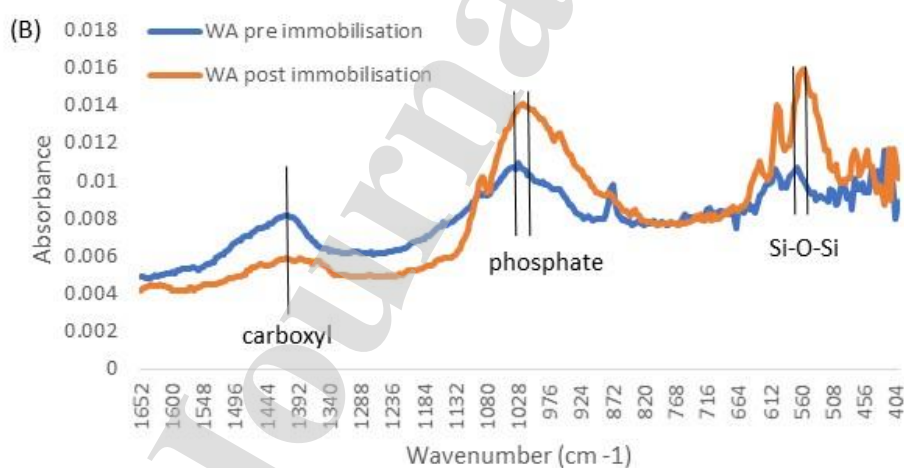
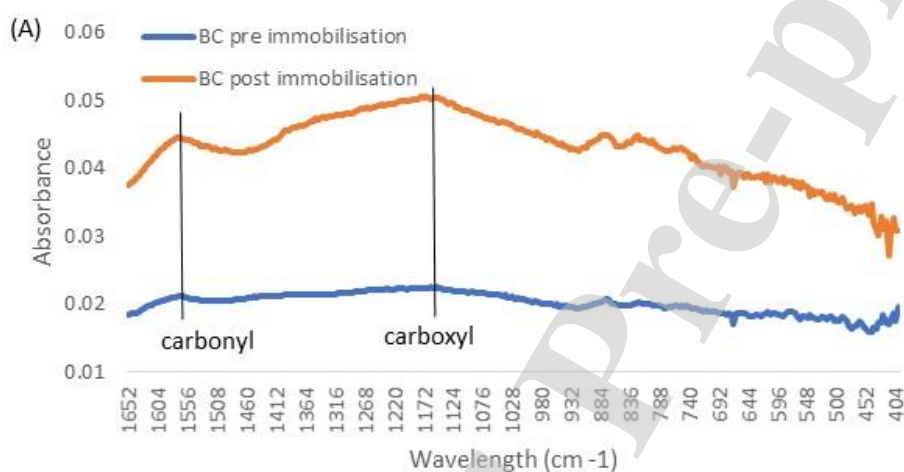
The FTIR results for BC pre and post adsorption of Cd, Cu, Pb and Zn show increases in the intensity of wavelengths attributed to carbonyl and carboxyl surface functional groups again indicating that ion exchange is taking place (Li *et al.*, 2014). However, BC's spectra show no indication of precipitation (figure 5A). The FTIR results for WA and WAS pre and post adsorption of Cd, Cu, Pb and Zn show shifts and a flattening of peaks attributed to carboxyl surface functional groups also indicating ion exchange (figures 5B and 5C). These shifts may be attributed to changes in the counterions associated with carboxylate anions (Iqbal *et al.*, 2009).

Studies have shown such shifts to demonstrate ion exchange for Pb, Cu, Zn and Cd (Iqbal *et al.*, 2009; Bandara *et al.*, 2020). Studies have also shown the ion exchange of carboxyl to be stronger for Pb and Cu than that of Cd resulting in lower levels of Cd adsorption agreeing with the sorption ordering of this study further pointing to the role of ion exchange for all of the

367 sorbents studied (Xu and Zhao, 2013). WA FTIR spectra show a shift and increase in intensity
1
2 368 for peaks assigned to both phosphate and Si-O-Si, WAS spectra also show a peak shift for
3
4 369 both phosphate and Si-O-Si. Xu *et al.* (2013) attributed similar shifts in peaks to the formation
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6 370 of metal precipitates.

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9 371 FTIR analysis indicates that ion exchange is an immobilisation mechanism for all three
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11 372 sorbents but only demonstrates precipitation with phosphate and Si-O-Si for wood ash
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13 373 amended biochars. This difference is likely to partially account for the difference in removal
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15 374 between BC and wood ash amended biochars.

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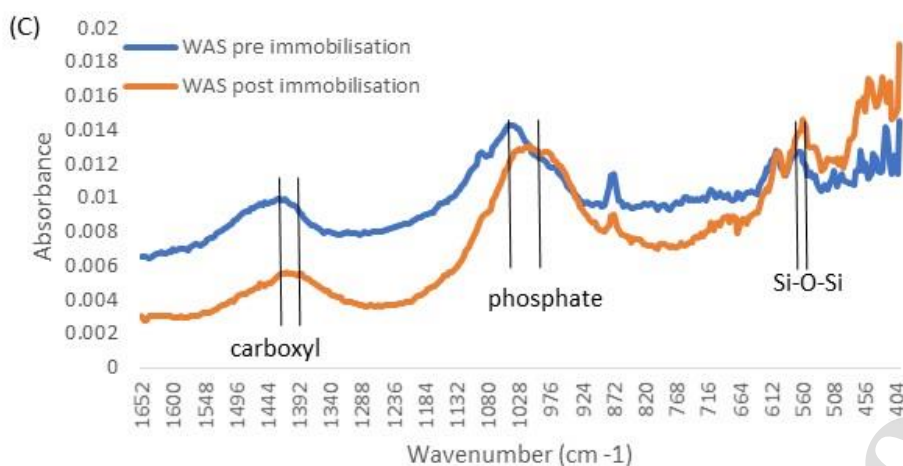


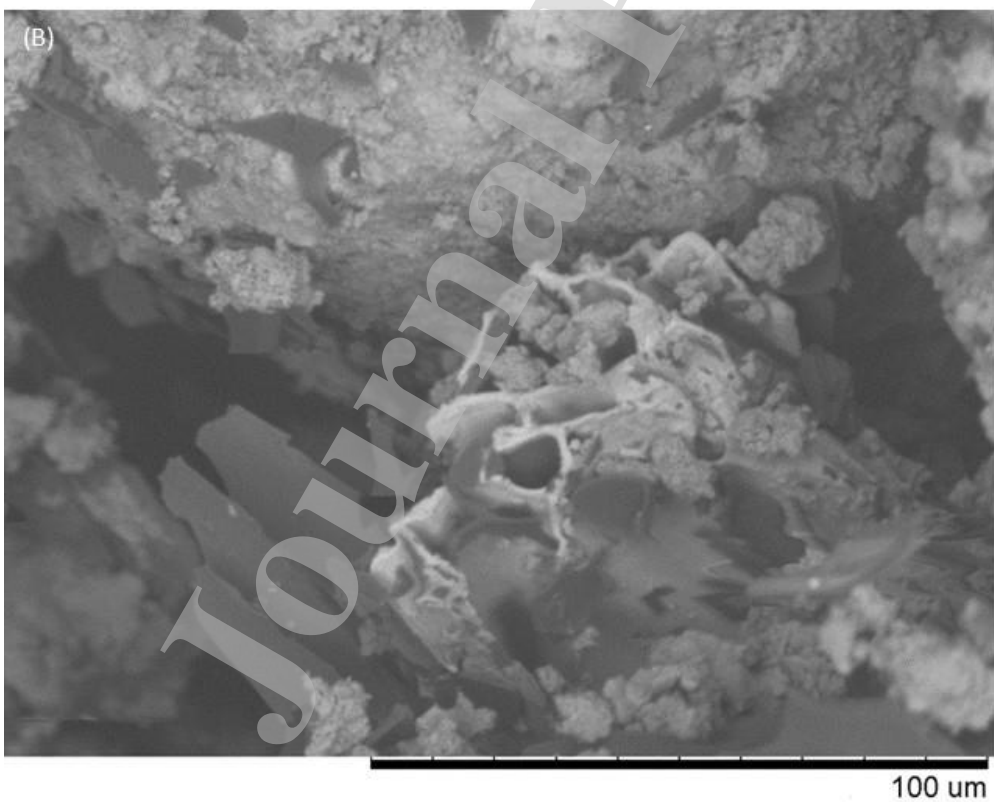
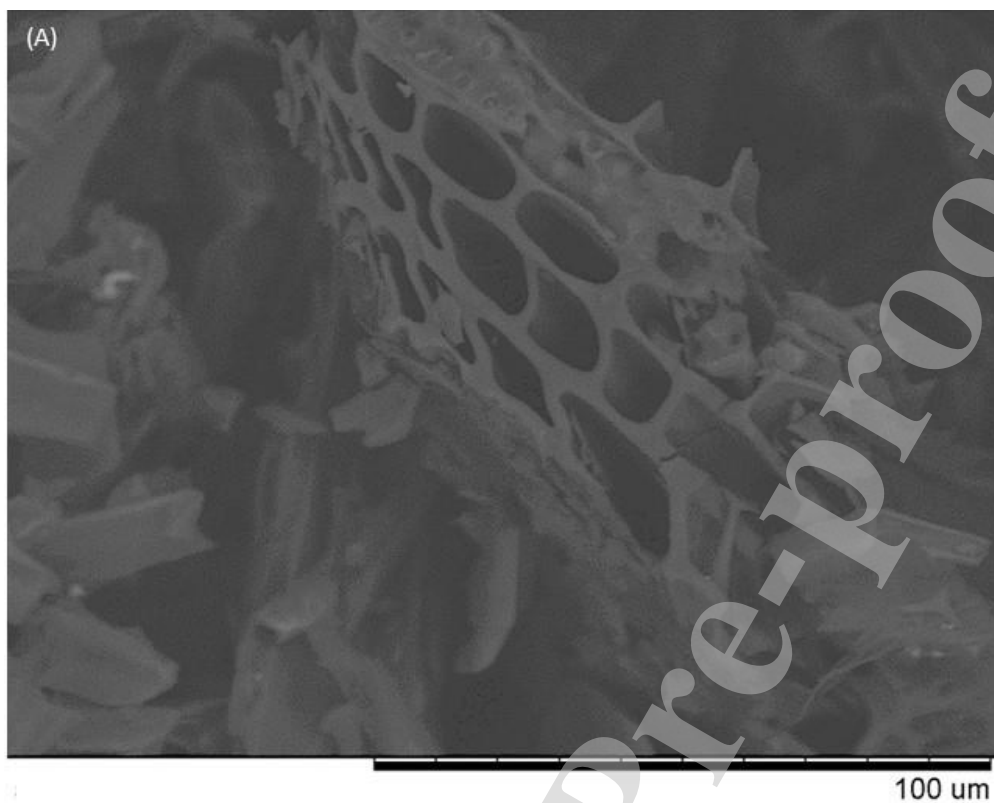
Figure 5: (A) FTIR spectra of larch biochar (BC) pre and post immobilisation of Pb, Cu, Zn and Cd (B) FTIR spectra of larch biochar cold mixed with wood ash (WA) pre and post immobilisation of Pb, Cu, Zn and Cd (C) FTIR spectra of larch biochar sintered with wood ash (WAS) pre and post immobilisation of Pb, Cu, Zn and Cd

SEM-EDX analysis was used to observe the morphology and structure of the sorbents and to ascertain the elemental composition and distribution including the presence of immobilised Pb, Cu, Zn and Cd. For BC SEM-EDX did not show signs of precipitation such as high levels of P or Si or bright areas on the surface of the char. In contrast, SEM images of WAS post adsorption did show bright areas on the surface of the char (SI 7A) which are Pb rich phases (Lu *et al.*, 2012). The EDX spectrum associated with this SEM image demonstrates the presence of P, O, Cl and C alongside Pb, Cu and Zn (SI 8A). SEM images of WA post adsorption also showed the bright areas associated with Pb alongside high levels of P, O, Si, C, Cl, Cu and Zn seen in the corresponding EDX spectra (SI 7B and SI 8B). Again, Cd was not present in this zone. In addition to the elemental results of EDX, XRD analysis indicated the presence of carbonates, siloxane and phosphates in both WA and WAS (SI 9). Where metals are seen in the presence of high levels of minerals such as P or Si precipitation between these metals and minerals should be expected (Trakal *et al.*, 2014) and as such

396 precipitation should again be considered a mechanism in the immobilisation of metals by wood
1
2 397 ash amended biochars, a mechanism not evidenced for BC. SEM images of BC post
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4 398 adsorption did not show large bright areas or crystalline structures which would indicate
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6 399 precipitation (SI7 C). EDX elemental data showed that Cu, Zn and Cd were not detected at all
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8
9 400 and that Pb is present in this zone but in small quantities when compared to wood ash
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11 401 amended biochars (0.51%) (SI 8 A, B, C). P, Cl and Si were all undetected, but K was
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13 402 evidenced in this zone again indicating the potential for ion exchange (SI8 C). There is also
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15 403 no evidence of carbonates, siloxane or phosphates for BC within the XRD analysis making
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17 404 precipitation unlikely as an important mechanism.

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21 405 The dominant mechanism for Pb, Cu, Zn and Cd removal by wood amended biochars is
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23 406 precipitation with ion exchange also playing a role. However, these mechanisms do not
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25 407 correlate to surface area. Although BC had the lowest measured removal of each contaminant
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27 408 its surface area (409 m²/g) is significantly higher than the surface area of WA (34.5 m²/g) or
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29 409 WAS (26.5 m²/g). Pore size distribution for WA and WAS follow similar patterns to each other
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31 410 both with a high concentration of pores with 41 Å diameter (SI 10A and B). BC however shows
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33 411 a high concentration of smaller pores with 31 Å diameter (SI 10C). SEM-EDX images show
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35 412 BC to have an unblocked honeycomb structure with 98% C (figure 6A). Although WA has a
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37 413 similar structure the pores are blocked with only 29% C due to the presence of other elements
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39 414 such as P, Si, K and Na (Figure 6B). Despite the addition of the wood ash being seen to
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41 415 reduce surface area by more than an order of magnitude this does not impact negatively on
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43 416 immobilisation. The wood ash amendment and resultant pH, mineral and functional group
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45 417 increases have proven to be more important than surface area. WA and WAS pores are
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47 418 blocked by the minerals added with the wood ash, such pore blocking has been seen by Hu
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49 419 *et al.*, (2015) in their study of iron impregnated biochar whereby the iron clogged pore
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51 420 openings on the biochar surface whilst increasing metal removal from solution. Although
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53 421 surface area is often seen as an important physical property for contaminant sorption,
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55 422 comparative studies have shown that when surface area of a char is lower but immobilisation
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423 is higher, as seen in this study, chemical processes such as ion exchange or more importantly
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2 424 precipitation supersede the importance of surface area (Wang et al., 2018).
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426 Figure 6 – (A) SEM image of the honeycomb structure of the pristine larch biochar (BC) (B)
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2 427 SEM image of the honeycomb structure of the larch biochar cold mixed with wood ash (WA)
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4 428 which is blocked with P, Si, K and Na.
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10 430 **4. Conclusion**

13 431 This study investigated if pristine larch biochar (BC) or wood ash amended biochar was
14 432 effective as an alternative and green remediator of the inorganic vehicular pollutants Pb, Cu,
15 433 Zn and Cd found in motorway runoff, **mine waters and industrially polluted rivers**. It also set
16 434 out to investigate why BC, larch biochar cold mixed with wood ash (WA) and larch biochar
17 435 sintered with wood ash (WAS) immobilised these contaminants and understand differences
18 436 between wood ash amended biochar and BC in terms of contaminant removal and
19 437 immobilisation mechanisms. Maximum measured removal of Pb, Cu, Zn and Cd by WA and
20 438 WAS were significantly higher than BC alone. This difference was the result of the wood ash
21 439 amendment increasing pH, thus shifting metal species, and increasing the presence of
22 440 minerals such as PO_4^{3-} causing immobilization of the metals through precipitation. The
23 441 proportion of hydroxides modelled for BC is far less than for wood ash amended biochars
24 442 likely resulting in precipitation accounting for less immobilisation of the contaminants. Although
25 443 precipitation with phosphate and silicates, was found to be an immobilisation mechanism for
26 444 WA and WAS, precipitation with silicates was not observed for BC further highlighting
27 445 differences in removal between wood ash amended biochars and BC. Ion exchange
28 446 contributed to the immobilisation of the contaminants for all three sorbents. Surface area was
29 447 not seen to be a dominant factor for metal removal with precipitation and ion exchange
30 448 superseding its importance.
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44 449 Sustainability of feedstock, maximum measured removal (61.5 mg/g, 38.9 mg/g, 12.1 mg/g
45 450 and 10.2 mg/g for Pb, Cu, Zn and Cd respectively) and low feedstock / production costs
46 451 indicate that wood ash amended biochar is a viable option to immobilise Pb, Cu, Zn and Cd
47 452 from motorway runoff.
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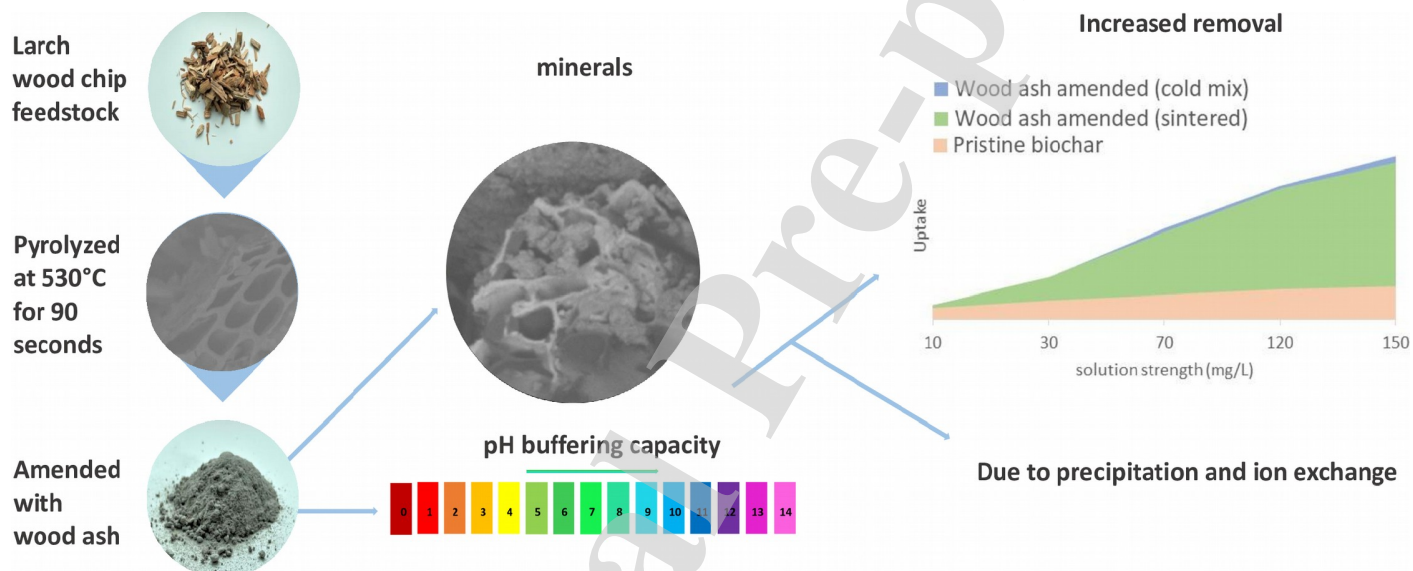
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1 Highlights

- 2 • The addition of wood ash to biochar increased metal removal by an order of
- 3 magnitude
- 4 • Immobilisation is correlated to pH
- 5 • Increased pH and the presence of minerals drive precipitation
- 6 • Precipitation and ion exchange dominate immobilization
- 7 • Wood ash amended biochar could remove heavy metals from motorway runoff



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1Declaration of competing interest

2The authors declare that they have no known competing financial interests or personal
3relationships that could have appeared to influence the work reported in this paper.

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