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1 Optimising the recovery and re-use of phosphorus from wastewater effluent for
2 sustainable fertiliser development

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11

12 **Abstract**

13 Recovery and re-use of phosphorus (P) from wastewater treatment systems as
14 agricultural fertiliser presents an important and viable target for P waste reduction and
15 recycling. In this study novel biochar materials for P filtration of wastewater were
16 designed and produced using waste feedstocks, with consideration of the plant
17 accessibility of the P captured by the biochars. The biochars were produced using batch
18 slow pyrolysis at 450°C and 550°C from a) AD: anaerobically digested sewage sludge
19 and b) OCAD: a 1:1 mixture of anaerobically digested sewage sludge and ochre, a
20 mineral product from mine drainage treatment. A set of experiments were designed
21 using pH buffering to provide a robust framework for assessing the P recovery capacity

22 and affinity of the biochars compared to other potential P recovery materials
23 (unprocessed ochre, activated carbon and zeolite). After 5 days of repeated exposure to
24 a P solution at a wastewater-relevant concentration (0.02 g P l^{-1}) replenished each 24
25 hours, relatively high masses of P were recovered by ochre ($1.73 \pm 8.93 \times 10^{-3} \text{ mg P g}^{-1}$)
26 and the biochars OCAD550 ($1.26 \pm 4.66 \times 10^{-3} \text{ mg P g}^{-1}$), OCAD450 ($1.24 \pm 2.10 \times 10^{-3}$
27 mg P g^{-1}), AD450 ($1.06 \pm 3.84 \times 10^{-3} \text{ mg P g}^{-1}$), and AD550 ($0.986 \pm 9.31 \times 10^{-3} \text{ mg P g}^{-1}$).
28 The biochar materials had higher removal rates than both activated carbon
29 ($0.884 \pm 1.69 \times 10^{-2} \text{ mg P g}^{-1}$) and zeolite ($0.130 \pm 1.05 \times 10^{-2} \text{ mg P g}^{-1}$). To assess the
30 extractability of recovered P, P exposure was followed by repeated extraction for 4 days
31 with pH 7-buffered deionised water. The AD biochars retained 55% of the P recovered,
32 OCAD biochars 78% and ochre 100%. Assessment of potentially toxic element
33 concentrations in the biochars against guideline values indicated low risk associated
34 with their use in the environment. Our successful demonstration of biochar materials
35 highlights the potential for further development of P filters for wastewater treatment
36 systems from anaerobic digestate produced and pyrolysed on-site with energy recovery.

37

38 **Keywords**

39 Phosphate adsorption, Phosphorus recovery, biochar, P recycling, wastewater, pH
40 buffering

41 **1. Introduction**

42 As a limiting factor for plant growth, the current food production system relies on
43 constant inputs of phosphorus (P) into soils to satisfy the growing demand of the human
44 population. Phosphate rock, the dominant source of P for phosphate fertilisers, is a
45 limited resource, with current world reserves estimated to last between 30 to 300 years
46 (Cordell and Neset, 2014; Reijnders, 2014). In contrast, eutrophication caused by the
47 discharge of excess P from wastewater and agricultural runoff into aquatic systems is a
48 global environmental problem (Dodds et al., 2009; Steffen et al., 2015). Worldwide
49 17.5 Mt a⁻¹ P is harvested from rock reserves and 9.5 Mt a⁻¹ released into inland and
50 coastal waters (Cordell et al., 2009). Human society currently perpetuates a P paradox
51 where both a problematic scarcity and a detrimental profusion of P exists in different
52 parts of the same system. P wastage occurs in almost all stages of the current food
53 system and there is therefore great potential to address this paradox (Cordell and White,
54 2013; Shepherd et al., 2015).

55 Recovery and redistribution of P from wastewater to agricultural land is one mechanism
56 for reconciling P wastage and scarcity. During wastewater treatment the majority of P is
57 precipitated into the solid sludge fraction using iron salts. Transfer of treated sludge to
58 agricultural land is already an important method of sludge disposal within the UK as
59 well as Cyprus, Denmark, France, Ireland, Luxemburg, Portugal and Spain (SEPA,
60 2015). Managed under the EU Sewage Sludge Directive (86/278/EEC), the UK Sludge
61 Use in Agriculture Regulations 1989 and Safe Sludge Matrix, 75% of treated sludge in
62 England and Wales is transferred in this way (Defra, 2011). In 2008 approximately two
63 thirds of the 1.6 Mt of sewage sludge produced in the UK was also treated by anaerobic
64 digestion before use (Defra, 2011). Anaerobic digestion reduces the pathogen load of

65 sewage sludge and produces methane, but does not address acceptability issues relating
66 to odour. Distribution of wet digestate is also expensive but drying followed by
67 granulation or pelletising is energy intensive. Another alternative for sludge treatment is
68 incineration, which reduces bulk, removes odours and yields P-rich ash from which P
69 can be recovered. Various processes for the extraction of P from incineration ash have
70 been developed (Donatello and Cheeseman, 2013) and the utility of the fertiliser
71 products demonstrated (Franz, 2008). However incineration converts nitrogen (N) and
72 carbon (C) to the gaseous phase, losing their potential value in agricultural re-use.
73 Whilst there are many sludge treatment methods in use which allow for the recycling of
74 P, few of the products of sludge treatment are truly optimised for agriculture.

75 Pyrolysis is an alternative thermal treatment technology in which a proportion of C is
76 conserved in solid phase as well as P and some N, depending on the highest treatment
77 temperature (HTT) (Xie et al., 2015). The term biochar has been adopted to describe the
78 solid product of pyrolysis, especially if it is designed for use in soil. Pyrolysis of
79 anaerobically digested sewage sludge has a better energy balance than its non-digested
80 counterpart (Cao and Pawłowski, 2012), possibly because methanogenesis does not
81 involve fractions that are volatile at pyrolysis temperatures. Sludge pyrolysis is
82 environmentally and economically viable for energy production and solid waste
83 treatment in the wastewater treatment industry (Mills et al., 2014). Productive uses of
84 biochar improve the economic case for this mode of sludge management, however
85 environmental regulators require evidence that addition of biochar from sludge
86 pyrolysis will not cause contamination of soils by potentially toxic elements (PTEs) that
87 they may contain.

88 In the near future the permissible concentrations of P in discharge from wastewater
89 treatment will decrease in the EU under the Water Framework Directive, from 1–
90 2 mg P l⁻¹ to 0.1 mg P l⁻¹. This may necessitate the use of tertiary treatment specifically
91 to meet these requirements. To date, various materials have been suggested for
92 removing P from wastewater effluent: ochre, zeolite, Polonite, opoka, blast furnace
93 slags and Filtra P, amongst others (Cucarella et al., 2008; Dobbie et al., 2005, 2009;
94 Heal et al., 2005). Ochre is produced during the treatment of metal-rich water from
95 flooded coal and metal mines. Each year around 50,000 t of ochre are produced from
96 UK coal minewater treatment plants (MWTPs) with no specific recycling option
97 (Johnston et al., 2008). Ochre from a variety of MWTPs and other sources has been
98 used previously to remove phosphate from wastewater in batch, column and field-scale
99 experiments (Adler and Sibrell, 2003; Fenton et al., 2009, 2012; Heal et al., 2005; Na
100 and Park, 2004; Sibrell and Tucker, 2012; Sibrell et al., 2009). However the properties
101 of each ochre are specific to the mine geochemistry, treatment processes and design at
102 the respective MWTP and thus not all are ideally suited for use in a flow-through
103 filtration system. Screening of ochre prior to use is required as leaching of toxic metals
104 from ochre from particular mine sources has been reported (Fenton et al., 2009, 2012).
105 Low hydraulic conductivity is an important current barrier to widespread use of ochre
106 for P filtration in wastewater treatment plants (WWTPs) (Heal et al., 2003, 2005). To
107 improve the hydraulic properties of ochre in P filtration systems, pelletised ochre-
108 composites bound using cement have been developed (Dobbie et al., 2009; Sibrell,
109 2007), but the use of cement is not consistent with the development of an energy and
110 resource-efficient system. The system would be improved if a successful alternative
111 binder and binding system were to be identified.

112 Purposeful precipitation of struvite (magnesium ammonium phosphate) is performed at
113 some treatment facilities to simultaneously manage both P and N, but some P remains in
114 the solid waste stream, requiring additional treatment. Despite encouraging results in
115 both P extraction and plant growth studies for products of P recovery systems,
116 traditional P management systems remain the most commonly utilised in the wastewater
117 and agricultural industries. Regulatory and industrial attitudes towards P have
118 nonetheless shifted and so technological innovations are focussing on treating P as an
119 increasingly scarce resource rather than an environmental pollutant (EC, 2013).

120 Biochars produced from anaerobically digested materials have been shown to recover P
121 from aqueous media in laboratory (Yao et al., 2011) and field (Streubel et al., 2012)
122 experiments. More recently, enhancement of biochar P recovery properties has been
123 achieved by chemical pre-treatment of feedstocks (Liu et al., 2015; Zhang et al., 2013,
124 2012) and post-treatment of biochar (Park et al., 2015; Ren et al., 2015). However, a
125 challenge in the assessment of biochars for P recycling is to make useful comparisons
126 with existing materials. Methods for characterising biochar have often been based on
127 existing soil science methods, perhaps since biochar is intended for addition to soil. Due
128 to several features of biochar, such as its hydrophobicity and the recalcitrance of the
129 carbon structure to chemical and biological breakdown, these methods may not provide
130 the intended information. The relative infancy of the topic means that new assessment
131 methods are under development and there is much scope for their testing and
132 improvement to better predict the potential of biochar for P recycling.

133 The overall aim of our research is to design and test novel materials for capture of P
134 from wastewater that are environmentally sustainable and economically viable. It is
135 desirable that the P captured can be subsequently recycled P to the soil as a fertiliser,

136 rather than becoming a waste product of the process. Our objective in the present study
137 was to develop a robust methodological framework to compare biochar P filters made
138 using materials already generated in wastewater treatment to other established materials
139 for P filtration, namely ochre, activated carbon and zeolite. Anaerobically digested (AD)
140 sewage sludge was selected to act as an alternative to cement as a binder for ochre to
141 produce a combined feedstock (OCAD) for pyrolysis. In addition to providing
142 additional nutrients to the ochre, it was hypothesised that the AD component in OCAD
143 feedstock would also exhibit P recovery characteristics. Both AD and OCAD feedstocks
144 were therefore assessed to determine whether P recovery in the composite OCAD
145 biochar materials would be due to each component or ochre alone. To test and rank the
146 diverse materials considered in our work, the design of novel batch recovery
147 experiments that considered the distinctive chemistry of biochar was required.
148 Specifically, methods for buffering solution pH were investigated due to the high
149 variability of P capture with changing pH. We allowed for P release as well as recovery,
150 so that our results would be relevant to both P recovery from wastewater and its
151 subsequent release into soil. We also tested for inherent nutrients and PTEs in the
152 materials and compared these against current biochar contaminant guidelines to assess
153 whether the use of these biochars posed any risk to the environment.

154 **2. Materials and Methods**

155 **2.1 Material selection and processing**

156 The ochre used in this study was selected for characteristics representative of coal mine
157 water treatment ochre, with typically low concentrations of PTEs but low hydraulic
158 conductivity. Ochre was collected from the Coal Authority Minto mine water treatment

159 scheme in Fife, Scotland. Anaerobically digested sewage sludge (AD) was collected
160 from the Newbridge WWTP, Edinburgh, Scotland. The AD feedstock (20% dry solids)
161 was prepared by first making a slurry from the untreated digestate cake and deionised
162 (DI) water, followed by shaking on an orbital platform shaker at 150 rpm overnight, and
163 then drying and sterilising by heating in an oven at 80°C for 12 h, 180°C for 2.5 h and
164 finally 80°C for a further 48 h. A mixed AD and ochre feedstock (OCAD) was
165 produced by making a slurry from the untreated digestate cake with the addition of air-
166 dried ochre (1:1 ratio, dry weight basis) in DI water, shaking to homogenise the sewage
167 solids and ochre, followed by drying and sterilising as above. In order to compare the
168 results of these experiments with experiments in the future, a commonly available
169 activated carbon produced from peat was sourced from Sigma Aldrich (St Louis,
170 Missouri, USA) to run as a standard. It was selected based on its easy acquisition and
171 the fact that it is structurally and chemically similar to biochar. A natural zeolite from
172 RS Minerals (Guisborough, UK) was also selected for comparison in these experiments
173 as zeolites, although cation exchangers like biochar, have also shown P filtration
174 properties (Agrawal et al., 2011; Sakadevan and Bavor, 1998).

175 Pyrolysis was undertaken at the UK Biochar Research Centre (University of Edinburgh,
176 UK) using the small-scale batch pyrolysis unit described in Crombie et al. (2013). The
177 surface chemistry of biochar is expected to be of primary importance to its phosphate
178 binding capacity. Electron donor groups are unlikely to interact directly with phosphate,
179 so adsorption and retention will likely take place via a metal-mediated mechanism. The
180 highest treatment temperature (HTT) is one of the most important pyrolysis parameters
181 for controlling chemical and physical properties of the resulting biochar. Structural
182 complexity, in both chemical and macro-physical terms, decreases with increasing HTT

183 (Brown et al., 2006; Downie et al., 2009; Lua et al., 2004), therefore two relatively low
184 HTTs were selected to increase the number of potential reactive sites in the biochar.
185 Samples of both feedstock types were heated at a rate of 25°C min⁻¹ to a HTT of 450°C
186 or 550°C, held for 30 min. The resulting biochars (AD450, AD550, OCAD450 and
187 OCAD550) were each left in the reactor with N₂ flow overnight to cool before being
188 transferred into a N₂-purged container. OCAD biochars were cooled to 4°C before air
189 was allowed to slowly diffuse into the container to prevent spontaneous combustion due
190 to rapid re-oxidation of reduced elements within the material.

191 **2.2 Characterisation of materials**

192 **2.2.1 Nutrients and potentially toxic elements (PTEs)**

193 The materials were digested and analysed by ICP-OES to determine the concentrations
194 of nutrients (Ca, K, Mg, Mn, P, S) and PTEs (Al, As, B, Cd, Co, Cr, Cu, Fe, Mo, Na,
195 Ni, Pb, Zn). All materials (biochars and biochar feedstocks) and blanks were prepared in
196 triplicate for analysis using the method described by Buss et al. (2016), which is based
197 on the modified dry ashing procedure proposed by Enders and Lehmann (2012) and
198 prescribed by IBI (2012). The purpose of the modifications was to improve element
199 detection by decreasing the dilution of samples during the digestion process. Due to the
200 high concentration of Fe in the biochars and ochre prepared for this study HCl was used
201 instead of H₂O₂.

202 Elemental quantification was performed on digests by ICP-OES, using a Perkin Elmer
203 Optima 5300DV instrument (Waltham, USA). The majority of elements were analysed
204 in axial mode, with the exception of Al, Ca, Fe, K, Mg and Na, which were present in
205 sufficient concentrations to necessitate the use of radial mode. Standards were prepared

206 and run during each analysis session for calibration and to check the accuracy of
207 measurements. The limit of detection of the instrument was determined as described in
208 Buss et al. (2016).

209 **2.2.2 pH and electrical conductivity (EC)**

210 The pH and EC of the materials were determined in DI water in duplicate using the
211 method recommended by the IBI (Rajkovich et al., 2012).

212 **2.3 Batch adsorption experiments**

213 As is standard for the investigation of material adsorption properties, a laboratory batch
214 adsorption experiment was conducted and both the Langmuir and Freundlich isotherms
215 fitted to the results.

216 The Langmuir equation describes single-layer adsorption and can be expressed as:

$$217 \quad S = \frac{S_{max}KC}{1 + KC}$$

218 Where S is the concentration of solute adsorbed by the material (mg g^{-1}), S_{max} is the
219 calculated maximum adsorption capacity of the material (mg g^{-1}), K is the Langmuir
220 coefficient, which refers to binding strength (higher K indicates stronger binding) and C
221 is the concentration of the solute remaining in solution at equilibrium (mg l^{-1}).

222 The Freundlich equation allows for multi-layer adsorption and can be expressed as:

$$223 \quad S = K_f C^n$$

224 Where S and C are the same as for the Langmuir equation, K_f is the Freundlich
225 coefficient which indicates relative adsorption capacity (but not specifically a maximum

226 adsorption capacity), and n is the Freundlich exponent which is a constant describing
227 heterogeneity of the material (Cucarella and Renman, 2006). The reciprocal of the
228 Freundlich exponent is also used in the literature to describe the adsorption affinity,
229 with higher values indicating higher affinity (Castaldi et al., 2014; Holford, 1982).
230 Therefore a lower n value also indicates a higher affinity for the solute.

231 While the pH in P batch adsorption experiments is usually adjusted manually to 7 using
232 acid or base at the beginning of the experiment, it is typical for phosphate adsorption
233 isotherms to be determined for biochar without the use of buffering or even without any
234 pH adjustment at the start of the experiment (Chen et al., 2011; Liu et al., 2015; Park et
235 al., 2015; Ren et al., 2015; Yao et al., 2012, 2011; Zhang and Zhang, 2013; Zhang et al.,
236 2013), even though P adsorption is generally highly dependent on pH (Antelo et al.,
237 2005; Kanematsu et al., 2011; Kumar et al., 2010). The pH of biochar measured using a
238 DI water–biochar mixture is typically between 6 and 11. When added to soil, biochar
239 tends to have a liming effect, raising soil pH over a period of time (Beesley et al., 2011;
240 Biederman and Harpole, 2013). This is, however, dependent on the initial soil pH and
241 associated buffering capacity as well as the biochar type. Hence, if relevant comparisons
242 are to be made between biochars and with other materials, the pH of batch experiments
243 should be controlled for the duration of the experiment. The effect of materials in
244 different soils can then be inferred separately, using information on specific soil
245 properties. Although most buffers may interfere with reaction conditions, some (known
246 as ‘Better Buffers’) have been developed for use in biological systems where buffer
247 interactions with cations are undesirable (Kandegedara and Rorabacher, 1999; Yu et al.,
248 1997). They are a set of tertiary amines with nitrogen substituents which are at least 2
249 carbon atoms in length, meaning they lack donor atoms on the α , β and γ carbons with

250 which a metal cation could react to form a closed ring structure with the nitrogen atom
251 (Yu et al., 1997). Within this group of compounds, MES (2-(N-
252 morpholino)ethanesulfonic acid) and MOPS (3-(N-morpholino)propanesulfonic acid)
253 have been found to have no effect on P adsorption (Mao et al., 2012). MOPS was tested
254 in our experimental system at increasing concentrations (see Supplementary
255 Information) and as in the literature, no interference was observed. Therefore phosphate
256 solutions of concentrations ranging from 0–800 mg P l⁻¹ were prepared for the batch
257 experiments using DI water buffered to pH 7 with 10 mM MOPS/NaNO₃ and K₂HPO₄.
258 The median particle size of the Minto ochre is 0.02-0.06 mm (Heal et al., 2003), which
259 is smaller than that of the other materials tested, however it does form natural
260 aggregates. Therefore it was prepared by breaking up the aggregates in a pestle and
261 mortar and removing manually any visible organic matter. Rather than matching the
262 primary particle size of ochre for all materials, the biochar (AD450, AD550, OCAD450,
263 OCAD550), activated carbon and zeolite samples were passed through a sieve to obtain
264 a 0.5–1.0 mm size fraction, since crushing of the OCAD materials may have separated
265 the ochre and AD components spatially and prevented direct interaction between
266 fractions relevant to P adsorption. Due to the highly hygroscopic nature of the biochars,
267 their moisture content at room temperature was determined by weighing, drying at
268 105°C overnight and re-weighing a subsample of each material immediately after
269 cooling in a desiccator. The calculated water content was accounted for in subsequent
270 calculations. Aliquots of MOPS buffered P solution (36 ml, prepared as outlined above)
271 were added to 0.100 g of each material in 50 ml centrifuge tubes. The tubes were laid on
272 their side and shaken on an orbital platform shaker at 150 rpm for 24 h. The samples
273 were centrifuged at 3500 rpm for 30 min and the supernatant filtered using 0.45 µm

274 syringe filters (Millipore, Watford, UK). All filtrates were refrigerated at 4°C before
275 analysis for soluble reactive P (SRP) by automated colorimetry (Auto Analyser III, Bran
276 & Luebbe, Norderstedt, Germany). Each adsorption experiment was performed with
277 four replicates and a set of blank samples, with results reported as means of the blanks
278 subtracted from the means of the treatment results ± 1 S.D. All experiments were
279 conducted at room temperature (21°C).

280 **2.4 Repeat exposure experiments**

281 To rank the materials, an experiment was designed to provide repeated exposure to P at
282 three different concentrations. The lowest P concentration used in the experiment
283 described in section 2.3 (0.02 g P l⁻¹) was selected to simulate the typical maximum P
284 concentration of tertiary wastewater effluent. Higher concentrations (0.8 and 3 g P l⁻¹)
285 were selected to probe the maximum P recovery rate. The experiments were designed
286 with repeated removal and replenishment of the P solution, rather than a flow-through
287 column system (which would more accurately simulate a wastewater treatment system),
288 as the objective was to design a simple screening method that could be adopted using
289 readily available equipment.

290 After the addition of the appropriate MOPS-buffered P solution in a 1:20 solid to liquid
291 ratio (m/v) in 50 ml centrifuge tubes, the samples were laid on their side and shaken on
292 an orbital platform shaker at 150 rpm for 20 h, stood for 4 h and then centrifuged at
293 3500 rpm for 30 min, filtered and analysed for P as described in 2.3. A fresh P solution
294 was added in the same solid to liquid ratio and the process repeated until the samples
295 had been exposed for 5 days. P recovery was determined by calculating the difference in
296 SRP concentration in the blank control samples and each treatment collected after 24 h

297 for each of the 5 days. Data were analysed using the Shapiro-Wilk test for normality,
298 followed by one-way ANOVA and Tukey HSD tests using RStudio (R Core Team,
299 2015) to identify any significant differences ($p < 0.05$) between the cumulative P
300 captured by the materials over the 5-day experiment. Where the data were not normally
301 distributed, the Wilcoxon rank sum test was used instead to identify any significant
302 differences.

303 **2.5 Phosphorus release from P-enriched materials**

304 To probe the potential for recovered P to be released from the materials, an extraction
305 experiment analogous to the repeat exposure experiment was designed, where the P
306 solutions were substituted by DI water buffered at pH 7. There are more than ten
307 standard soil-P bioavailability test methods in use but no clear ‘best method’, reflecting
308 the large number of variables which influence the plant availability of P in different
309 soils (Jordan-Meille et al., 2012). Biochar has strongly contrasting properties to soil and
310 no specific methods have so far emerged. Some guidelines (IBI, 2012) recommend 2%
311 formic acid extraction as described in Wang et al., (2012) but this method has limited
312 validation to date. In our study buffered DI water was chosen to simulate soil pore
313 water, which is buffered to varying extents in the soil system, based on the finding that
314 most native P in biochar is water extractable (Angst and Sohi, 2013). Therefore, the P
315 extracted represents the plant available P that might become immediately available in
316 soil at pH 7. The P-enriched materials from each treatment were oven-dried at 35°C for
317 3 days. Using pH 7 MOPS-buffered DI water, the samples were extracted over 4 days,
318 following the method described in 2.4, with SRP concentrations measured every 24 h.

319 **3. Results and Discussion**

320 **3.1 Biochar production and analysis**

321 **3.1.1 Feedstock processing**

322 The OCAD feedstock was prepared by combining AD sewage sludge with Minto ochre
323 in a 1:1 ratio (dry weight basis) therefore it was expected that the elemental
324 concentrations measured in the resulting OCAD biochar would approximate to the mean
325 of the sum of the concentrations of the two materials, expressed in g kg^{-1} . ICP-OES
326 analyses of digests of the OCAD feedstock revealed that, with the exception of S, which
327 was enriched by 51%, and Cu, which was 28% lower, all elements measured were
328 present at expected concentrations. Although it is difficult to explain the exceptions
329 with certainty and it should be noted that the mass amounts are small, it is probable that
330 Cu was lost during the altered modified dry-ashing protocol and S enrichment owed to
331 sample contamination during the same process or during pyrolysis.

332 **3.1.2 Assessment of potential toxic effects of the novel biochar materials**

333 Evaluation of the chemical composition of the novel biochar materials against the
334 International Biochar Initiative (IBI) Certification (IBI, 2012) and the European Biochar
335 Certificate (EBC) guidelines (EBC, 2012) provides an indication of the potential for re-
336 use of the filter materials as P (and other nutrient) fertiliser in soils within existing
337 environmental regulations. Although these certification systems are not officially
338 recognised by environmental regulators, they have been developed (primarily by
339 academics) to assist in the development of suitable frameworks. PTE concentrations
340 measured in all the biochars are reported in Table 1.

341 Of the elements listed by the IBI guidelines (IBI, 2012), no thresholds values were
342 breached by any of the biochars for As, Hg, Co, Cr, Cu, Ni, Pb, and Se. Of the EBC

343 guidelines (EBC, 2012), none of the premium biochar thresholds were exceeded for Cu,
344 Cr, Hg, Ni or Pb. With respect to PTE concentrations, both OCAD450 and OCAD550
345 were below thresholds in the IBI guidelines and EBC premium grade specification, but
346 close to exceeding Zn thresholds. Notably, the AD feedstock itself contains
347 $461 \pm 16.5 \text{ mg Zn kg}^{-1}$, so blending with ochre before pyrolysis reduced the final
348 concentration in OCAD450 and OCAD550 below threshold values. Concentrations of
349 PTEs in AD450 biochar exceeded the following threshold values (threshold values
350 given in parentheses): Cd (IBI 1.4-39 mg kg^{-1} and EBC basic grade 1.5 mg kg^{-1}), Mo
351 (IBI 5-75 mg kg^{-1}) and Zn (IBI 416-7400 mg kg^{-1} and EBC basic grade 400 mg kg^{-1}).
352 AD550 moderately exceeds the IBI threshold for Mo at $5.56 \pm 0.14 \text{ mg kg}^{-1}$ and exceeds
353 both the IBI and EBC basic grade threshold for Zn at $900 \pm 12.9 \text{ mg kg}^{-1}$.

354 **3.1.3 Fertiliser value**

355 Fertiliser value and relevant characteristics of the novel materials (Table 2) were
356 determined to assess their potential for use in agriculture. All the biochars had a pH
357 close to neutral (7.3-7.9), which is lower than typical for biochar, but expected due to
358 their high ash content as indicated by high yields and metal concentrations in Tables 1
359 and 2. Application of these biochars to acidic soil may still result in a liming effect but,
360 more importantly, application is not likely to have negative effects on pH of soil at ideal
361 pH values for optimum fertility (~7).

362 The concentration of P in each of the biochar materials before retention of additional P
363 is high in the context of the dose required to match fertiliser applications. Assuming all
364 biochar P is plant accessible in the first season after application, 0.4-1.1 t ha^{-1} of non-P-
365 enriched material would satisfy UK recommendations for barley grown on P-depleted

366 soil ($110 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$, equivalent to 48 kg P ha^{-1}) (DEFRA, 2010). In two previous
367 meta-analyses on crop and soil responses to biochar application, experimental doses
368 have been between approximately 0.08 and over 800 t ha^{-1} (Jeffery et al., 2011;
369 Biederman and Harpole, 2013), so there are examples in the literature of biochar
370 application at such rates. Production of biochar from sewage sludge should also be
371 economically feasible due to the low cost of sewage sludge as a feedstock (Shackley et
372 al., 2011).

373 Nutrient retention during pyrolysis is desirable as it preserves the fertiliser value of the
374 final biochar materials. Compared to their feedstocks, AD550, OCAD450 and
375 OCAD550 each were enriched in Ca, K, Mg, Mn, P and S, maintaining the fertiliser
376 value of the materials. This enrichment is expected as none of these elements are
377 extremely volatile at the pyrolysis temperatures used (although small amounts of Ca and
378 Mg can be lost), thus as C and other volatile elements are lost the relative concentration
379 of other nutrients increases.

380 **3.2 Phosphorus recovery**

381 **3.2.1 Batch adsorption experiments**

382 The calculated parameters for the best fits of the Langmuir and Freundlich isotherms are
383 shown in Table 3. The lowest fits of the Langmuir isotherm were found for ochre
384 ($R^2 = 0.400$), zeolite ($R^2 = 0.269$), activated carbon ($R^2 = 0.458$) and OCAD550
385 ($R^2 = 0.848$). In general, good fits were not obtained for any of the materials, indicating
386 that single-layer absorption does not describe the dominant adsorption kinetics in these
387 systems For the AD and OCAD biochars adsorption capacity (S_{max}) increased with

388 pyrolysis temperature, but binding strength decreased, suggesting that the additional P
389 may be more easily re-dissolved.

390 The Langmuir isotherm plot (Figure 1) has been extended to compare the theoretical P
391 adsorption at the highest concentration tested in the repeat uptake experiments. Visual
392 inspection of the plot indicates that the 550°C biochars should retain more P than the
393 450°C biochars at higher concentrations of P. It also shows the rapid reaction of ochre
394 with P compared to the other materials.

395 In general, the Freundlich isotherm did not provide good fits for the materials, with the
396 exception of AD550, OCAD450 and OCAD550 ($R^2 > 0.93$). The K_f for AD450 was more
397 than 5 times that for AD550, and the K_f for OCAD450 was more than 2 times greater
398 than that of OCAD550, suggesting that the lower temperature biochars should have
399 higher adsorption capacities, in contrast to those estimated from the Langmuir isotherm.
400 The K_f of ochre was 10 times higher than for the next highest material (OCAD450)
401 which, again, was not replicated in the Langmuir results. The smaller particle size of the
402 ochre compared to the other materials results in a higher surface area available to react
403 with P. Activated carbon and zeolite both had a K_f in the range of the biochar materials.
404 Sorption affinity ($1/n$) was in the order: ochre > OCAD450 > AD450 > activated carbon
405 > OCAD550 > AD550 > zeolite.

406 Examining these results in the context of the proposed use of the materials, whilst ochre
407 may be an excellent P filter, it may not readily release the P into soils. However this
408 may not mean that the P is inaccessible to plants, as P-enriched ochre has been shown to
409 be as effective as conventional phosphate treatment in a plant pot trial (Dobbie et al.,
410 2005). This finding is important as the experiments reported here were all buffered at

411 pH 7.0, at which phosphate is at its most soluble. Overall, the biochar materials and
412 activated carbon also demonstrate promising retention properties for recycling P. The
413 more similar results observed for the biochars and activated carbon are likely due to
414 their similar carbon structure. The higher concentration of metals in the biochars with
415 which P can interact compared to the activated carbon explains their superior retention
416 properties. Using these testing methods, the zeolite analysed is not suitable for P capture
417 from wastewater and subsequent release to soil.

418 **3.2.2 Assessment of P recovery characteristics of the novel biochar materials**

419 After 5 days repeated exposure to 0.02 g P l⁻¹ solutions, ochre removed the highest
420 amount of P, closely followed by OCAD550 and OCAD450 (Figure 2). As expected, P
421 removal rates of the OCAD biochars were in between those of ochre and the AD
422 biochars, and the values were closer to AD biochars than ochre. Significant differences
423 ($p < 0.01$) between all materials were found in the 0.02 g P l⁻¹ experiment except
424 OCAD550 and OCAD450 (Table 4). It appears that the co-pyrolysis of ochre with AD
425 sewage sludge may reduce the removal capacity of the ochre component (on a w/w
426 basis) of the biochar produced, although the differences in particle size between the
427 treatments may also contribute to the observed differences. All of the biochars removed
428 more P than activated carbon and zeolite. There was no significant effect of pyrolysis
429 temperature for the OCAD biochars, but AD450 removed significantly more P than
430 AD550 ($p < 0.001$). As AD550 contains a higher concentration of metals which are
431 expected to interact with P than AD450 (Ca: 2.4 times higher, Mg: 2.1, Al: 1.6 and Fe:
432 2.3) it was expected to remove more P, however this is not the case. It is possible that
433 the difference in pH (AD450: 7.3 vs AD550: 7.9) may have been the cause of the small
434 but significant difference in P retention due to increased electrostatic repulsion of

435 negatively charged phosphate (PO_4^{3-}) by more negatively-charged surfaces of AD550
436 compared to AD450.

437 Higher P solution concentrations were included to probe the actual recovery capacities
438 of the materials without a prolonged experiment. Rather than providing definitive
439 capacity results, however, these experiments highlighted the importance of solution
440 concentration on recovery kinetics. Whilst higher P recovery was measured for each
441 material in the 0.8 and 3 g P l⁻¹ experiments as expected, the relative ranking of the
442 materials was different. Most notable was the higher P recovery by zeolite, which
443 ranked lowest in the 0.02 g P l⁻¹ experiment but second highest in the 0.8 g P l⁻¹
444 experiment. With the exception of AD450, the other biochar materials were ranked in
445 decreasing order of P-interacting metal concentration (OCAD >AD, 550 >450), as
446 would be expected. Statistically however, the materials did not perform differently. For
447 the 3 g P l⁻¹ experiment, AD450 recovered more P than activated carbon and ochre
448 ($p < 0.05$), but no other significant differences were found between materials, noting
449 that 550°C biochars were not included in this experiment.

450 The P recovery observed in both the 0.8 g P l⁻¹ and 3 g P l⁻¹ experiments exceeded the
451 S_{max} values calculated by the Langmuir isotherm. The fits of the Langmuir isotherms
452 were generally poor, and so the calculated adsorption capacity values do not reflect
453 actual recovery capacities of these materials. Hence, as discussed by Cucarella and
454 Renman (2006) and Barrow (2015) with reference to other materials, despite being
455 widely used, batch adsorption experiments may not be an appropriate method for
456 estimating P recovery capacity for biochar materials. The repeated exposure
457 experiments show the capacity for biochar materials to continuously take up P from
458 solution as the biochar becomes less hydrophobic and, as a result, more of the reactive

459 sites come into contact with the P solution. The adsorption of P into soil (Barrow, 2015)
460 and ochre (Sibrell et al., 2009) particles has been shown to occur in two stages: initial
461 adsorption onto surfaces, followed by passive diffusion of P into the particle along a
462 concentration gradient until the particle is saturated. The energy required for the
463 forwards reaction is similar to that of the backwards reaction (Barrow, 1979) so a higher
464 concentration of P in solution increases the concentration gradient, allowing for P to be
465 taken up into the particle at a faster rate. This lends support to use of a method
466 involving repeated exposure to a constant concentration of P which is relevant for the
467 intended use of the material, in order to observe the relevant kinetics of the system. In a
468 flow-through filtration system, rate of recovery under the relevant conditions is just as
469 important as total capacity for P uptake.

470 **3.3 P release from enriched materials**

471 Whilst strong interactions with P are important characteristics of materials for P
472 extraction from wastewater, they may not be optimal for fertiliser re-use. Previous
473 studies of native P release from different biochars have shown continuous release over
474 repeated extractions and throughout a greenhouse experiment (Angst and Sohi, 2013;
475 Wang et al., 2014), suggesting that P interactions within biochar lattices were not so
476 strong as to prevent P release entirely. This also indicates high-P biochars should be
477 suitable P fertiliser alternatives. To estimate the accessibility of P recovered by biochar
478 to plants from soil pore water, repeated water extractions at each of the three
479 experimental P enrichment concentrations were conducted.

480 For the 0.02 g P l⁻¹ treatment, ochre was found to release the most recovered P, both in
481 concentration and percentage of recovered P (Figure 1, Supplementary Information

482 Table 1). It also released the smallest amount of P after 4 days of buffered DI water
483 extraction. As expected, both the OCAD450 and OCAD550 biochars had similar
484 behaviours to ochre, retaining more P and therefore having a higher concentration of
485 remaining P than the non-ochre containing materials. No difference was observed
486 between pyrolysis temperatures for the OCAD biochars in the release of adsorbed P.

487 In contrast, both the AD450 and AD550 biochars release a higher concentration of P
488 than any of the other materials (AD450 more so than AD550) and, apart from zeolite,
489 both released the greatest percentage of recovered P. Activated carbon ranked in
490 between the AD and OCAD biochars. As potential P fertilisers, these materials should
491 provide more readily-available P to plants than ochre-based products, but are less
492 effective at recovering P from solution, particularly zeolite.

493 Where release was less than the amount of P recovered, the released P was probably
494 derived from the pool of recovered P, rather than the P native to the materials. To
495 confirm this interpretation, extraction of non-enriched materials was undertaken which
496 demonstrated that water soluble P was much lower than that of the enriched samples
497 (See Table 2, Supplementary Information).

498 Comparison of the results from the 0.02 g P l⁻¹ treatments to the other treatments shows
499 differences in the rate of P loss over time. For example, the rate of P loss for the AD
500 biochars at the lowest concentration treatment was approximately constant, whereas in
501 the higher concentration treatments there was greater release on the first extraction than
502 in subsequent extractions. This suggests a different mechanism of P sorption and
503 retention at higher concentrations which results in less strongly bound P. Thus when

504 materials saturated with P are added to soil, P release could be faster initially, a pattern
505 that may be better synchronised with plant growth.

506 **3.4 Alternative P fertilisers from wastewater P**

507 Systems in which biochar production recycles P from sewage sludge and wastewater to
508 agriculture have great potential. Our results show that selected biochars can be used to
509 actively extract P from wastewater, and that they might subsequently function as
510 fertilisers with more favourable characteristics to established fertiliser products from
511 biosolids or phosphate rock.

512 Using these results, the biochar requirement to reduce the outflow P concentration in a
513 WWTP to 0.01 mg P l^{-1} from a concentration of 20 mg P l^{-1} (0.02 g l^{-1}), assuming
514 achievement of only 50% of the highest laboratory-measured efficiency in the
515 0.02 g P l^{-1} experiments after the first 24 h (see Sorp 1, Figure 2) is $114 \text{ g biochar l}^{-1}$.
516 For a WWTP producing $80 \cdot 10^3 \text{ l treated water d}^{-1}$, 9 t of biochar would be required to
517 bring all water to 0.01 mg P l^{-1} before discharge. For a plant producing $5 \cdot 10^6 \text{ l d}^{-1}$, 570 t
518 of biochar would be required. These are large quantities of biochar, but if a 50% total
519 recovery capacity is also assumed (using the highest P sorption values from the $3 \text{ g l}^{-1} \text{ P}$
520 experiment), the char would not be saturated with P until after 70 days. However,
521 applying these calculations and assumptions to achieve a WWTP outflow P
522 concentration of 0.1 mg P l^{-1} from the current limit of 2 mg l^{-1} , the biochar required
523 would be 0.9 t and 54 t respectively, which may be more feasible in terms of the
524 physical space required for filtration.

525 Using the approximate density of biochar of 0.3 g ml^{-1} , the smaller of the two WWTPs
526 would require a filter of dimensions $1 \text{ m} \times 2 \text{ m} \times 15.2 \text{ m}$ to treat an outflow P

527 concentration of 20 mg l⁻¹ or 1 m × 2 m × 1.45 m for an outflow of 2 mg P l⁻¹. The
528 larger WWTP would require 1 m × 2 m × 947 m and 1 m × 2 m × 90.4 m,
529 respectively. Whilst the largest of these volumes does appear unfeasible, the rest look to
530 be achievable. Biochar from WWTPs of these sizes would produce enough P enriched
531 material each year to fertilise between 1.8 and 3261 ha of Index 0 soil at the rates
532 calculated in section 3.3.1. These calculations support the assertion that these materials
533 could be used to supplement or replace conventional P fertiliser, especially for land in
534 the vicinity of individual WWTPs.

535 Understanding the chemical and physical properties of biochars used for P capture and
536 release from wastewater will be important for managing (for example) the diminishing
537 sorption expected when biochar surfaces become negatively charged through phosphate
538 sorption. It will also help to identify non-ochre mineral waste materials that might
539 improve sorption efficiency. Technical responses might also be considered, such as
540 filtration designs that permit periodic resting for diffusive penetration of phosphate into
541 biochar and which have been shown to increase phosphate sorption of other materials
542 (Barrow, 2015; Sibrell et al., 2009).

543 **4. Conclusion**

544 Biochars with promising P recovery and recycling properties can be made from
545 anaerobically digested sewage sludge. We show that addition of ochre to the feedstock
546 not only improves P recovery properties, but also produces biochars which comply with
547 guidelines relevant to possible future regulation of biochar application to soil. The
548 results also indicate that the ideal pyrolysis temperature for these materials depends on
549 feedstock characteristics, and that the P capture and retention properties of the biochars

550 were equal to or better than other potential P recycling materials tested for comparison.
551 Robust methods using pH buffering that are applicable to diverse, novel materials and
552 are meaningful in the context of their intended use as fertilisers have been demonstrated.
553 Future experiments should aim to improve the design of the biochars by probing the
554 sorption mechanisms more deeply, using plant growth experiments to directly evaluate
555 their potential use as fertilisers.

556

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567

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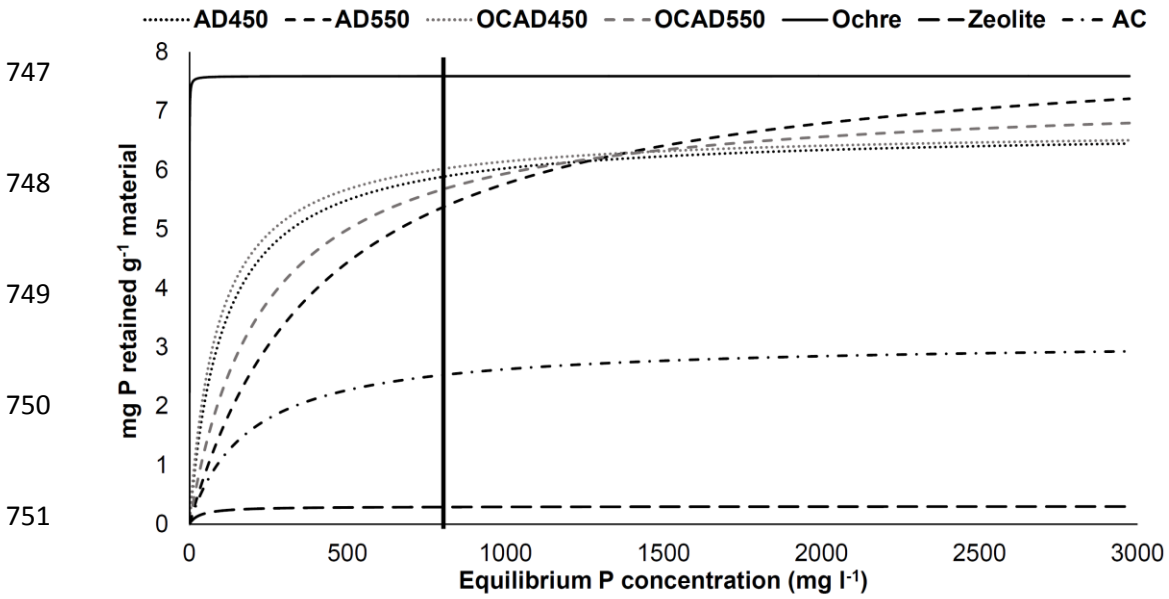
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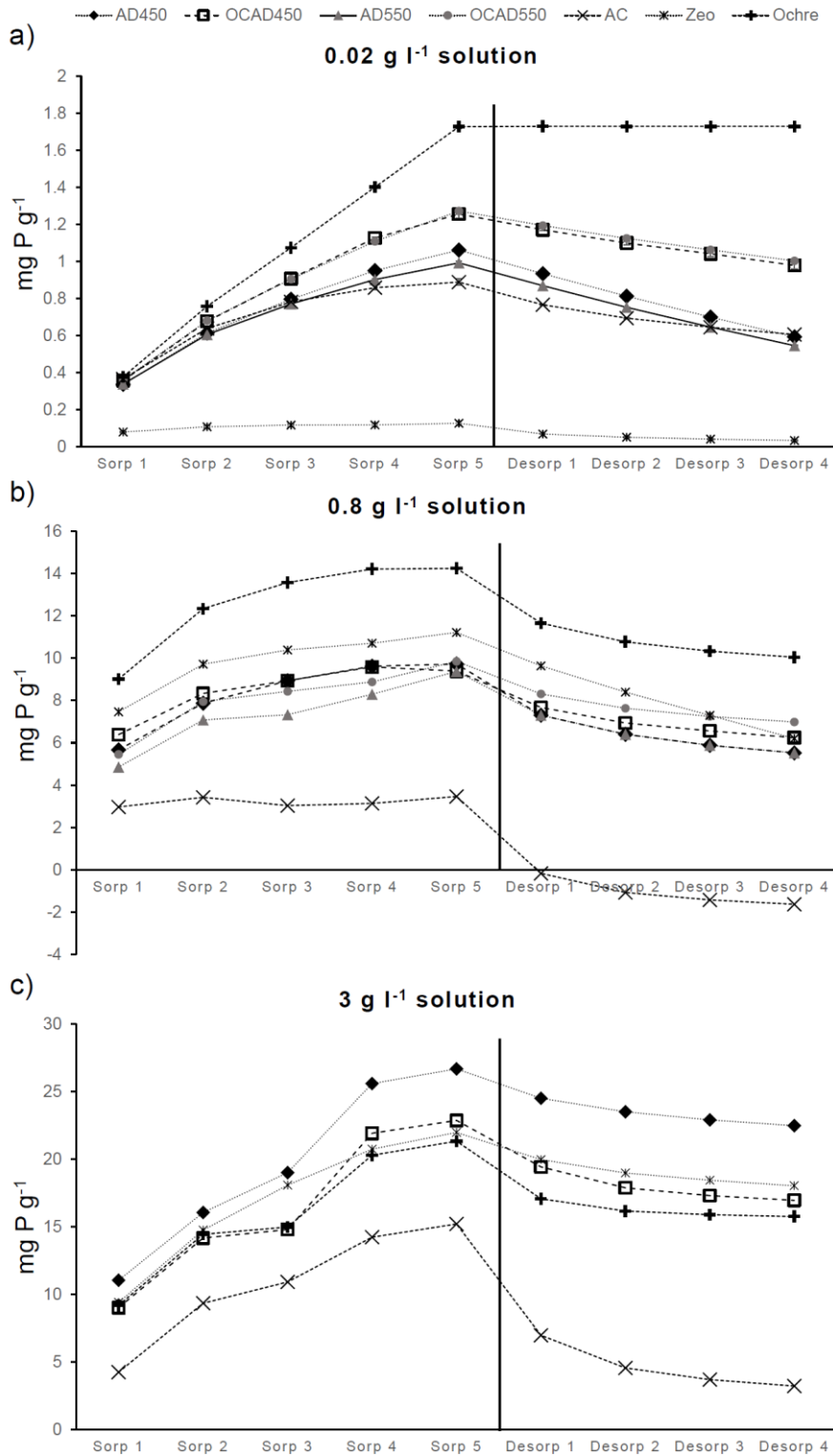
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752 Figure 1. Langmuir isotherms plotted for all materials. The vertical line on the x axis
753 shows the highest treatment concentration in the batch adsorption experiments (0.8 g P
754 l⁻¹). The isotherms have been extended to the highest treatment concentration in the
755 repeat uptake experiments (3 g P⁻¹) to show the predicted adsorption capacity at these
756 concentrations.

757



759 Figure 2. Capture and subsequent extraction of P from the materials in experiments with
760 solutions of (a) 0.02 g P l⁻¹, (b) 0.8 g P l⁻¹ and (c) 3 g P l⁻¹. Values are cumulative and
761 are the means of 4 replicates. Error bars are shown for the 0.02 g P l⁻¹ experiment (\pm 1
762 standard deviation from the mean) but most are not visible due to small deviations
763 between the replicates. Error bars are not shown for the 0.8 or 3 g P l⁻¹ experiments to
764 allow trends to be clear, but are presented in Supplementary Information Table 1.
765 Negative values for extraction of P for activated carbon (AC) in the 0.8 g P l⁻¹
766 experiment show release of native P rather than enriched P, as the values have been
767 calculated relative to total P recovery from solution.

| | AD | Ochre | OCAD | AD450 | OCAD450 | AD550 | OCAD550 | ZEO | AC |
|-----------|---|--|--|---|---|---|--|-------------------------------|-------------------------------|
| Al | 29.8×10 ³ ± 913 | 2.09×10 ³ ± 227 | 15.8×10 ³ ± 131 | 38.1×10 ³ ± 2.20×10 ³ | 20.1×10 ³ ± 3.59×10 ³ | 62.7×10 ³ ± 1.29×10 ³ | 24.9×10 ³ ± 689 | 19.6×10 ³ ± 357 | 649 ± 16.3 |
| As | < 0.72 | < 0.72 | < 0.72 | 1.42 ± 2.01 | < 0.72 | < 0.72 | < 0.72 | 44.0 ± 5.05 | < 0.72 |
| B | 16.7 ± 1.73 | 43.8 ± 6.09 | 28.3 ± 0.660 | 13.4 ± 1.53 | 45.1 ± 1.47 | 22.7 ± 0.569 | 46.8 ± 2.86 | 4.58 ± 1.63 | < 0.36 |
| Cd | 0.249 ± 3.29×10 ⁻² | < 0.04 | < 0.04 | 3.34 ± 0.400 | < 0.04 | 0.542 ± 4.16×10 ⁻² | < 0.04 | 0.591 ± 0.111 | 0.310 ± 0.202 |
| Co | 4.90 ± 0.163 | 9.65 ± 5.98×10 ⁻² | 7.56 ± 0.171 | 6.57 ± 0.530 | 11.7 ± 0.463 | 8.22 ± 0.203 | 11.2 ± 0.663 | 0.47 ± 0.04 | 0.25 ± 0.01 |
| Cr | 10.5 ± 0.487 | < 0.49 | < 0.49 | 15.3 ± 1.32 | < 0.49 | 21.8 ± 0.795 | < 0.49 | < 0.49 | 5.76 ± 0.170 |
| Cu | 41.7 ± 4.05 | < 0.06 | 15.1 ± 0.633 | 93.1 ± 3.79 | 23.5 ± 1.07 | 72.8 ± 1.56 | 33.8 ± 3.23 | 0.694 ± 9.66×10 ⁻² | 7.36 ± 0.50 |
| Fe | 72.8×10 ³ ± 1.37×10 ³ | 520×10 ³ ± 7.44×10 ³ | 352×10 ³ ± 14.1×10 ³ | 44.6×10 ³ ± 3.85×10 ³ | 406×10 ³ ± 86.0×10 ³ | 101×10 ³ ± 2.29×10 ³ | 451×10 ³ ± 20.7×10 ³ | 8.01×10 ³ ± 172 | 1.31×10 ³ ± 64.1 |
| Mo | 2.12 ± 0.231 | < 0.21 | < 0.21 | 7.62 ± 1.44 | < 0.21 | 5.56 ± 0.149 | < 0.21 | < 0.21 | < 0.21 |
| Na | 1.37×10 ³ ± 37.5 | 1.86×10 ² ± 30.3 | 863 ± 33.9 | 1.65×10 ³ ± 48.4 | 1.01×10 ³ ± 36.0 | 1.96×10 ³ ± 118 | 999 ± 55.8 | 1.26×10 ³ ± 102 | 406 ± 15.7 |
| Ni | 11.1 ± 0.368 | 5.90 ± 7.79×10 ⁻² | 9.53 ± 0.428 | 22.3 ± 2.38 | 15.9 ± 0.725 | 23.4 ± 0.692 | 15.7 ± 0.724 | <0.09 | 0.465 ± 6.43×10 ⁻² |
| Pb | 15.2 ± 0.804 | 10.1 ± 0.824 | 14.8 ± 3.84 | 34.9 ± 2.73 | 22.8 ± 4.14 | 36.4 ± 0.748 | 20.4 ± 2.18 | 17.0 ± 2.74 | 59.5 ± 10.5 |
| Zn | 461 ± 16.5 | 60.6 ± 0.985 | 270 ± 4.23 | 518 ± 41.7 | 397 ± 24.5 | 900 ± 12.9 | 400 ± 12.3 | 9.88 ± 1.02 | < 0.47 |

768 **Table 1** Mean PTE concentrations (n=3) of the materials as determined by ICP-OES of sample digests expressed in mg kg⁻¹ ± standard
769 deviation.

| | AD | Ochre | OCAD | AD450 | OCAD450 | AD550 | OCAD550 | ZEO | AC |
|--------------------------------------|----|-------------|------|-------------|----------|-------------|-------------|------------|--------------|
| Yield % | - | - | - | 52.6 | 67.3 | 50.5 | 65.1 | - | - |
| pH (n = 2) | - | 7.9 ± 0.014 | - | 7.3 ± 0.035 | 7.6 ± 0 | 7.9 ± 0.014 | 7.7 ± 0.078 | 8.1 ± 0.17 | 10.3 ± 0.042 |
| EC (µS cm ⁻¹) (n = 2) | - | 518 ± 20 | - | 596 ± 62 | 692 ± 28 | 375 ± 0.70 | 738 ± 200 | 223 ± 8.5 | 424 ± 52 |

Nutrients (g kg⁻¹)

| | | | | | | | | | |
|-----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Ca | 38.4 ± 1.05 | 18.8 ± 0.438 | 28.9 ± 0.633 | 28.7 ± 2.83 | 32.4 ± 8.27 | 70.0 ± 1.59 | 39.7 ± 1.55 | 16.6 ± 0.208 | 34.3 ± 0.254 |
| K | 2.12 ± 7.46×10 ⁻² | 0.349 ± 4.76×10 ⁻² | 1.35 ± 2.02×10 ⁻² | 2.75 ± 6.81×10 ⁻² | 3.05 ± 1.94 | 3.42 ± 9.30×10 ⁻² | 1.84 ± 0.0527 | 12.8 ± 0.151 | 2.29 ± 1.61×10 ⁻² |
| Mg | 7.39 ± 0.192 | 3.03 ± 5.88×10 ⁻² | 5.02 ± 0.122 | 6.03 ± 0.502 | 5.97 ± 1.15 | 12.8 ± 0.254 | 7.06 ± 0.236 | 2.72 ± 0.134 | 2.72 ± 8.02×10 ⁻³ |
| Mn | 0.286 ± 1.26×10 ⁻² | 0.891 ± 5.33×10 ⁻³ | 0.615 ± 1.54×10 ⁻² | 0.493 ± 4.58×10 ⁻² | 1.03 ± 4.89×10 ⁻² | 0.565 ± 8.31×10 ⁻³ | 0.961 ± 5.23×10 ⁻² | 0.120 ± 1.65×10 ⁻² | 0.528 ± 5.15×10 ⁻³ |
| P | 71.2 ± 2.62 | 1.92 ± 0.134 | 36.6 ± 0.629 | 46.9 ± 3.10 | 44.9 ± 1.70 | 126 ± 3.84 | 49.8 ± 1.64 | 0.301 ± 9.04×10 ⁻² | 24.5 ± 0.282 |
| S | 8.83 ± 0.236 | 3.32 ± 0.121 | 9.18 ± 0.219 | 8.25 ± 0.530 | 12.2 ± 0.176 | 15.6 ± 0.279 | 12.3 ± 0.228 | 0.207 ± 2.03×10 ⁻² | 2.78 ± 1.37×10 ⁻³ |

770 **Table 2** Characteristics of the biochar feedstock, biochar and comparison materials. Nutrient values were determined by ICP-OES of
771 samples and the mean values (n=3) ± standard deviation are given.

| | Langmuir parameters | | | Freundlich parameters | | |
|------------------|---------------------------------|-----------------------|-------|-----------------------|-------|-------|
| | S_{max} (mg g ⁻¹) | K | R^2 | K_f | n | R^2 |
| AD450 | 6.68 | 9.2×10^{-3} | 0.918 | 0.44 | 0.410 | 0.845 |
| AD550 | 8.25 | 2.32×10^{-3} | 0.935 | 8.41×10^{-2} | 0.636 | 0.965 |
| OCAD450 | 6.70 | 1.10×10^{-2} | 0.942 | 0.503 | 0.398 | 0.969 |
| OCAD550 | 7.33 | 4.26×10^{-3} | 0.848 | 0.202 | 0.516 | 0.934 |
| Ochre | 7.59 | 7.30 | 0.400 | 5.71 | 0.070 | 0.314 |
| Zeolite | 0.300 | 0.030 | 0.269 | 2.60×10^{-2} | 0.886 | 0.218 |
| Activated carbon | 3.11 | 5.40×10^{-3} | 0.458 | 0.139 | 0.450 | 0.672 |

772 **Table 3** Best-fit Langmuir and Freundlich parameters determined for the materials.

773

| P solution | Ranking | P sorption (mg P g⁻¹) |
|------------------------|----------------|---|
| 0.02 g l ⁻¹ | a | Ochre 1.73 ($\pm 8.93 \times 10^{-3}$) |
| | b | OCAD550 1.26 ($\pm 4.66 \times 10^{-3}$) |
| | b | OCAD450 1.24 ($\pm 2.10 \times 10^{-2}$) |
| | c | AD450 1.06 ($\pm 3.84 \times 10^{-3}$) |
| | d | AD550 0.986 ($\pm 9.31 \times 10^{-3}$) |
| | e | Activated carbon 0.884 ($\pm 1.69 \times 10^{-2}$) |
| | f | Zeolite 0.130 ($\pm 1.05 \times 10^{-2}$) |
| 0.8 g l ⁻¹ | g | Ochre 14.2 (± 1.77) |
| | h | Zeolite 11.2 (± 1.46) |
| | h,i | OCAD550 9.82 (± 2.01) |
| | h,i | AD450 9.72 (± 0.657) |
| | i | OCAD450 9.37 (± 0.872) |
| | i | AD550 9.35 (± 2.21) |
| | j | Activated carbon 3.47 (± 1.52) |
| 3 g l ⁻¹ | k | AD450 25.9 (± 5.10) |
| | k,l | Zeolite 21.5 (± 4.99) |
| | k,l | OCAD450 20.4 (± 6.35) |
| | l | Ochre 20.0 (± 5.71) |
| | l | Activated carbon 15.1 (± 4.35) |

774 **Table 4** Total P sorption of the materials after 5 days exposure to solutions of different P
775 concentrations. Materials are grouped according to statistical differences (ANOVA and
776 Tukey HSD tests, as indicated by the letters a–m) and ranked in descending order of P
777 sorption. Values for sorption reported are the mean of 4 replicates with propagated standard
778 error.

779

780 **Supplementary Information**

781 **Methods**

782 **Testing of buffers**

783 To determine whether buffer addition affected P sorption, a batch experiment was carried out
784 using AD550 and a 0.02 g P l⁻¹ solution (from K₂HPO₄) with either 5 mM or 10 mM MOPS,
785 following the procedure described in section 2.3. All supernatants were refrigerated at 4°C
786 before analysis for soluble reactive P (SRP) by automated colorimetry (Auto Analyser III,
787 Bran & Luebbe, Norderstedt, Germany). Each adsorption experiment was performed with
788 four replicates and results reported as means ± 1 S.D. All experiments were conducted at
789 room temperature (21°C) concentrations were measured as described above. 1-way ANOVA
790 and Tukey HSD tests were completed using RStudio and used to identify statistical
791 differences (p<0.05) between the total P adsorbed by the materials and no statistically
792 significant difference was found between the treatments.

793

794 **Supplementary Table 1** Percentage of P extracted from the P-enriched samples in pH 7
795 buffered deionised water after 24 h, repeated for four days. The concentration of material P
796 enrichment (in mg P g⁻¹) is shown for reference. The percentage of enriched P remaining after
797 the four extractions is also given. AD550 and OCAD550 were not included in the 3 g l⁻¹ P
798 experiment as they became available after the initial experiment was run. All values are the
799 mean of four replicates with propagated standard error shown, all to 3 significant figures.

| | | % enriched P extracted after 24 h treatment | | | | | |
|-----------|---|---|--------------|--------------|--------------|------------------------------|--|
| Treatment | P enrichment (mg P g ⁻¹) | Day 1 | Day 2 | Day 3 | Day 4 | % enriched P remaining | |
| AD450 | 0.02 g l ⁻¹ | 12.1 ± 0.317 | 11.4 ± 0.475 | 10.7 ± 0.612 | 10.1 ± 0.679 | 55.8 | |
| | 0.8 g l ⁻¹ | 25.8 ± 2.82 | 12.5 ± 2.89 | 6.68 ± 2.91 | 4.76 ± 2.92 | 50.3 | |
| | 3 g l ⁻¹ | 9.86 ± 3.05 | 4.05 ± 3.20 | 2.67 ± 3.55 | 1.87 ± 3.99 | 81.5 | |
| OCAD450 | 0.02 g l ⁻¹ | 6.78 ± 0.378 | 5.70 ± 0.564 | 4.61 ± 0.839 | 4.99 ± 0.995 | 77.9 | |
| | 0.8 g l ⁻¹ | 18.3 ± 1.21 | 7.85 ± 2.06 | 3.95 ± 2.15 | 3.41 ± 2.19 | 66.5 | |
| | 3 g l ⁻¹ | 18.7 ± 3.27 | 8.31 ± 5.65 | 3.10 ± 7.60 | 1.88 ± 9.33 | 68.0 | |
| AD550 | 0.02 g l ⁻¹ | 12.4 ± 0.0954 | 11.7 ± 0.138 | 10.8 ± 0.165 | 10.1 ± 0.176 | 54.9 | |
| | 0.8 g l ⁻¹ | 22.6 ± 4.96 | 9.68 ± 5.28 | 5.66 ± 5.37 | 3.90 ± 5.42 | 58.2 | |
| | 3 g l ⁻¹ | n/a n/a | n/a n/a | n/a n/a | n/a n/a | n/a | |
| OCAD550 | 0.02 g l ⁻¹ | 6.18 ± 0.219 | 5.43 ± 0.281 | 4.92 ± 0.312 | 4.65 ± 0.363 | 78.8 | |
| | 0.8 g l ⁻¹ | 15.8 ± 1.96 | 6.92 ± 2.15 | 3.97 ± 2.24 | 2.67 ± 2.29 | 70.6 | |
| | 3 g l ⁻¹ | n/a n/a | n/a n/a | n/a n/a | n/a n/a | n/a | |
| AC | 0.02 g l ⁻¹ | 13.8 ± 0.359 | 8.12 ± 0.474 | 5.57 ± 0.616 | 4.44 ± 0.733 | 68.1 | |
| | 0.8 g l ⁻¹ | 89.3 ± 11.6 | 22.2 ± 12.1 | 8.91 ± 12.2 | 5.19 ± 12.2 | -25.6 | |
| | 3 g l ⁻¹ | 64.1 ± 8.91 | 18.6 ± 13.6 | 6.63 ± 17.5 | 3.62 ± 20.8 | 7.03 | |
| OCHRE | 0.02 g l ⁻¹ | 0 n/a | 0 n/a | 0 n/a | 0 n/a | 100 | |
| | 0.8 g l ⁻¹ | 18.3 ± 1.88 | 6.14 ± 1.98 | 3.09 ± 2.01 | 2.02 ± 2.01 | 70.4 | |
| | 3 g l ⁻¹ | 23.2 ± 2.19 | 4.86 ± 3.29 | 1.45 ± 4.16 | 0.720 ± 4.92 | 69.8 | |
| ZEOLITE | 0.02 g l ⁻¹ | 46.3 ± 1.33 | 13.9 ± 4.19 | 8.18 ± 5.10 | 5.62 ± 6.08 | 26.0 | |
| | 0.8 g l ⁻¹ | 14.2 ± 1.79 | 10.9 ± 2.08 | 9.94 ± 2.27 | 9.62 ± 2.44 | 55.3 | |
| | 3 g l ⁻¹ | 12.5 ± 4.11 | 6.06 ± 7.24 | 3.27 ± 9.93 | 2.52 ± 12.4 | 75.6 | |

800

801

802

803 **Supplementary Table 2** Total concentration of P released from the materials after 5
804 consecutive extractions in deionised water.

| | mg P g ⁻¹ 805 |
|----------------|--------------------------|
| AD450 | 0.209 |
| OCAD450 | 0.101 |
| Zeolite | 0.001 |
| AC | 0.001 |
| Ochre | 0.000 |