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

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Abstract

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

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

Keywords

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

1. Introduction

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

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

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

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

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

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

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

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

2. Materials and Methods

2.1 Material selection and processing

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

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

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

(Brown et al., 2006; Downie et al., 2009; Lua et al., 2004), therefore two relatively low
HTTs were selected to increase the number of potential reactive sites in the biochar.
Samples of both feedstock types were heated at a rate of $25^{\circ}\text{C min}^{-1}$ to a HTT of 450°C
or 550°C , held for 30 min. The resulting biochars (AD450, AD550, OCAD450 and
OCAD550) were each left in the reactor with N_2 flow overnight to cool before being
transferred into a N_2 -purged container. OCAD biochars were cooled to 4°C before air
was allowed to slowly diffuse into the container to prevent spontaneous combustion due
to rapid re-oxidation of reduced elements within the material.

2.2 Characterisation of materials

2.2.1 Nutrients and potentially toxic elements (PTEs)

The materials were digested and analysed by ICP-OES to determine the concentrations
of nutrients (Ca, K, Mg, Mn, P, S) and PTEs (Al, As, B, Cd, Co, Cr, Cu, Fe, Mo, Na,
Ni, Pb, Zn). All materials (biochars and biochar feedstocks) and blanks were prepared in
triplicate for analysis using the method described by Buss et al. (2016), which is based
on the modified dry ashing procedure proposed by Enders and Lehmann (2012) and
prescribed by IBI (2012). The purpose of the modifications was to improve element
detection by decreasing the dilution of samples during the digestion process. Due to the
high concentration of Fe in the biochars and ochre prepared for this study HCl was used
instead of H_2O_2 .

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

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

2.2.2 pH and electrical conductivity (EC)

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

2.3 Batch adsorption experiments

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

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

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

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

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

$$S = K_f C^n$$

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

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

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

which a metal cation could react to form a closed ring structure with the nitrogen atom (Yu et al., 1997). Within this group of compounds, MES (2-(N-morpholino)ethanesulfonic acid) and MOPS (3-(N-morpholino)propanesulfonic acid) have been found to have no effect on P adsorption (Mao et al., 2012). MOPS was tested in our experimental system at increasing concentrations (see Supplementary Information) and as in the literature, no interference was observed. Therefore phosphate solutions of concentrations ranging from 0–800 mg P l⁻¹ were prepared for the batch experiments using DI water buffered to pH 7 with 10 mM MOPS/NaNO₃ and K₂HPO₄.

The median particle size of the Minto ochre is 0.02-0.06 mm (Heal et al., 2003), which is smaller than that of the other materials tested, however it does form natural aggregates. Therefore it was prepared by breaking up the aggregates in a pestle and mortar and removing manually any visible organic matter. Rather than matching the primary particle size of ochre for all materials, the biochar (AD450, AD550, OCAD450, OCAD550), activated carbon and zeolite samples were passed through a sieve to obtain a 0.5–1.0 mm size fraction, since crushing of the OCAD materials may have separated the ochre and AD components spatially and prevented direct interaction between fractions relevant to P adsorption. Due to the highly hygroscopic nature of the biochars, their moisture content at room temperature was determined by weighing, drying at 105°C overnight and re-weighing a subsample of each material immediately after cooling in a desiccator. The calculated water content was accounted for in subsequent calculations. Aliquots of MOPS buffered P solution (36 ml, prepared as outlined above) were added to 0.100 g of each material in 50 ml centrifuge tubes. The tubes were laid on their side and shaken on an orbital platform shaker at 150 rpm for 24 h. The samples were centrifuged at 3500 rpm for 30 min and the supernatant filtered using 0.45 µm

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

2.4 Repeat exposure experiments

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

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

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

2.5 Phosphorus release from P-enriched materials

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

3. Results and Discussion

3.1 Biochar production and analysis

3.1.1 Feedstock processing

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

3.1.2 Assessment of potential toxic effects of the novel biochar materials

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

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

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

3.1.3 Fertiliser value

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

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

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

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

3.2 Phosphorus recovery

3.2.1 Batch adsorption experiments

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

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

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

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

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

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

3.2.2 Assessment of P recovery characteristics of the novel biochar materials

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

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

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

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

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

3.3 P release from enriched materials

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

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

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

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

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

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

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

3.4 Alternative P fertilisers from wastewater P

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

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

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

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

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

4. Conclusion

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

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

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

Figure 2. Capture and subsequent extraction of P from the materials in experiments with 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 are the means of 4 replicates. Error bars are shown for the 0.02 g P l⁻¹ experiment (± 1 standard deviation from the mean) but most are not visible due to small deviations between the replicates. Error bars are not shown for the 0.8 or 3 g P l⁻¹ experiments to allow trends to be clear, but are presented in Supplementary Information Table 1. Negative values for extraction of P for activated carbon (AC) in the 0.8 g P l⁻¹ experiment show release of native P rather than enriched P, as the values have been 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.

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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)

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

Supplementary Information

Methods

Testing of buffers

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

Supplementary Table 1 Percentage of P extracted from the P-enriched samples in pH 7 buffered deionised water after 24 h, repeated for four days. The concentration of material P enrichment (in mg P g⁻¹) is shown for reference. The percentage of enriched P remaining after the four extractions is also given. AD550 and OCAD550 were not included in the 3 g l⁻¹ P experiment as they became available after the initial experiment was run. All values are the 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
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
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

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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