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Biochar phosphorus (P) release is limited by high pH and excess calcium (Ca)

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Core ideas

- P release from rice husk biochar was investigated
- Soil-free extractions were performed at different pH and solution compositions
- Lowest P release occurred at pH 7.6-8.6 and in the presence of excess Ca
- A conceptual model was developed of biochar P release in different soil conditions
- Biochars with Ca <1% and/or pH < 7.5 are optimal for maximum P release to soil

Abstract

Aside from its use for improving soil properties, biochar is increasingly promoted as a direct nutrient provider for sustainable recycling of waste materials. However, incomplete understanding of the interacting factors that determine phosphorus (P) release from biochar may limit the efficiency of P recycling from biochar to soil. In particular, the contrasting pH of biochar and soil need to be considered. In this study, soil-free biochar (rice husk 700°C) extractions were performed under different pH (4.6–9.9) and extractant conditions to test how solution composition affects biochar P release. When solution pH was in the range 7.6–8.6 and excess Ca was present in the solution or in biochar, P release was low; only 1-7% of the total P was released compared to ~20% under most other conditions. Importantly, we demonstrate that biochar total Ca concentration is closely related to P availability ($R^2 = 0.76$) and could be used to predict biochar P release. The results suggest that for maximum P release, low Ca concentrations in biochar and (soil) solution are needed and/or a pH <7.5

31 at the soil-biochar interface. This novel understanding will help engineer sustainable biochar
32 fertilisers optimised for P provision.

33 **Keywords**

34 Rice husk; biochar pH; soil pH; calcium; slow pyrolysis

35 1 Introduction

36 The distinct physical, chemical and surface properties of biochar as a matrix have to be considered in
37 understanding and assessing its nutrient value (Farrell et al., 2013; Shepherd et al., 2017; Harvey et
38 al., 2018). The typical high porosity (e.g. 62.5-85.1% (Gray et al., 2014)) and high pH of biochar (e.g.
39 pH 7 – 11 (Qambrani et al., 2017)) means that extraction methods optimised for soil are not
40 necessarily appropriate for biochar. For example, in Shepherd et al. nutrients were extracted using
41 different chemical extractants and the results were correlated with plant nutrient uptake from biochar
42 (Shepherd et al., 2017). For phosphorus (P) it was concluded that buffered 0.01 M CaCl₂ correlated
43 best with plant uptake, rather than Mehlich-3 and 2% formic acid which are typically used to
44 determine the P availability in soil.

45 A factor not sufficiently quantified for biochar-containing soil systems is the influence of pH and
46 elemental composition of the soil solution, particularly Ca for its importance in modifying P
47 availability (Blume et al., 2016; Sun et al., 2018). The relevance of pH in explaining the effects of
48 biochar addition to soil are evident from meta-analysis (Biederman and Harpole, 2013), but the local
49 effects at the interface of biochar and soil require examination. When predicting nutrient availability
50 in biochar, it is essential to consider the distinct difference in pH between biochar and soil. A pH
51 gradient between biochar and soil will form, which could affect the release of nutrients from biochar,
52 in particular P (Buss et al., 2018).

53 Hardwood and rice husk biochar released P readily and over several extraction steps when extracted
54 with deionised water (Angst and Sohi, 2013; Qian et al., 2013). However, it remains uncertain how
55 the interactive effect of soil solution composition and pH affects P release from biochar. Furthermore,
56 the % P extracted from different biochars varies significantly and is strongly dependent on the type of
57 feedstock used for pyrolysis (Buss et al., 2016a; Shepherd et al., 2017). So far it is unclear which
58 biochar characteristics influence the P release.

59 Our broader aim is to optimise the composition of biochar for managing nutrients in P-constrained
60 soils. To explore the P release from biochar, we applied conventional extractions under controlled and

61 uncontrolled pH conditions, mimicking different pHs and soil solution compositions at the soil-
62 biochar interface.

63 **2 Materials and methods**

64 **2.1 Biochar**

65 Standard biochar material manufactured from rice husk was used (UKBRC, University of Edinburgh)
66 (Mašek et al., 2018). The rice husk was sourced from Sri Lanka and produced using the UKBRC
67 Stage III Slow Pyrolysis Unit (rotary kiln pyrolyser), described in Buss and Mašek (2014), at a
68 highest treatment temperature of 700°C and a residence time in the heated zone of 20 min.
69 Characteristics of the biochar (referred to as RH 700) are given in Mašek (2014). The total nutrients
70 concentrations are (% dry basis): 1.6 ± 0.4 g kg⁻¹ P, 1.7 ± 0.58 g kg⁻¹ Ca, 1.1 ± 0.2 g kg⁻¹ Mg, 6.2 ± 0.2
71 g kg⁻¹ K. Further key characteristics of the biochar are as follows: ash content 47.9 ± 5.4 wt%,
72 electrical conductivity (EC) 690 ± 260 μS cm⁻¹ and pH 9.81 ± 0.64 (1:20 mass: volume in deionised
73 water (DI)).

74 **2.2 Rice husk biochar P extractions at different pH and soil** 75 **solution composition**

76 Soil-free batch extractions were conducted to minimise other influencing factors in order to clearly
77 identify the pH and solution composition effects. Different extractants were used to infer effects of
78 soil solution chemistry on P release. The extractants used were deionised (DI) water, 0.01 M CaCl₂
79 and 1 M NH₄NO₃, each widely applied for soil analysis and also tested on a range of biochar materials
80 (Angst and Sohi, 2013; Farrell et al., 2013; Zhang et al., 2016; Shepherd et al., 2017). Specifically,
81 NH₄NO₃ was used because it is a salt extraction similar to CaCl₂ but without ions that could bind to
82 and precipitate phosphate.

83 A fractional factorial experimental design was implemented in which all three extractants were tested
84 without buffering where the mean solution pHs (of the four replicates) after extraction of the biochar
85 sample were 6.7 (NH₄NO₃), 8.5 (CaCl₂) and 9.9 (DI). Further extractions conducted were CaCl₂ and

86 NH_4NO_3 both buffered at pH 4.6 and 7.6 and CaCl_2 and DI both buffered at pH 8.6. All extractions
87 were single step.

88 Buffering was implemented by the addition of the non-complexing ‘Better Buffers’ DEPP (N,N’-
89 diethylpiperazine) at pHs 4.6 and 8.6 (pKa 4.67 and 8.83) (Yu et al., 1997) and MOPS (3-(N-
90 morpholino) ethanesulfonic acid) at pH 7.6 (pKa 7.42) (Sari and Covington, 2005) to ensure no
91 interaction with sorption and desorption of P. Further details of both MOPS and DEPP and their use
92 in similar batch experiments has previously been reported (Shepherd et al., 2016, 2017). Based on this
93 prior work MOPS was used at a concentration of 0.01 M to buffer the extraction of rice husk biochar
94 using 0.01 M CaCl_2 and DI water. From our assessment of DEPP in a similar manner (Supplemental
95 Table 1), a DEPP buffer concentration of 0.04 M was adopted.

96 The design outlined above provided a total of nine buffered and unbuffered extractions in the pH
97 range of 4.6 to 9.9 (summarised in Table 1), each replicated four times. The extractions were
98 conducted with 20 mL of solution and 0.2 g biochar (particle size 1.0–2.0 mm, representing fresh,
99 non-weathered biochar) in 50 mL polypropylene centrifuge tubes with appropriate blanks containing
100 no biochar (9 different blanks were used with respective extractant and with/without respective
101 buffer). The tubes were shaken for 2 h at 150 rpm on an orbital shaker, centrifuged for 30 min at 3500
102 rpm and the supernatant was transferred into biotite vials using 3 mL Pasteur pipettes. The pH of the
103 extracts at the start and end of the extraction process were measured using a Mettler Toledo FE 30 pH
104 meter and probe calibrated with standards of pH 4.00 and 7.00 and corrected for temperature.

105 Table 1: Summary of the 9 extractions conducted showing concentrations of extractant and buffer (where used)
106 and mean pH of 4 replicates after extraction of biochar sample.

| Extractant and concentration | Buffer and concentration | Mean pH after extraction |
|------------------------------|--------------------------|--------------------------|
| 0.01 M CaCl_2 | 0.04 M DEPP | 4.6 |
| 0.01 M CaCl_2 | 0.01 M MOPS | 7.6 |
| 0.01 M CaCl_2 | Unbuffered | 8.5 |
| 0.01 M CaCl_2 | 0.04 M DEPP | 8.6 |
| 1 M NH_4NO_3 | 0.04 M DEPP | 4.6 |
| 1 M NH_4NO_3 | Unbuffered | 6.7 |
| 1 M NH_4NO_3 | 0.01 M MOPS | 7.6 |
| Deionised water (DI) | 0.04 M DEPP | 8.6 |
| Deionised water (DI) | Unbuffered | 9.9 |

107

108 **2.3 P analysis of rice husk biochar extracts**

109 The extracts were filtered with 0.45 µm syringe filters (X50 Millex, MCE sterile 33 mm, Millipore,
110 Watford, UK) and analysed for total P via inductively coupled plasma–optical emission spectrometry
111 as described in Buss et al. (2016a). In brief, five standards of 0.01, 0.1, 1, 10 and 100 ppm P and a
112 calibration blank were used to calibrate a Perkin Elmer Optima 5300DV. Subsequently, the extracts
113 were analysed, and a 1 ppm standard was analysed every 10 samples for quality control to monitor
114 any concentration shifts. Extraction blanks were measured and their concentrations subtracted from
115 the sample concentrations.

116 **2.4 Repeated rice husk biochar extraction with deionised water**

117 To assess the time-dependent release of P from the rice husk biochar, the RH 700 material was
118 reduced to smaller minimum dimension (0.5 - 1 mm) using a sieve and extracted using unbuffered DI
119 water. This reflects biochar that has been physically fragmented through exposure to physical,
120 biological and chemical processes (Liu et al., 2017). A non-ionic surfactant, 2-octanol (98% for
121 synthesis; Merck, Hohenbrunn, Germany) was included, to address any short-term effects of
122 hydrophobicity that rapidly diminish in soil, and consequently to reflect long-term P leaching
123 conditions (Ojeda et al., 2015).

124 Five g of RH 700 were weighed into glass bottles (Pyrex, polypropylene pour ring), and 100 mL DI
125 water and 0.05 mL 2-octanol (solubility 1.1 g L⁻¹; 2-octanol-biochar weight ratio 0.04:100) surfactant
126 were added. The experiment was performed in triplicate, with the bottles shaken on an orbital shaker
127 at 150 rpm for 1.5 h.

128 The mixture was filtered with Whatman No.1 filter paper and the extracts analysed for pH (as in
129 section 2.2), electrical conductivity (EC) (Hach HQ40d portable meter, conductivity probe CDC 401)
130 and P (see section 2.3). The filter with retained biochar was dried in an oven overnight at 80°C. The
131 water-extraction extraction was repeated with the dried biochar and appropriate adjustment of DI
132 water and surfactant volume to maintain the same biochar mass-to-solution volume ratio. Overall, the

133 extraction procedure was performed 6 times with assessment of the parameters after the 1st, 2nd and 6th
134 extraction step.

135 **2.5 Ammonium nitrate extractions of ten biochars**

136 Calcium (Ca) is a key element that determines the availability of P in soil at elevated pHs. Therefore,
137 1 M NH₄NO₃-extractable P concentrations and total Ca concentration were determined in 10 different
138 biochars produced at 550°C to investigate the relationship between the parameters. Details of the
139 biochars, analytical procedures and the results have previously been reported (Buss et al., 2016a; b).
140 The following feedstocks were used: demolition wood (DW), *Arundo donax* (ADX), sugarcane
141 bagasse (SBI), water hyacinth (WHI), wheat straw (WSI), willow logs (WLB), winter rye straw
142 (WRB), *Salix purpurea* (SLP), *Paulonia tomentosa* (PAT) and residues from anaerobically digested
143 food waste (FWD).

144 **2.6 Data analysis**

145 A Shapiro-Wilk test of the P concentrations showed that the data (experiment section 2.2) were non-
146 normally distributed. However, since one-way ANOVAs are robust against violation of the normality
147 assumption (Schmider et al., 2010) they were conducted followed by Tukey post-hoc tests.

148 An exponential curve of type $f = a * e^{-b*x}$ was fitted to previously published data for total Ca
149 concentrations in 550°C biochars (Buss et al., 2016b) and % P availability based on NH₄NO₃
150 extractions (Buss et al., 2016a) using the least-square method. All statistical analyses were conducted
151 using SigmaPlot 13 (Systat Software Inc., Chicago, IL) and a significance level of $p < 0.05$.

152 **3 Results and Discussion**

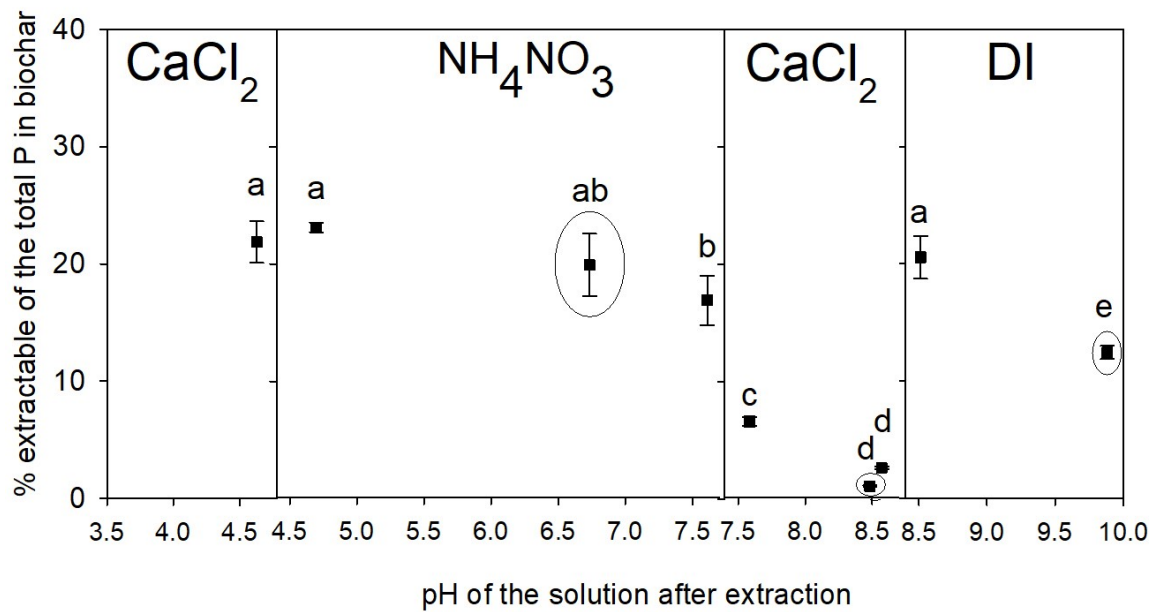
153 **3.1 Effect of pH on biochar P release**

154 In four of the nine extractions in the pH range 4.6 - 9.9 a similar proportion (~20%; not statistically
155 different) of the total P was extracted from the RH 700 biochar, independent of extractant and pH
156 (extractions indicated by “a” and “ab” in Figure 1). This is noteworthy since P becomes less available
157 in soils below pH 6.0 and between 7.5 and 9.0 (e.g. Ruyschaert et al. 2016) with the optimal P
158 availability at pH 6.0 - 6.5 (Blume et al., 2016). Below this range, P tends to bind to aluminum (Al)
159 and iron (Fe), while at higher pH it binds to Ca and Mg (Blume et al., 2016).

160 Our results suggest that inherent biochar P is released in equal amounts at pH 4.6, 6.7 and 8.6 in a
161 soil-free system. It is expected that the soil water environment (pH, cation composition and
162 concentration) will govern whether biochar-derived P can be utilised by plants, is leached or is
163 immobilised, e.g. Fe and Al will partially immobilise P at a pH of 4.6 (Blume et al., 2016). At an
164 extreme pH of 9.9, P availability assessed by DI water was significantly decreased to 12.5%,
165 compared to the DI extraction at lower pH (Figure 1). Furthermore, the NH_4NO_3 -extractable P was
166 significantly lower at a pH of 7.6 compared to lower pHs which can be explained by P precipitation as
167 struvite (Doyle and Parsons, 2002).

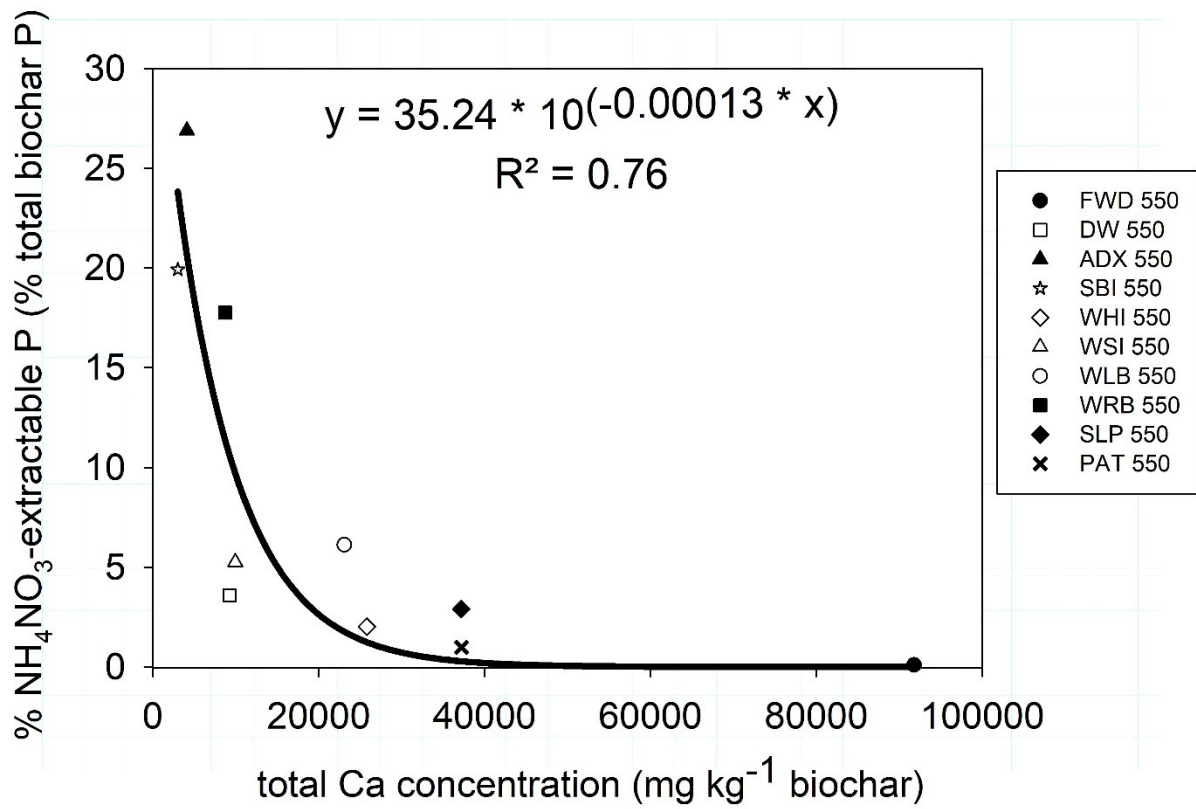
168 Repeated unbuffered DI water extraction was conducted with a lower biochar:solution ratio of 1:20,
169 smaller biochar particle size and a surfactant (see section 2.4) to assess the time-dependent P release.
170 In the 1st extraction step 16.6% of the total P present in RH 700 biochar was released and nearly 40%
171 after the 6th extraction step (Table 2). This indicates that P in our rice husk biochar is initially released
172 when extracted close to the native biochar pH (~9.5 in the first extraction step) and continues to be
173 released until at least 40% of the total P is extracted with potential further P release. These results
174 suggest that rice husk biochar is a suitable P fertiliser which is confirmed in other studies (e.g. Sun et
175 al., 2018).

176 Repeated extraction decreased the EC from $425 \pm 21 \mu\text{S cm}^{-1}$ in the initial extraction to $78 \pm 4 \mu\text{S cm}^{-1}$
177 after the 6th step (Table 2). At the same time, the solution pH gradually decreased, from 9.49 ± 0.12 to
178 8.83 ± 0.18 (Table 2).



179

180 Figure 1: Proportion of total P mass in RH 700 biochar (rice husk, 700°C) extracted using three different
 181 extractants (0.01 M CaCl₂, 1 M NH₄NO₃, deionised water (DI)) at different pH. All values are means and one
 182 standard deviation (n = 4). Unbuffered pH conditions (highlighted by the ellipses) and buffered pH conditions
 183 were used. The x-axis represents the pH values after the extraction (equal to the pH prior to extraction for
 184 buffered solutions, variable for unbuffered). Different lower-case letters indicate statistical differences
 185 determined via one-way ANOVA and Tukey post-hoc tests.



186

187 Figure 2: Relationship between % available of total P concentration in biochars determined via unbuffered 1 M
 188 NH_4NO_3 extractions and biochar total Ca concentration. Ten biochars produced at 550°C from ten different
 189 feedstocks are shown. Data based on Buss et al. (2016a, b). $R^2 = 0.76$, standard error of the estimate = 4.8762, p-
 190 value determined via ANOVA = 0.001.

191 **3.2 Effect of Ca on biochar P release**

192 The proportion of total P extracted from RH 700 biochar with CaCl₂ at a pH between 7.6 and 8.6 was
193 much lower than for other extractions, resulting in P release of only 1.1% (unbuffered pH), 2.9%
194 (buffered at pH 8.6) and 6.8% (buffered at pH 7.6) (Figure 1), whereas CaCl₂ at pH 4.6 extracted
195 21.9% of the total P. This clearly shows that the combination of CaCl₂ together with the higher pH
196 environment limits biochar P availability. At a pH between 7.5 and 9.0, P binds to Ca and forms di-
197 and tri-calcium phosphates (Chow, 2001; Blume et al., 2016). The low water solubility of these P
198 forms can result in precipitation on biochar surfaces as previously described for fast pyrolysis
199 biochars (Qian et al., 2013). At pH exceeding 9.0, di-calcium phosphates (anhydrous and dehydrate)
200 are more soluble (Chow, 2001).

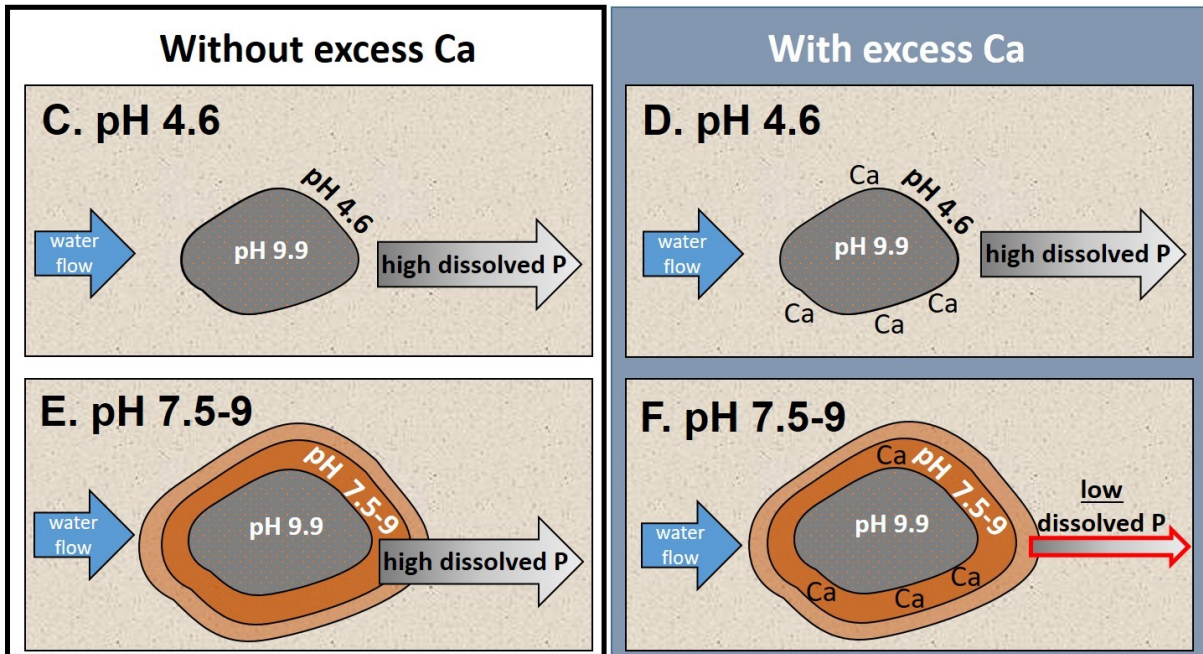
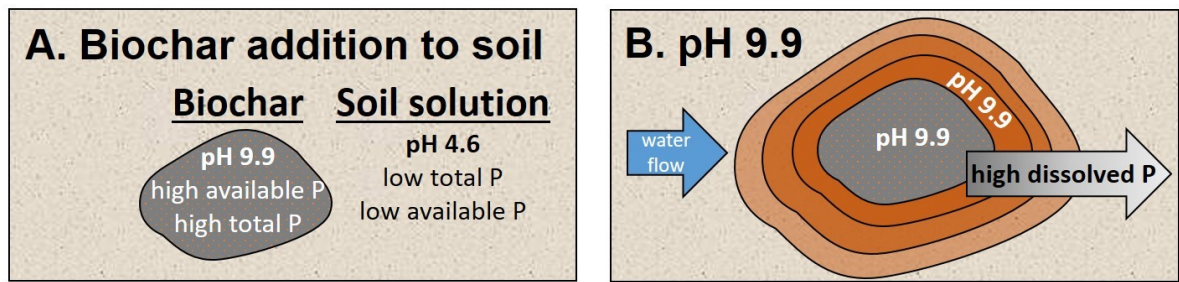
201 We investigated whether only external Ca immobilises P or whether internal Ca from the biochar
202 itself can immobilise P. Analysis of previously published data for 10 biochars (produced at 550°C to
203 exclude any effect of pyrolysis temperature) showed that higher biochar total Ca concentrations (Buss
204 et al., 2016b) are significantly associated with decreasing 1 M NH₄NO₃-extractable P (Buss et al.,
205 2016a) ($R^2 = 0.76$, $p = 0.001$; Figure 2). It is likely that calcium phosphates formed either during
206 pyrolysis and/or after initial P release from biochar which subsequently precipitated with biochar Ca.

207 The RH 700 biochar has a Ca concentration of ~1700 mg kg⁻¹ and released 19.9% of total P when
208 extracted under the conditions used to define the relationship above (unbuffered 1 M NH₄NO₃, final
209 pH 6.7) which fits well with the general exponential model (Figure 2). This provides strong evidence
210 that biochar P can be rendered unavailable through the effect of Ca supplied externally from the soil
211 solution or from within biochar itself. Ca concentrations in biochar below 1% are recommended
212 which is a threshold value where the concentration of available P increased drastically in our study.

213 Table 2: Quantitative and cumulative P release, solution pH and solution electrical conductivity (EC) for RH
 214 700 (rice husk, 700°C) biochar after extraction with unbuffered DI water in six repeated extractions. Means and
 215 one standard deviation depicted with n = 3.

| extraction step | biochar P released | | pH | EC |
|-----------------|----------------------------------|-----------------------------|-------------|----------------------------------|
| | mg kg ⁻¹ mean ± SD | % of total P, cumulative | mean ± SD | μS cm ⁻¹ mean ± SD |
| 1 | 258 ± 2.9 | 16.6 | 9.49 ± 0.12 | 425 ± 20.5 |
| 2 | 137 ± 2.4 | 25.4 | 9.57 ± 0.05 | 221 ± 15.3 |
| 6 | 34 ± 0.8 | 38.9 | 8.83 ± 0.18 | 77.8 ± 4.2 |

216



219 Figure 3: Model for P release from alkaline biochar in an acidic, nutrient-poor soil showing different scenarios
 220 of biochar-soil interaction with and without excess Ca (originating from the soil solution or from the biochar
 221 itself). The biochar-soil interface pH is depicted in each figure in the upper left-hand corner. Panel A shows the
 222 initial state when biochar is added to soil. In B the development of a pH gradient between biochar and the soil
 223 due to ash leaching out of biochar is depicted (concentric rings) which increases the pH at the biochar-soil
 224 interface. Scenarios C and D represent a well buffered soil environment so there is no pH gradient between the
 225 biochar particle, in contrast to less buffered conditions in scenarios E and F.

226 **3.3 A model for P release as affected by biochar-soil pH gradient** 227 **and Ca concentration**

228 Our results demonstrate that P release from biochar is limited by the same factors that govern P
229 availability in soil. The difference is, however, that when biochar is applied to soil, soil solution
230 composition and pH are affected by both soil and biochar. Therefore, here we propose a conceptual
231 model to delineate the P release from rice husk biochar when applied to acidic soil with different
232 buffering capacity as affected by CEC, soil texture and mineralogy. The starting conditions after
233 biochar addition to the soil are shown in Figure 3A.

234 The pH at the interface of biochar and soil is expected to be determined by the pH of the biochar
235 resulting from migration of soluble alkaline elements from biochar ash (Figure 3B). These
236 components lead to a pH gradient developing around the biochar particle reflecting the limited
237 buffering capacity of strongly weathered or sandy soils. Under these conditions with pH at the soil-
238 biochar interface similar to the biochar pH measured in water (9.9), P flows readily (12.5% of P
239 extracted), although not as readily as at lower pH.

240 In a well buffered soil environment, such as a clay soil, where bulk soil pH is barely affected by
241 biochar pH, there is no pH gradient and the pH surrounding the biochar will be governed by soil pH
242 (Figure 3C). Our results suggest that in this scenario, biochar P will be released initially (20% of total
243 P in our study). However, it will depend on the composition of soil and soil solution (in particular Al
244 and Fe) whether the P continues to be released or becomes immobilised (Blume et al., 2016). Excess
245 Ca from the soil solution or leached from the biochar in this case would not affect the P release
246 (Figure 3D) since the solubility of calcium phosphates is high at low pH (Chow, 2001).

247 A scenario between these two extremes is likely in most situations, for a soil with average buffering
248 capacity. Here a gradient of pH develops between the biochar and the soil, and the resulting pH
249 around the biochar will be in the range 4.6–9.9. P will be readily released independent of Ca, Fe and
250 Al in soil solution at a pH between 6.0 and 7.0 (Blume et al., 2016; Ruyschaert et al., 2016). When
251 the pH around the biochar is in the range ~7.5–9.0 (Figure 3E), it can be assumed that P moves

252 readily from biochar to soil. In contrast, a high concentration of Ca around the biochar in combination
253 with a pH of ~7.5–9.0 (Figure 3F) may lead to very low availability and delivery of P to the soil
254 (around 1% of total P) due to the precipitation of calcium phosphates. The excess Ca needed for P
255 precipitation can originate from the soil solution (represented in our study by the CaCl₂ extractions) or
256 from the biochar itself (demonstrated by the relationship between biochar extractable P and biochar
257 total Ca). Biochars typically display pHs of 7–11 (Qambrani et al., 2017) and it is highly likely that in
258 biochar-amended soil the pH at the soil-biochar interface will be 7.5–9.0, leading to P precipitation.
259 The key unknown then concerns the effect of direct interaction between plant roots and the biochar
260 interface, and whether the biochar composition can be manipulated, in order to maximise transfer of
261 recycled P. Characterising P-Ca speciation in biochar using XANES (e.g. Liang et al. (2017)) could
262 facilitate further understanding of the mechanisms and controls on P release from biochar.

263 **4 Conclusion**

264 The release of P in biochar was reduced at a pH of 7.5-9.0 and when excess Ca was present. We
265 anticipate that biochar total Ca concentration will provide a good predictor of its P availability. To
266 increase the P delivery, low Ca concentrations (<1%) in biochar and/or a pH lower than ~7.5 are
267 required. Conversely, higher Ca concentrations support some chemical restriction on biochar P
268 release. Whilst based on results for one biochar only, the new conceptual model proposed here
269 provides a framework that can be developed further to assess the potential of different biochars to
270 provide P for crops under different soil pH and buffering conditions.

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276 **Supplemental material.** Supplemental material contains results of tests of DEPP buffer concentration
277 on extractable nutrients from biochar (Supplemental Table S1).

278 **5 References**

- 279 Angst, T.E., and S.P. Sohi. 2013. Establishing release dynamics for plant nutrients from biochar. *GCB*
280 *Bioenergy* 5(2): 221–226. doi: 10.1111/gcbb.12023.
- 281 Biederman, L.A., and W.S. Harpole. 2013. Biochar and its effects on plant productivity and nutrient
282 cycling: a meta-analysis. *GCB Bioenergy* 5(2): 202–214. doi: 10.1111/gcbb.12037.
- 283 Blume, H.-P., G.H. Brümmer, H. Fleige, R. Horn, E. Kandeler, I. Kögel-Knabner, R. Kretschmar, K.
284 Stahr, and B.-M. Wilke. 2016. Chapter 9: Soil-plant relations. p. 409–484. *In*
285 Scheffer/Schachtschabel: Soil Science. Springer, Berlin, Heidelberg.
- 286 Buss, W., M.C. Graham, J.G. Shepherd, and O. Mašek. 2016a. Risks and benefits of marginal
287 biomass-derived biochars for plant growth. *Sci. Total Environ.* 569–570: 496–506. doi:
288 10.1016/j.scitotenv.2016.06.129.
- 289 Buss, W., M.C. Graham, J.G. Shepherd, and O. Mašek. 2016b. Suitability of marginal biomass-
290 derived biochars for soil amendment. *Sci. Total Environ.* 547: 314–322. doi:
291 doi:10.1016/j.scitotenv.2015.11.148.
- 292 Buss, W., and O. Mašek. 2014. Mobile organic compounds in biochar – a potential source of
293 contamination – phytotoxic effects on cress seed (*Lepidium sativum*) germination. *J. Environ.*
294 *Manage.* 137: 111–119. doi: 10.1016/j.jenvman.2014.01.045.
- 295 Buss, W., J.G. Shepherd, K. V. Heal, and O. Mašek. 2018. Spatial and temporal microscale pH
296 change at the soil-biochar interface. *Geoderma* 331(April): 50–52. doi:
297 10.1016/j.geoderma.2018.06.016.
- 298 Chow, L.C. 2001. Solubility of Calcium Phosphates. p. 94–111. *In* LC, C., ED, E. (eds.), *Octacalcium*
299 *Phosphate. Monographs in Oral Science* Basel, Karger.
- 300 Doyle, J.D., and S.A. Parsons. 2002. Struvite formation, control and recovery. *Water Res.* 36(16):
301 3925–3940. doi: 10.1016/S0043-1354(02)00126-4.
- 302 Farrell, M., G. Rangott, and E. Krull. 2013. Difficulties in using soil-based methods to assess plant
303 availability of potentially toxic elements in biochars and their feedstocks. *J. Hazard. Mater.* 250–
304 251: 29–36. doi: 10.1016/j.jhazmat.2013.01.073.
- 305 Gray, M., M.G. Johnson, M.I. Dragila, and M. Kleber. 2014. Water uptake in biochars: The roles of
306 porosity and hydrophobicity. *Biomass and Bioenergy* 61: 196–205. doi:
307 10.1016/j.biombioe.2013.12.010.
- 308 Harvey, O.R., B.C. Leonce, and B.E. Herbert. 2018. A Flow Adsorption Microcalorimetry-Logistic

309 Modeling Approach for assessing heterogeneity of Bronsted-type surfaces: Application to
310 Pyrogenic Organic Materials. *Environ. Sci. Technol.* doi: 10.1021/acs.est.8b00104.

311 Liang, X., Y. Jin, M. He, C. Niyungeko, and J. Zhang. 2017. Phosphorus speciation and release
312 kinetics of swine manure biochar under various pyrolysis temperatures. *Environ. Sci. Pollut.*
313 *Res.* published.

314 Liu, Z., B. Dugan, C.A. Masiello, and H.M. Gonnermann. 2017. Biochar particle size, shape, and
315 porosity act together to influence soil water properties. *PLoS One* 12(6): 1–19. doi:
316 10.1371/journal.pone.0179079.

317 Mašek, O. 2014. UKBRC Standard Biochar specification sheet RH700, v. 1.0. accessed 08/12/2017.
318 https://www.biochar.ac.uk/standard_materials.php.

319 Mašek, O., W. Buss, A. Roy-Poirier, W. Lowe, C. Peters, P. Brownsort, D. Mignard, C. Pritchard, and
320 S. Sohi. 2018. Consistency of biochar properties over time and production scales: A
321 characterisation of standard materials - Available online 24 February 2018. *J. Anal. Appl.*
322 *Pyrolysis* 132: 200–210. doi: 10.1016/j.jaap.2018.02.020.

323 Ojeda, G., S. Mattana, A. Àvila, J.M. Alcañiz, M. Volkmann, and J. Bachmann. 2015. Are soil-water
324 functions affected by biochar application? *Geoderma* 249–250: 1–11. doi:
325 10.1016/j.geoderma.2015.02.014.

326 Qambrani, N.A., M.M. Rahman, S. Won, S. Shim, and C. Ra. 2017. Biochar properties and eco-
327 friendly applications for climate change mitigation, waste management, and wastewater
328 treatment: A review. *Renew. Sustain. Energy Rev.* 79(November 2016): 255–273. doi:
329 10.1016/j.rser.2017.05.057.

330 Qian, T., X. Zhang, J. Hu, and H. Jiang. 2013. Effects of environmental conditions on the release of
331 phosphorus from biochar. *Chemosphere* 93(9): 2069–2075. doi:
332 10.1016/j.chemosphere.2013.07.041.

333 Ruyschaert, G., V. Nelissen, R. Postma, E. Bruun, A. O’Toole, J. Hammond, J. Rödger, L. Hylander,
334 T. Kihlberg, K. Zwart, H. Hauggaard-Nielsen, and S. Shackley. 2016. Field applications of pure
335 biochar in the North Sea region and across Europe. p. 99–135. *In* *Biochar in European Soils and*
336 *Agriculture: Science and Practice*.

337 Sari, H., and A.K. Covington. 2005. Dissociation constants of morpholino- and piperidino-
338 methylphosphonic acids and stability constants of their copper, nickel, and zinc complexes. *J.*
339 *Chem. Eng. Data* 50(4): 1438–1441. doi: 10.1021/je0500983.

340 Schmider, E., M. Ziegler, E. Danay, L. Beyer, and M. Bühner. 2010. Is it really robust?

341 Reinvestigating the robustness of ANOVA against violations of the normal distribution
342 assumption. *Methodology* 6: 147–151.

343 Shepherd, J.G., W. Buss, S.P. Sohi, and K. V. Heal. 2017. Bioavailability of phosphorus, other
344 nutrients and potentially toxic elements from marginal biomass-derived biochar assessed in
345 barley (*Hordeum vulgare*) growth experiments. *Sci. Total Environ.* 584–585: 448–457. doi:
346 10.1016/j.scitotenv.2017.01.028.

347 Shepherd, J.G., S.P. Sohi, and K. V. Heal. 2016. Optimising the recovery and re-use of phosphorus
348 from wastewater effluent for sustainable fertiliser development. *Water Res.* 94: 155–165. doi:
349 10.1016/j.watres.2016.02.038.

350 Sun, D., L. Hale, G. Kar, R. Soolanayakanahally, and S. Adl. 2018. Phosphorus recovery and reuse by
351 pyrolysis: Applications for agriculture and environment. *Chemosphere* 194: 682–691. doi:
352 10.1016/j.chemosphere.2017.12.035.

353 Yu, Q., A. Kandegedara, Y. Xu, and D.B. Rorabacher. 1997. Avoiding interferences from Good's
354 buffers: A contiguous series of noncomplexing tertiary amine buffers covering the entire range
355 of pH 3-11. *Anal. Biochem.* 253(1): 50–56. doi: 10.1006/abio.1997.2349.

356 Zhang, H., C. Chen, E.M. Gray, S.E. Boyd, H. Yang, and D. Zhang. 2016. Roles of biochar in
357 improving phosphorus availability in soils: A phosphate adsorbent and a source of available
358 phosphorus. *Geoderma* 276: 1–6. doi: 10.1016/j.geoderma.2016.04.020.

359