SUPPORTING INFORMATION

for the article

Tailoring the phosphorus release from biochar-based fertilizers: role of magnesium or calcium addition during co-pyrolysis

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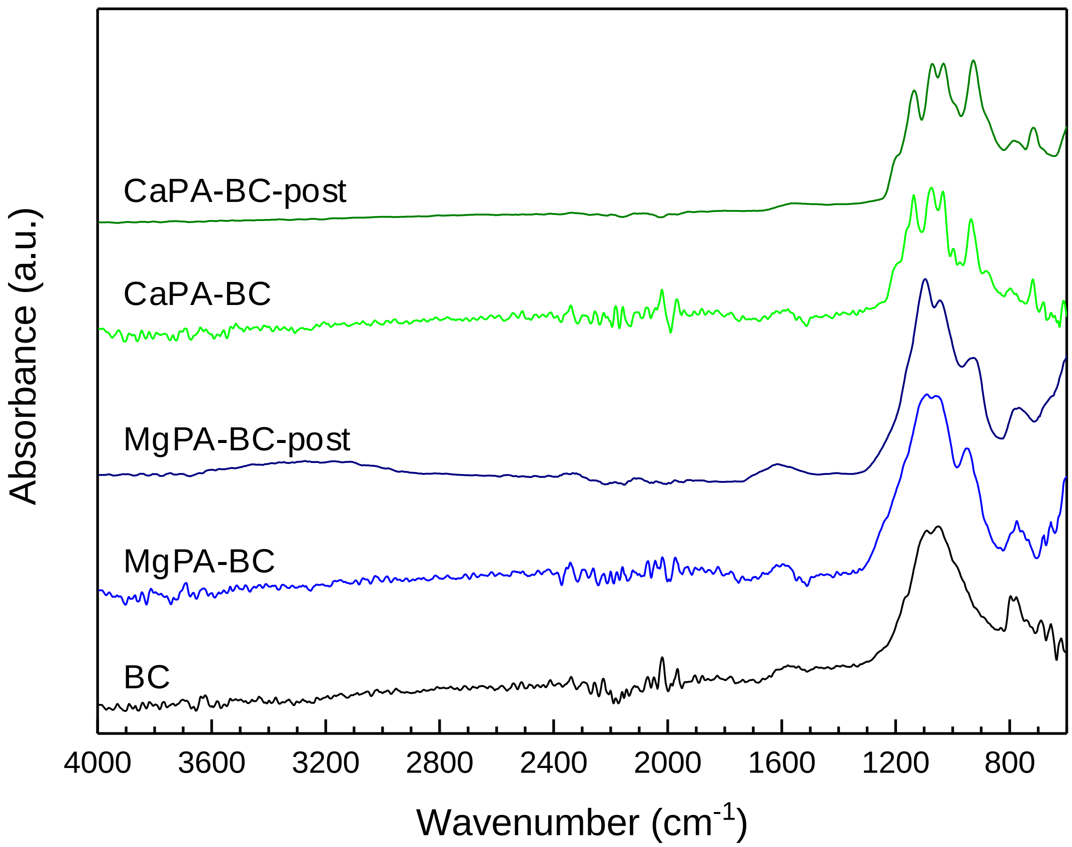

Fig. S1. FTIR spectra (4000-600 cm^{-1}) of pristine BC and MgPA-BC and CaPA-BC, and the modified biochars after the 240 hours kinetic release experiment (MgPA-BC-post and CaPA-BC-post, respectively).

Table S1. Equations that were used to model the P release from the biochars.

Model	**Equation**
Zero order	$q_t = a_0 + k_0 t$
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$
Elovich	$q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t$
Parabolic diffusion	$q_t = A + R \cdot t^{1/2}$
Power model	$\ln q_t = \ln a + b \ln t$

Note: q_t (g·kg^{-1}) is the P released at time t; q_e (g·kg^{-1}) is the P released at equilibrium, a_0 (g·kg^{-1}) is a constant; k_0 (h^{-1}), k_1 (h^{-1}), and k_2 (kg·g^{-1}·h^{-1}) are rate constants; α (g·kg^{-1}·h^{-1}) is a constant describing initial P release; β (kg·g^{-1}) is a release constant; R (mg·g^{-1}·h$^{-0.5}$) is the intraparticle diffusion rate; A (g·kg^{-1}) is a constant proportional to the boundary layer thickness; a (g·kg^{-1}·h^{-b}) is a constant describing the initial P release; b (-) is a release constant that indicates the variation in release rate over time.

Table S2. Solubility products (K_{sp}) that were used to calculated the solubility of the Mg phosphates and Ca phosphates.

Compound	**Reaction**	**K_{sp}**	**Reference**
$Mg_3(PO_4)_2{\cdot}22H_2O$	$3Mg^{2+} + 2PO_4^{3-} \Leftrightarrow Mg_3(PO_4)_2 \cdot 22H_2O$	23.10	Lindsay[1]
$Mg_3(PO_4)_2{\cdot}8H_2O$	$3Mg^{2+} + 2PO_4^{3-} \Leftrightarrow Mg_3(PO_4)_2 \cdot 8H_2O$	25.00	Lindsay[1]
$Mg_3(PO_4)_2$	$3Mg^{2+} + 2PO_4^{3-} \Leftrightarrow Mg_3(PO_4)_2$	25.20	Krauskopf[2]
$MgHPO_4{\cdot}3H_2O$	$Mg^{2+} + HPO_4^{2-} \Leftrightarrow MgHPO_4 \cdot 3H_2O$	5.82	Taylor et al.[3]
$MgNH_4PO_4{\cdot}6H_2O$	$NH_4^{+} + Mg^{2+} + PO_4^{3-} \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O$	13.20	Lindsay[1]
$MgKPO_4{\cdot}6H_2O$	$K^{+} + Mg^{2+} + PO_4^{3-} \Leftrightarrow MgKPO_4 \cdot 6H_2O$	10.60	Lindsay[1]
α-$Ca_3(PO_4)_2$	$3Ca^{2+} + 2PO_4^{3-} \Leftrightarrow \alpha\text{–}Ca_3(PO_4)_2$	25.50	Lindsay[1]
β-$Ca_3(PO_4)_2$	$3Ca^{2+} + 2PO_4^{3-} \Leftrightarrow \beta\text{–}Ca_3(PO_4)_2$	28.90	Lindsay[1]
$Ca_{10}(OH)_2(PO_4)_6$	$10Ca^{2+} + 6PO_4^{3-} \Leftrightarrow 2H^{+} + Ca_{10}(OH)_2(PO_4)_6$	88.40	Lindsay[1]
$Ca_8H_2(PO_4)_6{\cdot}5H_2O$	$8Ca^{2+} + 6PO_4^{3-} \Leftrightarrow 2H^{+} + Ca_8H_2(PO_4)_6 \cdot 5H_2O$	80.60	Lindsay[1]
$CaHPO_4{\cdot}2H_2O$	$Ca^{2+} + H^{+} + PO_4^{3-} \Leftrightarrow CaHPO_4 \cdot 2H_2O$	18.92	Lindsay[1]
$CaHPO_4$	$Ca^{2+} + H^{+} + PO_4^{3-} \Leftrightarrow CaHPO_4$	19.24	Lindsay[1]

Table S3. The pH and dissolved concentrations of P (before and after persulfate digestion) and additive element (Mg or Ca) after 240 hours in DI water. Values in brackets indicate percentages of total element in the biochar that has been dissolved.

Material	pH (-)	P ($mg{\cdot}L^{-1}$)	P (persulfate digestion) ($mg{\cdot}L^{-1}$)	Mg or Ca ($mg{\cdot}L^{-1}$)
MgPA-BC	8.4±0.1	49.6±1.4 (13%)	80.5±4.8 (22%)	Mg: 34.3±1.5 (17%)
CaPA-BC	7.4±0.1	6.1±0.5 (1.7%)	7.0±0.3 (1.9%)	Ca: 2.5±0.3 (0.5%)

Additional references:

1. W. Lindsay, *Chemical equilibria in soils*, Wiley, New York, 1979.
2. K. B. Krauskopf, *Introduction to geochemistry*, McGraw-Hill, New York, 2nd edn., 1979.
3. A. W. Taylor, A. W. Frazier, E. L. Gurney and J. P. Smith, *Trans. Faraday Soc.*, 1963, **59**, 1585-1589.