

# Biochar-induced soil stability influences phosphorus retention in a temperate agricultural soil

Vanita Sachdeva<sup>a</sup>, Naseer Hussain<sup>a</sup>, Barry R. Husk<sup>b</sup>, Joann K. Whalen<sup>a,\*</sup>

<sup>a</sup> Department of Natural Resource Sciences, Macdonald Campus of McGill University, Ste-Anne-de-Bellevue, Quebec H9X 3V9, Canada

<sup>b</sup> BlueLeaf Inc., Drummondville, Quebec J2B 5E9, Canada

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## ABSTRACT

Surface runoff from agricultural fields is the largest non-point source of phosphorus (P) that pollutes surface water in humid temperate regions. Best management practices have attempted to reduce P loading and improve P retention in agricultural soils, but significant losses continue to occur, emphasizing the need for novel solutions. The objective of this study was to determine whether wood-based biochars applied to an agricultural field, 3 years earlier, could reduce P loss in surface runoff by increasing water infiltration or by improving soil stability. Field plots amended with Dynamotive, Basques and Pyrovac biochars (5 and 10 t ha<sup>-1</sup>) or without biochar were subjected to 30-min of simulated rainfall to determine runoff volume, time-until-ponding, infiltration rate, and water holding capacity, as well as the P concentration and P load in runoff. The distribution of soil macro- and micro-aggregates and their total organic C and total P content was measured. Soil water dynamics were not affected by biochar amendments, however, runoff contained significantly less ortho-P in field soil amended with Dynamotive and Basques biochar at 5 t ha<sup>-1</sup> and significantly less particulate P when amended with biochar at 10 t ha<sup>-1</sup>. Biochar-amended soil had significantly greater microaggregate stability, organic C and total P content than the control soil without biochar. The reduction in particulate P concentration in runoff may be the result of biochar integration within the microaggregate structure, which indirectly promotes P retention in macro-aggregates.

## 1. Introduction

Dissolved P and particulate P compounds in fertilized agricultural soils are susceptible to transport through hydrologic pathways to aquatic ecosystems. Globally, as much as 60% of the annual P load in waterways may originate from agricultural runoff (Jamieson et al., 2003; Macintosh et al., 2018). One way to reduce P loss through runoff is to increase water infiltration. Jamieson et al. (2003) reported that water infiltrating through soil profile that drained through subsurface outlets had 80% lower P concentration than surface runoff. Agricultural soils with tile drainage systems have greater water-holding capacities (WHC) and higher hydraulic conductivity in the soil profile than undrained soils, which increases water infiltration and prevents saturation (Renck and Lehmann, 2004). Therefore, farm managers may rely on tile drainage systems to improve water infiltration, increase WHC, and expedite drainage to reduce runoff volume and lower the P load associated with runoff (Sprague and Gronberg, 2012). Still, the agricultural sector is responsible for an estimated 50% of the non-point source P load entering aquatic ecosystems globally (Carpenter et al., 1998; Ortiz-

Reyes and Anex, 2018), therefore solutions are needed to reduce P loss from agricultural fields.

Biochar is an emerging soil amendment with potential to modify soil water dynamics. It can hold water within its micro- and mesopores and increase infiltration by contributing to the formation of soil macropores and soil macroaggregates, which expands the soil pore network (Renck and Lehmann, 2004; Asai et al., 2009; Basso et al., 2013). The WHC of a sandy-loam soil increased by 57% when amended with 5% (w/w) of pine biochar prepared by slow pyrolysis at 450 °C (Briggs et al., 2012). In addition, biochar is implicated in the formation of de novo soil macropores and soil macroaggregates, which increases soil porosity and leads to greater water infiltration. For instance, water infiltration increased by 112% in a Norfolk fine-loam soil amended with 2% (w/w) of pine chip biochar pyrolyzed at 500 °C (Novak et al., 2016). As the biochar-mediated increase in soil porosity is expected to facilitate water infiltration, biochar-amended soils may have a lower water volume and smaller P load in agricultural runoff (Bronick and Lal, 2005). Beck et al. (2011) reported that the total P concentration in green roof discharge water was reduced by as much as 52% with soil containing 7% biochar,

\* Corresponding author.

E-mail address: [joann.whelan@mcgill.ca](mailto:joann.whelan@mcgill.ca) (J.K. Whalen).

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compared to the unamended control soil.

Biochar has capacity to adsorb and retain P compounds, which is another way that biochar amendments may reduce the P load in agricultural runoff. Zhang et al. (2016) observed a 16% increase in P retention ability in soils amended with hardwood biochar (5% w/w; produced from *Eucalyptus polybractea* at 720 °C) after treatment with 200 mg P L<sup>-1</sup> phosphate solution. The reactive surface of biochar can directly sorb phosphate ions to anion exchange sites on the biochar surface (Chen et al., 2011; Hale et al., 2013) or via associated organo-minerals, clay, and cation bridges (Laird et al., 2010). Biochars that contribute to the formation of soil macroaggregates may indirectly increase P retention, as greater aggregation should stabilize the soil matrix and reduce the water-erodible particulate P fraction associated with total suspended solids (> 0.053 mm) in runoff. Whether biochar-mediated P stabilization occurs at the field scale is unknown, and warrants investigation.

The objectives of this study were to determine whether biochar can (1) reduce P loss from runoff by increasing the soil infiltrability and WHC and (2) increase P retention through the formation of soil aggregates. The study occurred on a clay-loam agricultural soil in a humid, temperate climate that was amended with wood-based biochar in 2010, three years before this study was conducted. We hypothesized that (1) biochar-amended soil will have greater water infiltration and lower P concentrations in runoff than unamended soil, and (2) biochar-amended soil will have more macroaggregates with greater P content than unamended soil.

## 2. Methods and materials

### 2.1. Experimental site, soil and biochar

The experimental site was located on a working dairy farm in the St. Francis River watershed, Quebec (45°30' N, 72°01' W, elevation 243 m). The monthly mean temperatures ranged from -10 °C in January to 21 °C in July, with a mean annual precipitation of 1230 mm, based on a 30 yr average data (1980–2010) from Environment Canada (2012). The soil is part of the Brompton stony loam series, classified as a poorly drained Podzol (Lamontagne and Nolin, 1997). Soil surface (0–12 cm) is a black loam above a compact grey white sandy loam with many small stones (5–17 cm). Surface soil contains 190 g kg<sup>-1</sup> of clay, 380 g kg<sup>-1</sup> of sand, and 430 g kg<sup>-1</sup> of silt, with 33 g total C kg<sup>-1</sup>, 2.3 g total N kg<sup>-1</sup>, 5.2 g total P kg<sup>-1</sup> and pH of 5.9. Biochar from three suppliers – Dynamotive, Pyrovac, and Basques – were used in the study. Substrate used for the production of biochar, production process and the physico-chemical characteristics of biochar are detailed in Table 1.

### 2.2. Experimental design

The experimental field was established in May 2010 in a farm field that was conventionally tilled and amended with a single application of biochar applied by hand-weighing and spreading. Experimental treatments were arranged in a randomized complete block design and

**Table 1**

Physical and chemical properties of biochar applied to agricultural field plots in the St. Francis River watershed, Quebec, Canada.

	Dynamotive	Pyrovac	Basques
Feedstock	Hardwood	Softwood bark	Hardwood
Pyrolysis temperature	> 500 °C	> 500 °C	< 500 °C
Texture	Fine powder	Granular	Powder
pH	8.6	8.3	7.8
Organic Carbon, g kg <sup>-1</sup>	740	460	670
Total Nitrogen, g kg <sup>-1</sup>	4.2	5.9	5.1
Total Phosphorus, mg kg <sup>-1</sup>	300	978	1763
Ash content, g kg <sup>-1</sup>	9.80	44.2	10.9

included three biochar types (Dynamotive, Pyrovac, and Basques) applied at two rates (5 and 10 t biochar ha<sup>-1</sup>) plus an unamended control (0 t biochar ha<sup>-1</sup>). There were three blocks (replicates) with these treatments, for a total of 21 field plots. The plot size was 5 × 6 m with 1 m buffer between each plot and 2 m between each block. The year before this study, in 2011, the field was sown with mixed cereals (oat/barley; *Avena sativa*/*Hordeum vulgare*). Crops were fertilized with inorganic NPK fertilizers plus dairy cattle slurry according to crop-specific provincial recommendations (CRAAQ, 2010) and other agronomic practices such as weed and pest control were done according to the farmers' usual practice.

### 2.3. Rainfall simulation and infiltration rate

A portable rainfall simulator (Cornell Sprinkle Infiltrometer, Cornell University, Ithaca, United States) was used to determine soil infiltrability and collect runoff from the soil surface of each field plot in the spring, before seeding, when soil was bare and most vulnerable to surface erosion. As described by Ogden et al. (1997), the simulator was an airtight 20 L vessel filled with water that sits on a metal ring (457.3 cm<sup>2</sup>) inserted at a depth of 7 cm equipped with capillary tubes that delivered water from a height of 15 cm above the soil surface. In this study, the rainfall rate ( $r_f$ ) was adjusted to 25–30 cm h<sup>-1</sup> to ensure ponding for each measurement. Each simulation lasted 30 min ( $T_f$ ), with runoff water samples collect every 6 min in 125 mL polycarbonate bottles. Water samples were transported in a cooler with icepacks to the laboratory and stored in a 4 °C fridge prior to analysis. Total volume of simulated rain used on each plot ( $V_t$ , in L), the time to ponding, and the volume of runoff ( $V_{ro}$ , in mL) were measured to calculate runoff rate ( $ro_t$ , L min<sup>-1</sup>) and soil infiltration ( $i_t$ , mL cm<sup>-2</sup> h<sup>-1</sup>), according to Ogden et al. (1997).

### 2.4. P measurements in water samples

Phosphorus concentration was determined in composite water samples, made from equal volumes of water collected at each 6-minute interval during the simulation. We prepared samples for total P (TP), dissolved P (DP) and particulate P (PP) concentrations following the APHA (1992) method. The digested (filtered and unfiltered) and undigested water samples were analyzed with the malachite green method (D'Angelo et al., 2001) at 650 nm using a microplate reader (Biotech, Winooski, USA, Model EL312). The P load (mg) in runoff generated during the rainfall simulation was the TP concentration in runoff (mg TP L<sup>-1</sup>) × runoff volume (L).

### 2.5. Aggregate size fractionation

Soil samples collected from each plot at 15 cm depth were sieved through 6 mm mesh sieve and distributed evenly atop a sequentially arranged nest of mesh sizes 2 mm, 0.85 mm, 0.5 mm, 0.25 mm, and 0.15 mm. The sieves were then gently submerged in distilled water for 10 min to hydrate the soil samples. After the soil was moistened, aggregates were separated by repeatedly moving the sieves vertically 29 times per minute for 10 min, using an apparatus similar to that described by Kemper and Rosenau (1986). At the end of wet-sieving, the soil remaining on each sieve was collected, dried at 105 °C for 24 h, and weighed. Soils were considered large macroaggregates if in the range > 2 mm, small macroaggregates in the range 0.25–2 mm, microaggregates at 0.15 mm and the soil that passed through all the sieves was considered as unaggregated soil.

Subsamples from each soil aggregate fraction were analyzed for C and P content. Organic C was determined using a Flash EA 1112 NC soils analyzer (Carlo-Erba, Milan, Italy), assuming that total C was equivalent to organic C. For determination of the total P content, soil samples were digested with H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, and analyzed colorimetrically using a Lachat Quick-Chem AE flow injection auto analyzer (Lachat

Instruments, Milwaukee, WI, United States; Parkinson and Allen, 1975). Total P digestions cannot discern P originating from the biochar or soil, so to correct biochar added P the C differential between amended and non-amended soil was attributed to biochar and the expected P content from the present biochar was extrapolated using the P values from the biochar analysis. The difference between total P and biochar-P was assumed to be increased P-laden clay sediments, organic matter, or microbial matter.

Fractionated soil samples underwent further dispersion with 50 mL of 0.5% (w/v) sodium hexametaphosphate solution by shaking at 60 rpm for 45 min. The samples were then passed through the same sieves to extract the water-stable aggregates, dried and weighed. The water-stable aggregates (WSA<sub>i</sub>, expressed as a % for each aggregate fraction) and mean weight diameter (MWD, in mm) were calculated according to Van Bavel (1949):

$$WSA_i = \frac{w_{2i} - w_{3i}}{\frac{w_1}{1 + w_c} - \sum_{i=1}^n w_{3i}} \quad (1)$$

$$MWD = \sum_{i=1}^n x_i WSA_i \quad (2)$$

A modification was made to the W3i variable to compensate for the subsample taken for the C and P analyses. The percentage of soil lost during the dispersion was calculated and was used to estimate the original weight of the W3i fraction.

## 2.6. Statistical analysis

The effects of biochar type and biochar application rate on soil water dynamics, P concentration, aggregate distribution and strength, and C and P content was determined by analysis of variance (ANOVA), following the procedure of Piepho et al. (2006) to accommodate the untreated controls in the 3 × 2 factorial structure. Normal distribution of the residuals was verified using the UNIVARIATE procedure and the percentage distribution data for the aggregates were log transformed before evaluation by ANOVA. When the main effect was significant ( $p < 0.05$ ), means were compared with a post-hoc Tukey's test using SAS statistical software (version 9.2, SAS Institute Inc., Cary, NC). Pre-planned orthogonal contrasts were done to compare the effect of biochar type, biochar rate, and biochar versus the unamended control, which were considered significant at  $\alpha < 0.05$ .

## 3. Results and discussion

### 3.1. P loss and water infiltration

Total P concentration in runoff was significantly lower than controls in the soil amended with Dynamotive and Pyrovac biochar at 5 and 10 t ha<sup>-1</sup>, and in Basques biochar at 10 t ha<sup>-1</sup> (Table 2). Particulate P was significantly lower in all the biochar treatments at 10 t ha<sup>-1</sup>, while no difference was observed in DP concentrations between biochar-amended and unamended plots except Dynamotive biochar at 5 t ha<sup>-1</sup>. The water dynamics in terms of moisture content, time-until-ponding, runoff volume, and infiltration rate in biochar-amended soil were not significantly different than the controls, therefore no effect was observed on the P load (Supplementary table S1).

Contrary to the hypothesis that biochar-amended soil would exhibit greater water infiltration and WHC and hence reduce the P loss in runoff, the results showed no significant effect of biochar on soil water dynamics. There are two explanations for this finding: 1) biochar application rates were not sufficiently high (0.23 and 0.45%; w/w), compared to application rates in other studies (2 to 45%, which is equivalent to 45 to 1080 t ha<sup>-1</sup>), to induce changes in soil water dynamics (Joseph et al., 2010; Kinney et al., 2012; Novak et al., 2012; Basso et al., 2013); 2) biochar micropores, which adsorb and retain water molecules, were obstructed with silt, clay or organic particles and

**Table 2**

Total phosphorus (TP), dissolved phosphorus (DP) and particulate phosphorus (PP) loss in runoff from simulated rainfall applied with a Cornell Sprinkle Infiltrometer to biochar-amended field plots in the St. Francis River watershed, Quebec, Canada. Values for each treatment are the mean ± standard deviation ( $n = 5$ ). Results with the same letter are not significantly different ( $p < 0.05$ ), with a post-hoc Tukey's test. NS = not significant ( $p > 0.05$ ).

Biochar treatments		P concentration loss (mg L <sup>-1</sup> )		
Type	Rate (t ha <sup>-1</sup> )	TP	DP	PP
Control	0	0.25 ± 0.04 a	0.14 ± 0.01 a	0.12 ± 0.04
Dynamotive	5	0.14 ± 0.03 c	0.05 ± 0.01 b	0.09 ± 0.03
	10	0.16 ± 0.02 bc	0.13 ± 0.02 a	0.03 ± 0.03
Pyrovac	5	0.21 ± 0.05 ab	0.13 ± 0.01 a	0.08 ± 0.05
	10	0.14 ± 0.01 c	0.13 ± 0.01 a	0.01 ± 0.01
Basques	5	0.22 ± 0.02 a	0.12 ± 0.02 a	0.11 ± 0.02
	10	0.16 ± 0.02 bc	0.13 ± 0.01 a	0.03 ± 0.01
ANOVA	Biochar type	< 0.001	< 0.001	0.009
(p-value)	Biochar rate	< 0.001	< 0.001	< 0.001
	Type × rate	0.004	< 0.001	NS
Contrast analysis (p-value)				
	Control vs. biochar (5 t ha <sup>-1</sup> )	0.02	0.04	NS
	Control vs. biochar (10 t ha <sup>-1</sup> )	< 0.001	NS	< 0.001

hence prevented water from reaching micropores (Novak et al., 2009; Kameyama et al., 2012; Soenne et al., 2014). The most likely explanation was that biochar application rates in the present study were too low to affect soil water dynamics. Therefore, the reduction of the PP fraction in runoff from biochar-amended field soils could be due to small-scale processes occurring within soil aggregates.

### 3.2. Aggregate distribution, stability and total P content

The proportion of water-stable aggregates and the aggregate MWD after dispersion did not significantly differ for any of the biochar treatments individually, nor when pooled by type or rate, compared to the control (Table 3). However, the proportion of undispersed water-stable microaggregates was significantly higher compared to the control. No significant difference was observed in water-stable aggregates prior to dispersion between biochar-amended and unamended plots (Supplementary table S2). Biochar rate, but not biochar type, affected nutrient composition; therefore, the data across biochar types was pooled to isolate rate effects. Microaggregates contained 40 and 68% more organic C, while macroaggregates contained from 26 and 32% more organic C in biochar-amended plots at 5 and 10 t ha<sup>-1</sup>, respectively, then the unamended controls (Fig. 1a). Total P concentration in > 2 mm macroaggregates was significantly higher in 5 and 10 t ha<sup>-1</sup> treatments compared to the control, however the difference was not significant in the < 2 mm aggregate fractions (Fig. 1b).

The chemical recalcitrance and aromatic ring structures of biochar render it unlikely to serve as an adequate substrate to stimulate microbially-mediated formation of larger aggregates (Lin et al., 2012). In tropical regions, Major et al. (2012) speculated that it would take several decades to form larger aggregates in biochar-amended soil. Higher P concentration within the macroaggregates collected from biochar-amended soil suggests that biochar may be facilitating additional P retention within the macroaggregate (Zimmerman et al., 2011). It is possible that organic matter adsorbed onto biochar surfaces contains organic P, which is thereby protected from decomposition. Another explanation is that biochar indirectly alters microbial decomposition rates or community composition in a way that slows down organic P turnover, which would explain the greater P concentration in macroaggregates, but not in microaggregates. High carbon content in both macro- and microaggregates could be explained using a soil C

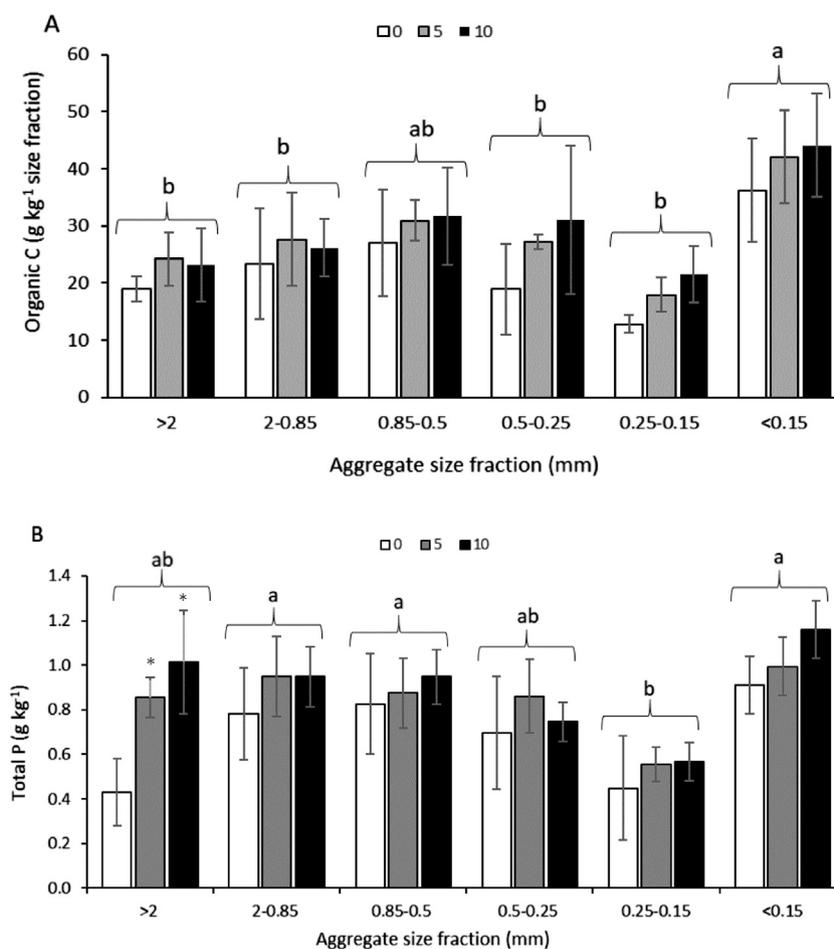
**Table 3**

Distribution of water stable aggregates (WSA), expressed as the percentage (%) of soil mass that remained intact after the dispersion of each size fraction of soil from biochar-amended field plots in the St. Francis River watershed, Quebec, Canada. The mean weight diameter (MWD, in mm) is reported for soil aggregates from 0.15 to > 2 mm. Values for each treatment are the mean  $\pm$  standard deviation ( $n = 5$ ). NS = not significant,  $p > 0.05$ .

Biochar treatments		WSA-size fraction (mm)					MWD (mm)
Type	Rate ( $\text{t ha}^{-1}$ )	> 2	2–0.85	0.85–0.5	0.5–0.25	0.25–0.15	
Control	0	56 $\pm$ 12	56 $\pm$ 15	53 $\pm$ 7.6	3.6 $\pm$ 0.3	3.8 $\pm$ 0.6	0.73 $\pm$ 0.2
Dynamotive	5	56 $\pm$ 3.7	55 $\pm$ 12	45 $\pm$ 4.2	3.7 $\pm$ 0.3	5.4 $\pm$ 0.1	0.87 $\pm$ 0.4
	10	65 $\pm$ 13	65 $\pm$ 3.9	56 $\pm$ 3.0	3.7 $\pm$ 0.2	6.5 $\pm$ 0.5	0.83 $\pm$ 0.4
Pyrovac	5	60 $\pm$ 17	54 $\pm$ 20	50 $\pm$ 18	3.6 $\pm$ 0.2	5.0 $\pm$ 0.8	0.78 $\pm$ 0.5
	10	50 $\pm$ 18	55 $\pm$ 11	52 $\pm$ 4.5	3.7 $\pm$ 0.4	5.0 $\pm$ 0.2	0.97 $\pm$ 0.4
Basques	5	59 $\pm$ 6.5	54 $\pm$ 10	47 $\pm$ 14	3.6 $\pm$ 0.1	5.9 $\pm$ 0.4	0.70 $\pm$ 0.3
	10	58 $\pm$ 3.5	62 $\pm$ 8.7	58 $\pm$ 9.2	3.9 $\pm$ 0.4	6.7 $\pm$ 0.1	1.1 $\pm$ 0.4
ANOVA		NS	NS	NS	NS	< 0.001	NS
(p-value)		NS	NS	NS	NS	0.015	NS
Type $\times$ rate		NS	NS	NS	NS	NS	NS
Contrast analysis (p-value)							
Control vs. biochar ( $5 \text{ t ha}^{-1}$ )		NS	NS	NS	NS	0.002	NS
Control vs. biochar ( $10 \text{ t ha}^{-1}$ )		NS	NS	NS	NS	< 0.001	NS

input model that shows C preferentially associates with different fractions as it shifts along a conceptual C-saturation continuum (Six et al., 2002). Carbon inputs into soil initially form chemical bonds with organo-mineral complexes, but once this fraction becomes saturated, additional C becomes compartmentalized within microaggregates. Brodowski et al. (2006) suggests that biochar is a core component of microaggregates and is gradually coated by clay, silt, and organic

matter particles and then colonized and encapsulated by soil microorganisms. Although this is a logical explanation, we cannot rule out the possibility that some of the C-enriched microaggregates are incorporated within macroaggregates in the short- to medium-term, based on the theory of hierarchical macroaggregate formation (Six et al., 2002).



**Fig. 1.** Organic C and total P content of aggregate size fractions collected from plots amended with 0, 5 and 10  $\text{t biochar ha}^{-1}$ . Values for each treatment are the mean  $\pm$  standard deviation ( $n = 5$ ). Bars with an asterisk are significantly different from the unamended control (0  $\text{t biochar ha}^{-1}$ ) at  $p < 0.05$ . Aggregate fractions with the same letter over the bracket are not significantly different at  $p < 0.05$ .

#### 4. Conclusion

Biochar used in the present study did not alter soil physical properties enough to change WHC, runoff volume, or infiltration rate, probably because the application rate was too low to induce changes in these soil parameters. As a result, biochar did not reduce P loss in runoff. However, the gain in organic C and total P content in macroaggregates > 2 mm suggests that biochar amendment could contribute to soil P retention. Larger macroaggregates tend to be more stable to dispersive forces and this could possibly reduce soil P loss via wind and water erosion. However, further studies are needed to explore how the physicochemical properties of biochar could be adjusted, based on choice of a suitable feedstock and pyrolysis conditions, to increase the P retention capacity of biochar-amended soils. Follow-up studies require confirmation with field experiments because the proposed mechanism is related to macroaggregate formation, a dynamic process that is affected by climatic conditions, soil properties and agricultural practices.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2019.05.029>.

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