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ARTICLE

Soil phosphorus fractionation after co-applying biochar and paper mill biosolids[1]

Noura Ziadi, Xiangru Zhang, Bernard Gagnon, and Eric Manirakiza

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Abstract: In recent decades, there has been a growing interest in the recycling of organic materials such as paper mill biosolids (PB) and biochar for use as soil amendments. However, the benefits of co-application of PB and biochar and its effects on soil phosphorus (P) availability remain unknown. An incubation study was conducted on two acidic soils to assess the effect of two PB types (2.5% *w/w*) co-applied with three rates (0%, 2.5%, and 5% *w/w*) of pine (*Pinus strobus* L.) biochar on soil P fractions. An unfertilized control and a mineral NP fertilizer were used as a reference. Soil P fractions were determined by Hedley procedure after 2 and 16 wk of incubation. Material fractionation indicated that the PB containing the highest total P and the lowest Al content had the highest proportion of labile P, whereas most P in the biochar was in a stable form. The incubation study revealed that the P-rich PB increased P availability in both soils to a level comparable to mineral fertilizer at the end of the incubation. The addition of biochar to PB, however, did not affect soil P availability, but the highest rate induced a conversion of P fixed to Al and Fe oxides towards recalcitrant forms, particularly in the sandy loam soil. We conclude that co-applying biochar and PB could be more beneficial than application biochar alone and soils amended with such a mixture would be expected to release part of their P slowly over a longer period of time.

Key words: paper mill biosolids, P availability, phosphorus fractions, soil incubation, wood biochar.

Résumé : Depuis quelques décennies, on s'intéresse de plus en plus au recyclage des matières organiques, les biosolides des papetiers (BP), par exemple, ou le biocharbon, qu'on utilise pour amender le sol. Cependant, on ignore les effets bénéfiques d'une application combinée de BP et de biocharbon, ainsi que ses conséquences sur le phosphore (P) disponible dans le sol. Les auteurs ont procédé à une étude d'incubation sur deux sols acides afin d'évaluer les effets de deux sortes de BP (2,5 % en poids), appliqués avec trois taux (0 %, 2,5 % et 5 % en poids) de biocharbon de pin (*Pinus strobus* L.), sur les fractions du P du sol. Un traitement non amendé et un autre fertilisé avec un engrais NP minéral ont servi de point de comparaison. Les auteurs ont dosé les fractions de P du sol selon la technique de Hedley après deux et seize semaines d'incubation. Les résultats du fractionnement des matériaux ont indiqué que les BP renfermant le plus de P total et le moins d'aluminium ont la plus forte proportion de P sous forme labile, alors que la plupart du P dans le biocharbon est sous une forme stable. L'étude a révélé qu'au terme de l'incubation, les BP riches en P avaient accru la quantité de P disponible dans les deux types de sol, à un niveau comparable à celui de l'engrais minéral. Cependant, l'ajout du biocharbon aux BP n'a pas modifié le P disponible dans le sol mais le taux le plus élevé d'application a produit une conversion du P fixé à l'aluminium et aux oxydes de fer vers des formes récalcitrantes, surtout dans le loam sablonneux. Les auteurs en concluent que l'application simultanée de BP et de biocharbon pourrait s'avérer plus bénéfique que celle de biocharbon seul, et que les sols

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amendés de cette façon devraient libérer le P qu'ils contiennent plus lentement sur une plus longue période. [Traduit par la Rédaction]

Mots-clés : biosolides de papeterie, disponibilité du P, fractions du phosphore, incubation du sol, biocharbon de bois.

Introduction

The use of paper mill biosolids (PB) in agriculture has been a common practice in Canada for many decades. This material is produced mainly from combined primary and secondary wastewater treatment, and it is a valuable source of nutrients for increasing crop performance and soil quality, including soil organic matter and nitrogen (N) and phosphorus (P) availability (Camberato et al. 2006). Moreover, the use of PB may be a good alternative to the continued depletion of phosphate rock reserves (Cordell et al. 2009), by recycling P at the agroecosystem level. However, few studies have been reported on the efficiency of PB as a source of P forms and availability (Fan et al. 2010; Zhang et al. 2020).

Biochar is a carbon-rich material produced through the pyrolysis of organic materials under low-oxygen environments and can be used as a soil amendment (Lehmann and Joseph 2015). A biochar production sector is gradually emerging in Canada, and biomass of little economic value such as wood chips and insect-infested trees is of particular interest (Matovic 2011; Biopterre 2018). However, few studies have assessed the impact of biochar application on soil properties in eastern Canada (Lévesque et al. 2020; Manirakiza et al. 2020).

Biochar is viewed as a way to sequester carbon, but it has also the capacity to enhance soil fertility by providing a long-lasting P source while minimizing the loss of P applied to soil (Dai et al. 2016). This is because pyrolysis converts labile P in the original biomass to less available and occluded forms that are slowly released over time (Xu et al. 2016; Li et al. 2018; Adhikari et al. 2019). In addition, increasing the pyrolysis temperature increases the surface area and adsorption capacity of biochar (Gul et al. 2015; Adhikari et al. 2019) and induces the formation of insoluble amorphous P complexes and organic salts with the multivalent cations (Dai et al. 2016; Zornoza et al. 2016). Although not readily available, the insoluble P complexes can serve as a long-term source of P through processes involving soil organisms (Gao and DeLuca 2016).

Addition of biochar may significantly increase P availability in agricultural soils, but this impact varied with the feedstock used (Glaser and Lehr 2019). Biochar made from manure or crop residues tended to increase soil P (Chan et al. 2008; Novak et al. 2009), whereas biochar made from softwood or pine chips had no effect (Gaskin et al. 2010; Tammeorg et al. 2014; Backer et al. 2016; Foster et al. 2016). Xu et al. (2018) reported a positive effect of wheat straw biochar relative to uncharred material on many P fractions of an acidic soil. A further analysis of P forms both in the material and in the amended soil may contribute to the understanding of the reaction of biochar once land applied. Biochar P forms have been the subject of several studies (Xu et al. 2016; Li et al. 2018; Adhikari et al. 2019), but less is known about the amended soil.

The agronomic effectiveness of biochars of lower P content can be improved by mixing them with other materials, such as compost, manure, or inorganic fertilizers, prior to soil amendment. This is thanks to the effects on soil organic matter, nutrient retention, and water-holding capacity (Liu et al. 2012; Agegnehu et al. 2017). Organic materials following mineralization produce organic acids that may exert strong competition on the P sorption sites, making P fertilizer use more efficient (Nelson et al. 2011; El-Naggar et al. 2015). In addition, microbial decomposition of organic matter also releases CO_2 that can form carbonic acid with water and indirectly solubilize the Ca- and Mg-phosphate, two very stable P forms (El-Naggar et al. 2015). Furthermore, co-applying biochars and PB may influence the effectiveness of PB and synergistically improve soil properties. However, there is very limited information on the co-application of PB and biochar, particularly related to P forms and availability.

The objective of this study was to assess the impact of co-applied PB and biochar on soil P fractions under controlled conditions after 2 wk (short-term) and 16 wk (typical duration of growing season). We hypothesized that co-applied biochar modifies the effect of PB on soil P forms as a function of biochar rate, PB type, and incubation time.

Materials and Methods

The experiment is a part of a large 32 wk incubation study on the effect of co-application of biochar and PB on soil chemical and biological properties at five sampling dates (Manirakiza et al. 2019, 2020). For this particular study, soil P fractions based on Hedley sequential extraction were determined at two sampling dates, namely after 2 and 16 wk of incubation.

Description of soils

Composite soil samples were collected from the upper layer (0–15 cm) of two fields located near Quebec City, QC, Canada (47°N, 71°W). The soils were air-dried and sieved to 2 mm before incubation. Each soil was characterized for biochemical properties and reported in Manirakiza et al. (2019). Briefly, the Kamouraska clay was an Orthic Humic Gleysol from a corn (*Zea mays* L.) field. It had a pH_{water} of 5.32, a total C

Table 1. Main properties of selected paper mill biosolids (PB) and pine biochar (dry matter basis except moisture).

Parameter	PB1	PB2	Biochar
pH (H$_2$O)	7.8	4.5	7.4
Moisture (g·kg^{-1})	707	693	68
Ash (g·kg^{-1})	—	—	48
Volatile matter (g·kg^{-1})	—	—	158
Fixed C (g·kg^{-1})	—	—	794
Total C (g·kg^{-1})	315	485	761
Total N (g·kg^{-1})	12.8	39.7	12.4
C/N ratio	25	12	61
H/C molar ratio	—	—	0.30
O/C molar ratio	—	—	0.10
Total P (g·kg^{-1})	4.2	7.3	0.4
Total Ca (g·kg^{-1})	8	2	6
Total Al (g·kg^{-1})	36.5	9.1	1.2

of 30.2 g·kg^{-1}, a Mehlich-3 P of 36 mg·kg^{-1}, a P/Al ratio of 0.028, and a total P of 1236 mg·kg^{-1}. The St-Antoine sandy loam was an Orthic Humo-Ferric Podzol from a field under alfalfa (*Medicago sativa* L.)/timothy (*Phleum pratense* L.) pasture. It had a pH$_{water}$ of 5.89, a total C of 16.3 g·kg^{-1}, a Mehlich-3 P of 33 mg·kg^{-1}, a P/Al ratio of 0.030, and a total P of 446 mg·kg^{-1}. Based on soil P saturation, each soil was considered low to medium in regards to available P content (0.025 < P/Al$_{M-III}$ < 0.050; CRAAQ 2010) and had a high capacity to retain P (Pellerin et al. 2006; Wang et al. 2015).

Material characterization

Two PB and one biochar were used in this study. The two PB consisted of mixed primary and secondary wastewater-treated sludge from thermomechanical pulp (PB1; Kruger, Trois-Rivières, QC, Canada) or from acid-treated bleached Kraft pulp (PB2; Kruger Wayagamack, Trois-Rivières, QC, Canada). The biochar consisted of pine chips pyrolyzed at 700 °C in a BEC Beta base unit (Biochar Engineering Corporation, Golden, CO, USA).

The main chemical properties of each material were reported in Table 1. Chemical analysis was provided in detail in Gagnon and Ziadi (2012) for PB and in Lévesque et al. (2018) for the biochar. The selected PB differed significantly in their properties, notably pH, total N and P, and C/N ratio, with PB2 showing a higher potential nutrient value. For its part, the biochar should have high stability against degradation in soils due to its high fixed C content and low volatile matter and H/C and O/C ratio which in counterpart should reduce its role in supplying major nutrients for crops (Domingues et al. 2017).

Incubation study

The experiment consisted of eight treatments (unfertilized control, mineral NP fertilizer, and two PB types × three biochar rates) for each soil arranged in a completely randomized block design with three replicates for each sampling date. Biosolids were thoroughly mixed with 100 g of air-dried soil at a rate of 2.5% (*w*/*w*), equivalent to 30 Mg wet·ha^{-1} considering a depth incorporation of 10 cm and a soil bulk density of 1.2 g·cm^{-3}. This rate is typical of the mean applied in field in Québec (Hébert 2016). The biochar was added at three rates (0%, 2.5%, and 5% *w*/*w*) which gave a field application equivalent to 0, 30, and 60 Mg dry·ha^{-1} in the 10 cm surface layer, respectively. The highest rate was used to amplify any impact of biochar on the P dynamic of PB even if this rate exceeded the agronomic and economic acceptance (Dai et al. 2017). The mineral NP fertilizer treatment consisted of 30 kg KH$_2$PO$_4$-P·ha^{-1} along with 120 kg NH$_4$NO$_3$-N·ha^{-1} added to evaluate the relative P contribution of each treatment combination.

Every amended soil mixture was incubated in 500 mL Mason™ glass jars during a 32 wk incubation period with periodic destructive samplings. In this study, samplings of weeks 2 and 16 were used for soil P fractionation. These two sampling periods were chosen to simulate short-term (early root growth) and typical duration for a growing season in eastern Canada. Distilled water was added to adjust water-filled pore space to 60%. The lids of the jars were inverted to allow aeration while limiting the loss of moisture. The jars were incubated in the dark in a controlled environment chamber at 25 °C. Water loss was monitored twice a week by weighing and corrected as necessary.

Soil P fractionation

At each sampling date, subsamples of the amended soil mixture were air-dried, sieved to pass a 2 mm screen, and then ground to 0.2 mm. The Hedley sequential extraction procedure was performed as described by Tiessen and Moir (2008), with modifications for soil digestion as proposed by Zheng et al. (2001) and performed in the same laboratory by Zhang et al. (2020). Briefly, 0.5 g ground soil subsample was weighed into 50 mL centrifuge tubes and sequentially extracted according to the following scheme:

1. Resin P [(inorganic P (Pi)]: 25 mL of water and two resin strips, shake for 16 h at 25 °C, remove the strips, centrifuge, decant, and discard supernatant. Phosphorus was recovered from strips in 25 mL of 0.5 mol·L^{-1} HCl.
2. NaHCO$_3$ [(Pi and organic P (Po)]: 25 mL of 0.5 mol·L^{-1} NaHCO$_3$ pH 8.5, shake for 16 h at 25 °C, centrifuge, and collect supernatant.
3. NaOH (Pi and Po): 25 mL of 0.1 mol·L^{-1} NaOH, shake for 16 h at 25 °C, centrifuge, and collect supernatant.
4. HCl (Pi): 25 mL of 1.0 mol·L^{-1} HCl, shake for 16 h at 25 °C, centrifuge, and collect supernatant.
5. Residual-P: 10 mL of 0.9 mol·L^{-1} H$_2$SO$_4$ and 0.5 g K$_2$S$_2$O$_8$, digestion at 121 °C in an autoclave for 90 min.

Table 2. Phosphorus (P) fractionation of paper mill biosolids[a] and pine biochar.

Fraction	PB1 (mg·kg^{-1} dry weight)	PB2 (mg·kg^{-1} dry weight)	Biochar (mg·kg^{-1} dry weight)
Inorganic			
Resin	577 ± 45 (13)	3273 ± 102 (47)	50 ± 8 (13)
NaHCO$_3$	400 ± 32 (9)	196 ± 5 (3)	11 ± 3 (3)
NaOH	1293 ± 117 (29)	0 ± 0 (0)	24 ± 4 (6)
HCl	894 ± 26 (20)	84 ± 3 (1)	192 ± 14 (50)
Total Pi	3164 ± 178 (72)	3554 ± 107 (51)	277 ± 21 (73)
Organic			
Resin + H$_2$O	66 ± 22 (2)	818 ± 221 (12)	1 ± 1 (0)
NaHCO$_3$	94 ± 3 (2)	708 ± 37 (10)	7 ± 4 (2)
NaOH	397 ± 33 (9)	1180 ± 115 (17)	2 ± 3 (1)
HCl	48 ± 6 (1)	98 ± 18 (1)	19 ± 30 (5)
Residual	625 ± 14 (14)	594 ± 48 (9)	74 ± 22 (19)
Total Po	1230 ± 34 (28)	3397 ± 215 (49)	104 ± 13 (27)
Total			
Σfraction P	4394 ± 173	6951 ± 113	380 ± 24
Total P digestion	4754 ± 99	6904 ± 156	331 ± 15
P recovery (%)[b]	93	101	115

Note: Value in parenthesis represents percentage of specific form P in the sum of fraction P.
[a]PB1, paper mill biosolids with a C/N ratio of 25; PB2, paper mill biosolids with a C/N ratio of 12.
[b]P recovery = (resin-Pi + NaHCO$_3$-Pi + NaOH-Pi + HCl-Pi + resin+H$_2$O-Po + NaHCO$_3$-Po + NaOH-Po + HCl-Po + residual P) × 100/total P in digestion.

The concentration of Pi in extracts and digests was determined using the ascorbic acid molybdenum blue method (Murphy and Riley 1962). The concentrations of Po in each of these two extractions (NaHCO$_3$ and NaOH) were calculated as the difference between total P determined after oxidation with potassium persulfate and Pi. Total P in soils was also determined in the same way as for residual P with 0.1 g ground soil. This made it possible to evaluate the P recovery from fractionation which varied from 81% to 97% (91% ± 3%).

Total Pi was the sum of resin-P, NaHCO$_3$-Pi, NaOH-Pi, and HCl-Pi, whereas total Po was the sum of NaHCO$_3$-Po, NaOH-Po, and residual-P. Usually but not exclusively, resin-P is considered as freely available Pi; NaHCO$_3$-P is assigned to Pi sorbed on crystalline Al and Fe oxides and to easily mineralized Po; NaOH-P is assigned to Pi sorbed to amorphous Al and Fe oxides and to stable Po; and HCl-P is considered to be Ca-P-compounds (Negassa and Leinweber 2009). Usually, the sum of resin-P and NaHCO$_3$-P was considered as labile P, whereas HCl-P and residual P were considered as P stable over time.

Material P fractionation

Each material P was also fractionated before application using the same method as reported in Zhang et al. (2020). Briefly, fresh PB and biochar (0.150 g dry basis for P fractionation and 0.030 g dry basis for total P) were used for the extraction, as suggested by Ajiboye et al. (2004). The supernatant of the resin step was kept to determine both Pi and Po (after digestion) in the water extract. No Pi was found in the water extract. Organic P

in 1.0 mol·L^{-1} HCl was also determined as recommended by He et al. (2010) to provide a more accurate P characterization of the materials. Usually, this fraction is recovered in the residual P pool and has been simply assumed to be negligible. Finally, extracts of residual P and total P were digested twice to completely release Pi from materials. This step did not give more Pi in the case of biochar.

Statistical analysis

All data for soil P incubation were checked for normality with the Shapiro–Wilk's test, and square-root transformation was needed for residual P at 16 wk to improve the normality of distribution. Treatment effects were evaluated as a factorial of two soils × eight treatments replicated three times using the MIXED procedure (SAS Institute Inc. 2004). Due to interaction effects with soil type, analysis was performed by soil, with replicates and replicates × treatments as random effects, treatments as fixed effects, and incubation time as repeated effect. Main treatment effects and their interactions were tested using differences of least squares means. Differences were considered statistically significant at $P < 0.05$.

Results and Discussion

Material P fractionation

The P recovery from the fractionation of the three materials was high, ranging from 93% to 115% (Table 2). Compared with biochar, the total P content in the PB was very high; more specifically, total Po accounted for about 50% of total P in PB2. This situation was common

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for several PB (Zhang et al. 2020) and was related to the fact that this material had been subjected to a secondary biological treatment for further purification and stabilization before discharge to the water bodies, which stimulated microbial activities. By contrast, PB1 comprised most of its P in inorganic form (72%) and could be more closely compared with municipal biosolids in which Pi is dominant (Sui et al. 1999; Ajiboye et al. 2004).

The relative contribution of P in each fraction varied widely with the material used (Table 2). The resin-P (Pi + H$_2$O-Po), the most readily available form, and the labile P (resin + NaHCO$_3$), which is considered plant available, accounted, respectively, for 59% and 72% of total P in PB2. In the PB1, labile P constituted only 26% of total P, whereas stable P (HCl + residual) accounted for 35% of total P. This could be attributed to its high pH, which may contribute to the formation of recalcitrant Ca-phosphate minerals and to the high total Al content (Table 1), which reduced the P availability (Krogstad et al. 2005; Torri et al. 2017).

Most P in biochar was in stable form (75%, HCl + residual), whereas the labile fraction accounted for only 18% of total P, with 13% as resin-P (Table 2). The method of producing biochar alters the forms of P in the original feedstock. The total P and the proportion of Pi fraction at the expense of Po generally increase with pyrolysis treatment, but the solubility of P is reduced, forming orthophosphate and immobilizing P into minerals or complexes with Al, Ca, Mg, and Fe ions (Dai et al. 2016; Xu et al. 2016; Zornoza et al. 2016; Li et al. 2018; Adhikari et al. 2019). Schneider and Haderlein (2016) reported that the HCl fraction, representing Ca-bound P in minerals of low solubility, might act as a reservoir of intrinsic P to slowly replenish labile P in acidic soils.

Soil P fractionation

The soil resin and labile P, two fractions representing plant available P, were strongly influenced by treatments on both soils at the two sampling dates: after 2 wk and 16 wk of incubation (Tables 3 and 4). The PB2, which was the richest material in total P (Table 1), increased most of these fractions. Indeed, PB2 supplied 56 mg total P·kg^{-1}, of which 59% was in resin form and 72% was in labile form (Table 2). The PB1 supplied less total P (31 mg·kg^{-1}), which was in more recalcitrant forms and also contained higher Al. As a consequence, PB1 contributed less to increasing soil resin- and labile-P fractions. In terms of mineral P fertilizer, the P recovery in labile form corresponded to 29% and 59% of total P applied for PB1 and PB2, respectively, at week 2, and 53% and 98% for PB1 and PB2 at week 16 (Table 5). This indicated that PB had a good potential for P mineralization. This agrees with our previous finding (Zhang et al. 2020) where we reported a recovery of labile P that increased with time and reached 48% for PB1 and 87% for PB2 at the end of a 16 wk incubation.

Fig. 1. Effect of co-application of pine biochar and paper mill biosolids on the soil NaOH-Pi fraction of the St-Antoine sandy loam. PB1, paper mill biosolids with a C/N ratio of 25; PB2, paper mill biosolids with a C/N ratio of 12.
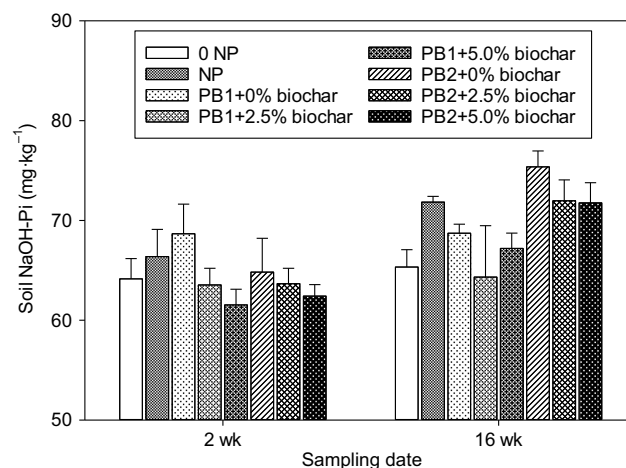
In contrast to PB, the pine chip biochar had little impact on the resin and labile P fractions on both soils (Tables 3 and 4). Despite the fact that this biochar supplied 11 and 22 kg total P·ha^{-1} with the two application rates, it did not increase the content of these fractions compared with the PB (Table 5). This was related to its low total P content (0.4 g·kg^{-1}; Table 1) and very recalcitrant P forms (75% HCl + residual; Table 2). This finding is in agreement with results obtained by Manirakiza et al. (2020), who reported that co-applying biochar and PB did not change soil Mehlich-3 extractable P concentration compared with the application of PB alone. Several studies reported increases in available P following biochar addition to soil (Glaser and Lehr 2019), but those applying biochars of softwood or pine chips did not show any effect (Gaskin et al. 2010; Tammeorg et al. 2014; Backer et al. 2016; Foster et al. 2016). In addition, increasing pyrolysis temperature to >600 °C significantly reduced the effect that biochar might have on P availability (Zornoza et al. 2016; Glaser and Lehr 2019, Li et al. 2020).

The pine biochar, however, affected the moderately (NaOH) and stable (HCl + residual) fractions, particularly in the low total-P sandy loam (Table 4). The highest rate decreased the NaOH-Pi and -Po content and caused a conversion to more stable forms (HCl and residual). The effect took place earlier for the alkaline PB1 than for the acidic PB2 (Fig. 1). The P release from biochar is characterized by two mechanisms: (1) an instantaneous direct release and (2) a long-term slow release by alteration of soil pH, microbial mineralization, and co-precipitation with cations present in the soil (Xu et al. 2013; Gao and DeLuca 2016; Li et al. 2020). Qian and Jiang (2014) reported that a more severe pyrolysis process promoted the migration of P to the long-term available HCl-P pool. The direct contribution of pine biochar or induced

Table 3. Effects of co-application of pine biochar and paper mill biosolids[a] on the soil phosphorus (P) fractions of the Kamouraska clay.

P form	Resin-P (mg·kg^{-1})	NaHCO$_3$-Pi (mg·kg^{-1})	NaHCO$_3$-Po (mg·kg^{-1})	Labile P (mg·kg^{-1})	NaOH-Pi (mg·kg^{-1})	NaOH-Po (mg·kg^{-1})	HCl-P (mg·kg^{-1})	Residual P (mg·kg^{-1})	Total Pi (mg·kg^{-1})
Control (0 NP)	58	31	46	135	125	329	411	266	625
NP fertilizer	66	33	47	146	128	334	420	253	647
PB1 + 0% biochar	60	34	49	142	125	330	414	267	632
PB1 + 2.5% biochar	61	35	47	142	124	330	421	264	640
PB1 + 5.0% biochar	62	34	46	142	125	325	408	265	629
PB2 + 0% biochar	72	37	49	158	129	338	409	256	647
PB2 + 2.5% biochar	72	36	45	153	128	329	414	268	651
PB2 + 5.0% biochar	74	35	47	156	124	327	410	271	643
LSD$_{0.05}$	5	5	5	8	9	13	24	16	22
Analysis of variance (*F* value)									
Treatment	14.0***	1.6	0.8	10.4***	0.4	0.9	0.4	1.3	1.7
Date	13.9**	0.9	2.8	8.7**	17.5***	0.1	19.9***	4.1	22.6***
Treatment × date	0.6	0.1	0.5	0.5	0.5	0.6	0.5	0.4	1.0
Contrasts									
NP vs. 0 NP	12.7**	1.5	0.0	10.0**	0.5	0.7	0.5	3.1	4.8*
PB vs. 0 NP	16.0***	6.1*	1.7	24.3***	0.2	1.2	0.0	0.4	2.9
PB vs. NP	0.0	1.2	1.4	1.6	0.1	0.0	0.6	1.8	0.7
PB1 vs. PB2	25.4***	2.8	0.1	20.6***	0.9	1.6	0.2	2.2	2.0
Biochar, linear rate	1.5	0.4	2.5	0.3	0.6	3.6	0.1	1.4	0.3
Biochar × PB1, lin.	1.0	0.0	1.5	0.0	0.0	0.8	0.3	0.1	0.1
Biochar × PB2, lin.	0.6	1.0	1.0	0.5	1.2	3.2	0.0	3.5	0.2

Note: ***, $P = 0.001$; **, $P = 0.01$; *, $P = 0.05$.

[a]PB1, paper mill biosolids with a C/N ratio of 25; PB2, paper mill biosolids with a C/N ratio of 12.

Table 4. Effects of co-application of pine biochar and paper mill biosolids[a] on the soil phosphorus (P) fractions of the St-Antoine sandy loam.

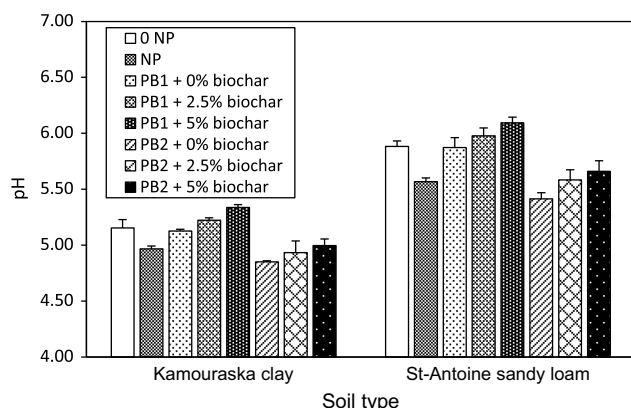| P form	Resin-P (mg·kg^{-1})	NaHCO$_3$-Pi (mg·kg^{-1})	NaHCO$_3$-Po (mg·kg^{-1})	Labile P (mg·kg^{-1})	NaOH-Pi (mg·kg^{-1})	NaOH-Po (mg·kg^{-1})	HCl-P (mg·kg^{-1})	Residual P (mg·kg^{-1})	Total Pi (mg·kg^{-1})
Control (0 NP)	24	20	27	71	65	100	117	103	226
NP fertilizer	36	25	28	89	69	106	117	103	244
PB1 + 0% biochar	27	22	29	78	69	109	116	99	234
PB1 + 2.5% biochar	28	20	27	75	64	100	120	103	232
PB1 + 5.0% biochar	31	22	29	82	64	92	131	105	249
PB2 + 0% biochar	40	27	30	97	70	107	113	103	250
PB2 + 2.5% biochar	37	27	28	93	68	103	114	101	242
PB2 + 5.0% biochar	36	27	28	91	67	104	115	100	244
LSD$_{0.05}$	5	3	2	7	2	13	13	4	17
Analysis of variance (*F* value)									
Treatment	11.1***	6.9***	1.6	16.7***	8.4***	1.6	1.9	2.4	2.3
Date	17.3***	1.2	9.2**	0.9	48.4***	7.4*	5.7*	2.9	4.2
Treatment × date	1.2	2.0	0.3	2.3	3.8*	0.5	2.2	1.1	3.8*
Contrasts									
NP vs. 0 NP	24.3***	11.3**	0.4	31.3***	14.4**	0.9	0.0	0.1	5.2*
PB vs. 0 NP	21.1***	13.1**	4.1	35.5***	21.8***	2.5	0.4	0.9	5.4*
PB vs. NP	1.2	0.1	1.8	0.3	0.1	0.2	0.2	1.9	0.1
PB1 vs. PB2	28.2***	10.2**	0.9	34.9***	1.5	0.1	0.3	5.1*	4.0
Biochar, linear rate	0.0	0.1	0.4	0.2	20.3***	5.8*	4.3	0.8	0.7
Biochar × PB1, lin.	2.5	0.0	0.0	1.8	14.1**	7.9*	6.3*	9.7**	3.4
Biochar × PB2, lin.	3.0	0.3	1.1	3.6	6.8*	0.3	0.2	3.4	0.4

Note: ***, $P = 0.001$; **, $P = 0.01$; *, $P = 0.05$.
[a]PB1, paper mill biosolids with a C/N ratio of 25; PB2, paper mill biosolids with a C/N ratio of 12.

Table 5. Recovery of total applied phosphorus (P) as labile P form from paper mill biosolids[a] and pine biochar addition average over soil types.
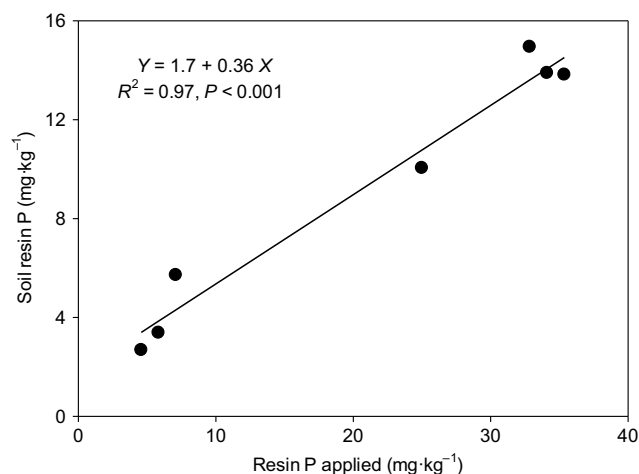
Treatment	Total P applied (kg·ha^{-1})	2 wk incubation		16 wk incubation	
		% Total P	Relative to NP fertilizer	% Total P	Relative to NP fertilizer
NP fertilizer	30.0	66	—	50	—
PB1, no biochar	37.3	19	29	26	53
PB2, no biochar	66.9	39	59	49	98
Biochar, 2.5%	11.2	−26	−39	−39	−79
Biochar, 5.0%	22.4	−1	−1	−11	−21

[a]PB1, paper mill biosolids with a C/N ratio of 25; PB2, paper mill biosolids with a C/N ratio of 12.

Fig. 2. Effect of co-application of pine biochar and paper mill biosolids on the soil pH after 16 wk of incubation. PB1, paper mill biosolids with a C/N ratio of 25; PB2, paper mill biosolids with a C/N ratio of 12.

Fig. 3. Relationship between the amount of resin phosphorus (P) applied and the net increase (treated soil minus control) in soil resin P average over soil types and sampling dates.

increase in soil pH is less plausible here because the material contained low amounts of labile P (Table 2) and caused only a small increase in soil pH after 16 wk (Fig. 2) and during the entire incubation study (0.1–0.2 units; Manirakiza et al. 2020). Hence, the pine biochar may have a limited impact on crop P nutrition in the year of application but may serve as a reservoir to improve soil P availability over the long term. As reported in the literature, the increase in soil pH following biochar addition may also be caused by the presence of ash in the biochar (Glaser et al. 2002). Smider and Singh (2014) reported that applying 1.5% tomato green waste biochar (ash content = 562 g·kg^{-1}) increased soil pH by between 0.76 and 1.93 units. The ash content of the biochar used in our study was low (48 g·kg^{-1}; Table 1) and may explain the weak increase in soil pH and consequently the soil P release (Gagnon and Ziadi 2020).

Biochar can be co-applied with an organic material to increase the P availability to crops (Liu et al. 2012; El-Naggar et al. 2015). It can also alleviate loss of dissolved P in runoff and reduce nonpoint source pollution by sorbing soluble P (Laird et al. 2010). Biochars produced

at high pyrolysis temperatures show more promise in this regard (Mukherjee and Zimmerman 2013; Yuan et al. 2016) because these conditions induced a larger surface area (Gul et al. 2015; Adhikari et al. 2019) and increased the Ca-bound P (Xu et al. 2016; Li et al. 2018; Adhikari et al. 2019), contributing to soil P sorption (Xu et al. 2014). However, Soinne et al. (2014) reported that biochar made of a mixture of softwood chips had very low affinity to sorb phosphate but can retain some P in high phosphate solution (Zhang et al. 2016). In our study, pine biochar seemed to have a limited impact on soil P retention apart from that attributed to the conversion of a portion of P associated with Al and Fe oxides to recalcitrant P pools, which are more slowly available in time.

Relationships between P fractions in materials and soils

Several attempts have been made to establish relationships between material P properties including fractionation and soil P availability. In this study, soil resin-P was highly and positively related to the amount of resin-P added by the different treatments (Fig. 3). It was the

Fig. 4. Relationship between the amount of labile phosphorus (P) applied and the net increase (treated soil minus control) in soil labile P average over soil types and sampling dates.
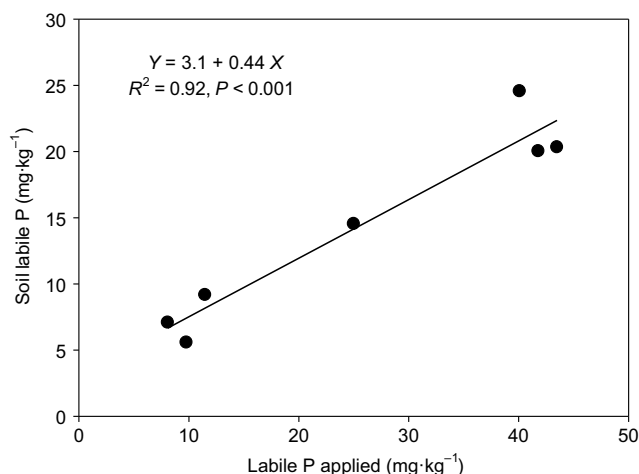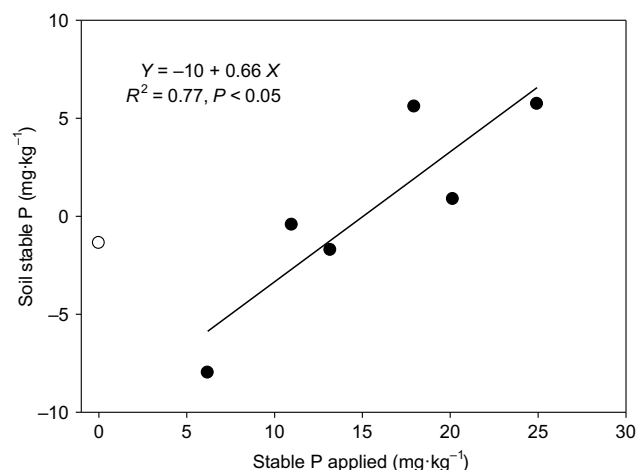

$Y = 3.1 + 0.44\ X$
$R^2 = 0.92, P < 0.001$

Fig. 5. Relationship between the amount of stable phosphorus (P) applied and the net increase (treated soil minus control) in soil stable P average over soil types and sampling dates. White dot from NP treatment was excluded of the regression.

$Y = -10 + 0.66\ X$
$R^2 = 0.77, P < 0.05$

same for the labile P (Fig. 4), indicating that it is important to characterize these pools when applying biochars to agricultural soils. This was caused by the very high proportion of recalcitrant P forms in biochar total P, which did not exist to the same degree with uncharred materials (Xu et al. 2016; Li et al. 2018; Adhikari et al. 2019). Total P concentration and water-extractable P have been reported as best predicting P release from manures and PB (Zvomuya et al. 2006; Zhang et al. 2020).

In contrast, the proportion of P in stable form (HCl + residual fractions) can be used as an index of material vulnerability to P loss by runoff water (Li et al. 2018). This pool was positively correlated to soil stable P (Fig. 5). This means that pine biochar contributed

actively, through its stability, to minimize the environment P risk following land application. Recently, Li et al. (2020) concluded, from an incubation study, that biochar produced from corn stalks released P slowly and could increase P use efficiency if used as a P fertilizer.

Conclusion

The objective of this study was to assess the effect of co-applying PB and pine biochar on soil P availability under controlled conditions. Based on P fractionation results, we conclude that PB applied alone could be a potential efficient P source for fertilizing crops on both soils. The material containing the highest total and labile P and lowest Al content enhanced the available P in soil more significantly, reaching a level equivalent to mineral P fertilizer at the end of the 16 wk incubation period. The addition of pine biochar to PB did not affect soil P availability, but the highest rate induced a conversion of P fixed to Al and Fe oxides to recalcitrant forms, particularly in the sandy loam. The P fractionation analysis showed that the majority of P in pine biochar was in stable form. Therefore, soils amended with both PB and biochar would be expected to release part of their P slowly over a longer period of time. Additional studies under field conditions and (or) with crops under controlled conditions are needed to evaluate P availability to plants as well as P uptake. The use of other biochars derived from richer P materials is also of interest in respect to soil P availability and needs to be included in future studies particularly under different field conditions.

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