# Changes in soil pH and nutrient extractability after co-applying biochar and paper mill biosolids1

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ARTICLE

# Changes in soil pH and nutrient extractability after co-applying biochar and paper mill biosolids[1]

Eric Manirakiza, Noura Ziadi, Mervin St. Luce, Chantal Hamel, Hani Antoun, and Antoine Karam

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**Abstract:** Acidification and metal mobility may present challenges in soil receiving paper mill biosolids (PB). Co-applying biochar and PB could help prevent these issues, but its effect must be assessed. The objective of this 224 d incubation study was to evaluate the effect of amending two acidic soils, a clay and sandy loam, with two PB types varying in pH (PB1, pH = 7.80; and PB2, pH = 4.51) co-applied with three rates (0%, 2.5%, and 5% *w*/*w*) of pine (*Pinus strobus* L.) biochar on soil pH and macro- (P, K, Ca, and Mg) and micronutrients (Cu, Zn, Fe, and Mn). In both soils, co-applying biochar and PB significantly increased soil pH and extractable K concentration compared with PB-only application, whereas amending with PB significantly increased soil extractable P concentration compared with the unamended soil. In comparison with PB only, co-applying 5% biochar and PB decreased extractable Cu concentration in both soils and extractable Fe concentration in the sandy loam soil. This study showed that co-applying biochar and PB can be more beneficial to agricultural soils than application of PB alone by supplying nutrients and helping prevent metal toxicity by raising pH, especially in acidic sandy soils.

*Key words:* pH, nutrients, paper mill biosolids, biochar, co-application.

**Résumé :** L'acidification et la mobilité des métaux peuvent poser un problème dans les sols recevant les biosolides papetiers (BP). Cependant, on pourrait atténuer celui-ci en appliquant simultanément du biocharbon et des BP, mais il faut d'abord en préciser les effets. Les auteurs ont entrepris une expérience d'incubation de 224 jours pour déterminer quel effet l'addition de deux sortes de BP de pH différents (BP1, pH = 7,80 et BP2, pH = 4,51) et trois taux d'application (0 %, 2,5 % et 5 % poids/poids) de biocharbon de pin (*Pinus strobus* L.) auraient sur le pH de deux sols acides (argile et loam sablonneux) et sur la concentration d'oligoéléments (P, K, Ca, Mg, Cu, Zn, Fe et Mn). Dans les deux cas, l'application simultanée de biocharbon et de BP a passablement rehaussé le pH du sol et la concentration de K extractible, comparativement à l'application de BP uniquement. D'autre part, l'addition de BP a sensiblement augmenté la concentration en P extractible dans le sol amendé, comparativement au sol témoin. À l'inverse des BP appliqués seuls, l'application de 5 % de biocharbon avec les BP a diminué la concentration en Cu extractible dans les deux sols et celle en Fe extractible dans le loam sablonneux. Cette étude révèle que l'application de biocharbon avec des BP s'avère plus bénéfique pour les sols

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**Abbreviations: CEC**, cation-exchange capacity; **PB**, paper mill biosolids; **PB1**, paper mill biosolids from thermomechanical pulping; **PB2**, paper mill biosolids from acid treatment and bleaching.

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*N. Ziadi currently serves as an Associate Editor and Guest Editor, and M. St. Luce currently serves as an Associate Editor; peer review and editorial decisions regarding this manuscript were handled by B.W. Thomas.

agricoles que l'application de BP seuls, car l'apport d'éléments nutritifs est plus important et on arrive à prévenir la toxicité des métaux en augmentant le pH, surtout dans les sols sablonneux acides. [Traduit par la Rédaction]

*Mots-clés :* pH, éléments nutritifs, biosolides papetiers, biocharbon, application simultanée.

## Introduction

Pulp and paper mills generate wood-derived organic by-products from the primary and secondary treatment of wastes such as fiber sources, recycled paper products, and non-wood fibers (Zibilske et al. 2000; Camberato et al. 2006). The application of paper mill biosolids (PB) to agricultural soils has been practiced for decades in Canada (Bellamy et al. 1995; Simard 2001; Gagnon and Ziadi 2012). Of the 977 000 wet Mg of PB generated annually in Quebec, 34% was land applied in 2018 (Recyc-Québec 2019). Co-applying biochar and PB may influence the effectiveness of PB and synergistically improve soil properties. However, there is very limited information related to the co-application of PB and biochar.

Many studies reported improvements in soil physicochemical and biological properties and increased crop yields following the application of PB on agricultural soils in Quebec (Gagnon et al. 2003; N'Dayegamiye 2006; Bipfubusa et al. 2008), and an annual application rate of 20–40 Mg ha$^{-1}$ is recommended to maintain the beneficial effects of PB (CRAAQ 2010). Paper mill biosolids supply plant nutrients such as N, P, and K as well as essential micronutrients, increase soil organic matter levels, improve soil structure and water-holding capacity (Zibilske et al. 2000; Gagnon et al. 2003, 2010; Bipfubusa et al. 2008), and promote microbial biomass growth and activity (Camberato et al. 2006; N'Dayegamiye 2006). However, the application of PB may decrease soil pH through nitrification and PB decomposition (Bolan et al. 1991; Gagnon et al. 2003). When applied annually at excessive rates, PB may increase leaching of nutrients, especially N and P, and raise the extractability of trace metals (Gagnon et al. 2010, 2013).

Biochar is a carbon-rich material produced from the pyrolysis of organic materials such as wood, crop residues, or manure, and used as a soil amendment (Lehmann and Joseph 2009). In Quebec, the pyrolysis and biochar production sector is gradually being developed and structured (Biopterre 2018), but very few studies have assessed the impact of biochar application on the properties of Quebec agricultural soils (Husk and Major 2010; Allaire et al. 2015; Backer et al. 2016). The application of biochar can increase and buffer soil pH (Yuan et al. 2011; Zhao et al. 2015; Fidel et al. 2017). Through its higher charge density and surface area for cation adsorption, biochar can increase soil cation-exchange capacity (CEC) when applied to soils (Liang et al. 2006; Cheng et al. 2008; Fidel et al. 2017) and thus improve nutrient and metal retention (Zhao et al. 2015; Liang et al. 2017; Limwikran et al. 2018). However, biochar application, especially on a large scale, faces limitations due to its cost and the variability of biochar properties (El-Naggar et al. 2019). Many studies suggested co-application of biochar and organic amendments as an effective way to alleviate some of the limits to the use of these soil amendments (Agegnehu et al. 2017; Liang et al. 2017; Yang et al. 2018; El-Naggar et al. 2019). Therefore, there is a need to determine how co-applied PB and biochar impact soil pH and extractable macro- and micronutrients and whether co-application of PB and biochar has more value than individual application of PB. It was shown that the mineralization of PB and thus its effects on soil properties (Gagnon et al. 2003, 2013) are dependent on time since application. When added to the soil, biochar undergo surface modifications due to oxidation and adsorption processes (Liang et al. 2006; Cheng et al. 2008), and this influences its effects over time (Farkas et al. 2018). Therefore, time is an important parameter to consider for assessing the effects of co-applied PB and biochar on soil pH and extractable macro- and micronutrients.

The objective of this study was to assess the impact of co-applied PB and biochar over time on soil pH and extractable macro- and micronutrients under controlled laboratory conditions. We hypothesized that co-applied biochar modifies the impact of PB on soil pH and extractable macro- and micronutrients as a function of biochar rate, PB type, and incubation time.

## Materials and Methods

### Experimental design

The experimental design and the materials used were previously described in detail in Manirakiza et al. (2019). Briefly, this study used three rates (0%, 2.5%, and 5% *w*/*w*) of pine (*Pinus strobus* L.) chip biochar produced at 700 °C and two PB types (PB1, paper mill biosolids from thermomechanical pulping; and PB2, paper mill biosolids from acid treatment and bleaching) varying in C/N ratio, pH, and total phosphorus (TP), each at 2.5% rate (wet basis, *w*/*w*). With a soil bulk density of 1.2 g cm$^{-3}$ and a 0–10 cm soil layer, the rates of 2.5% and 5% (*w*/*w*) were equivalent to 30 and 60 Mg ha$^{-1}$, respectively.

The 224 d microcosm incubation study was conducted under controlled conditions at 25 °C and 60% water-filled pore space on two acidic soils from Quebec, Canada, a Kamouraska clay (Orthic Humic Gleysol) and St-Antoine sandy loam (Orthic Humo-Ferric Podzol) (Table 1). The experimental design was a randomized complete block with eight treatments (unamended control, mineral-fertilized reference treatment, PB1 without biochar, PB1 + 2.5% biochar, PB1 + 5% biochar, PB2 without biochar, PB2 + 2.5% biochar, and PB2 + 5% biochar) and

**Table 1.** Chemical characteristics of the soils used in the incubation study.

| | Kamouraska clay | St-Antoine sandy loam |
|---|---|---|
| pH | 5.32 | 5.89 |
| Sand (g kg$^{-1}$) | 302 | 683 |
| Silt (g kg$^{-1}$) | 292 | 164 |
| Clay (g kg$^{-1}$) | 406 | 152 |
| Total C (g kg$^{-1}$) | 30.2 | 16.3 |
| Total N (g kg$^{-1}$) | 2.46 | 1.27 |
| C/N | 11.89 | 13.2 |
| $NO_3$-N (mg kg$^{-1}$) | 2.0 | 2.2 |
| $NH_4$-N (mg kg$^{-1}$) | 17.6 | 53.9 |
| $PO_4$-P (mg kg$^{-1}$) | 36.3 | 32.7 |
| K (mg kg$^{-1}$) | 108 | 129 |
| Ca (mg kg$^{-1}$) | 2569 | 1068 |
| Mg (mg kg$^{-1}$) | 302 | 164 |
| Fe (mg kg$^{-1}$) | 206 | 391 |
| Mn (mg kg$^{-1}$) | 116 | 14 |
| Cu (mg kg$^{-1}$) | 4.5 | 2.1 |
| Zn (mg kg$^{-1}$) | 10.7 | 1.4 |

**Table 2.** Physicochemical characteristics of the paper mill biosolids and biochar used in the incubation study.

| | PB1 | PB2 | Biochar |
|---|---|---|---|
| CEC (cmol kg$^{-1}$) | 187.63 | 162.7 | 96.2 |
| pH | 7.8 | 4.5 | 7.4 |
| Total porosity (cm$^3$ cm$^{-3}$) | ND | ND | 0.90 |
| Moisture (%) | 70.7 | 69.3 | 6.8 |
| Ash content (g kg$^{-1}$) | ND | ND | 48 |
| Total N (g kg$^{-1}$) | 13.1 | 36.4 | 12.4 |
| Total C (g kg$^{-1}$) | 315 | 485 | 761 |
| Total P (g kg$^{-1}$) | 4.3 | 7.4 | 0.4 |
| Total K (mg kg$^{-1}$) | 2500 | 1000 | 2500 |
| Total Ca (mg kg$^{-1}$) | 8000 | 2200 | 6000 |
| Total Mg (mg kg$^{-1}$) | 700 | 500 | 1400 |
| Total Fe (mg kg$^{-1}$) | ND | 855 | 2309 |
| Total Mn (mg kg$^{-1}$) | 1723 | 148 | 361 |
| Total Cu (mg kg$^{-1}$) | 5 | 16 | <5 |
| Total Zn (mg kg$^{-1}$) | 32 | 104 | 38 |
| C/N | 24.1 | 13.3 | 61.4 |
| $NO_3$-N (mg kg$^{-1}$) | 0.5 | 0.4 | 1.53 |
| $NH_4$-N (mg kg$^{-1}$) | 1108 | 154 | 1.04 |
| $PO_4$-P (mg kg$^{-1}$) | 72 | 1051 | ND |

**Note:** ND, not determined; CEC, cation-exchange capacity.

three replications. Mineral-fertilized reference treatment consisted of the rates recommended for the fertilization of corn (*Zea mays* L.) produced in Quebec, Canada (120 kg N ha$^{-1}$ as $NH_4NO_3$ and 30 kg P ha$^{-1}$ and 37 kg K ha$^{-1}$ as $KH_2PO_4$) (CRAAQ 2010). After 14, 28, 56, 112, and 224 d of incubation, soils were sampled destructively and analyzed. A total of 240 microcosms were used (eight amendments × five incubation times × two soils × three replications), and each consisted of 100 g (dry weight equivalent) of treated soil in a 500 mL Mason jar. Biochar and PB characteristics were reported in Table 2.

**Soil analyses**

The treated soils were analyzed for pH, CEC, and extractable P, K, Ca, Mg, Cu, Zn, Fe, and Mn. Soil pH was measured with a glass electrode using 10 g soil in 20 mL deionized water. The CEC was determined by the ammonium acetate method (pH 7.0) (Hendershot et al. 2008). Extractable P, K, Ca, Mg, Cu, Zn, Fe, and Mn were determined by Mehlich-3 extraction (Ziadi and Tran 2008). The P concentration of extracts was measured by colorimetry with the ascorbic acid – molybdate reaction (Murphy and Riley 1962). Concentrations of K, Ca, Mg, Cu, Zn, Fe, and Mn were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Perkin Elmer, Waltham, MA, USA, ICP-AES 4300 DV).

**Statistical analysis**

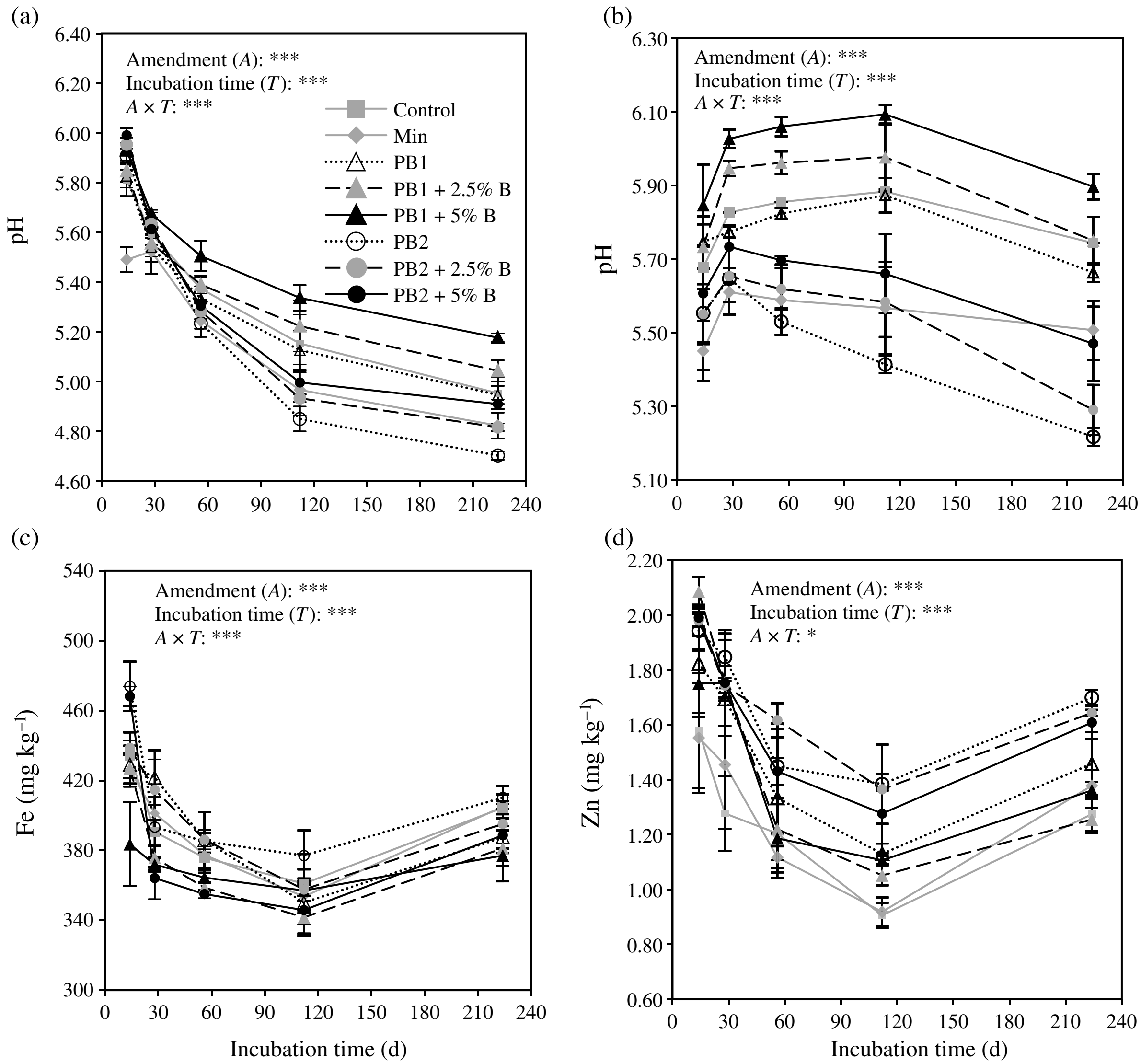
All statistical analyses were performed on each soil separately using the PROC MIXED procedure in SAS software (SAS version 9.4, SAS Institute Inc., Cary, NC, USA). The residuals were tested for normality with the Shapiro–Wilk's test, and the data were log or square root transformed when necessary. The experiment was analyzed according to a randomized complete block design. A two-way analysis of variance was performed to test the effects of incubation time and amendment and their interaction on pH, CEC, and extractable P, K, Ca, Mg, Cu, Zn, Fe, and Mn concentrations. Differences between treatment means were considered statistically significant at $P < 0.05$, according to Tukey's test.

## Results

**Soil pH and CEC**

Amendment, incubation time, and their interaction significantly influenced soil pH in both soils (Figs. 1*a* and 1*b*). Soil pH declined during the incubation period in the Kamouraska clay soil except in mineral-fertilized soils where a diverging trend was observed at day 14 (Fig. 1*a*). The pH of the St-Antoine sandy loam soil increased until day 112 when PB1 was applied with biochar, but a decreasing trend was observed from day 28 when PB2 was applied with or without biochar and in mineral-fertilized soils (Fig. 1*b*). No significant pH change was observed over the incubation period for the unamended soil and PB1-only amended St-Antoine sandy loam soils (Fig. 1*b*). Compared with PB only, co-applying biochar and PB significantly increased soil pH in both soils (Figs. 1*a* and 1*b*), to the extent of the biochar rate. We noted that mean soil pH after 224 d of incubation increased by 0.06–0.2 units in soils receiving biochar and PB compared with those amended with PB only. Amending with PB1 did not significantly affect soil pH compared with the control in both soils (Figs. 1*a* and 1*b*). However, co-applying PB1 and 5% biochar raised soil pH above that of the control in both soils (Figs. 1*a* and 1*b*).

**Fig. 1.** Effect of the interaction between amendment and incubation time on soil pH in the Kamouraska clay (*a*) and St-Antoine sandy loam soil (*b*), extractable Fe (*c*) and Zn (*d*) concentrations in the St-Antoine sandy loam soil during a 224 d incubation period. Measurement was done on days 14, 28, 56, 112, and 224. Bars represent standard errors of the mean ($n = 3$). Control, unamended soil; Min, mineral fertilization; PB1, paper mill biosolids from thermomechanical pulping; PB1 + 2.5% B, PB1 + 2.5% biochar; PB1 + 5% B, PB1 + 5% biochar; PB2, paper mill biosolids from acid treatment and bleaching; PB2 + 2.5% B, PB2 + 2.5% biochar; PB2 + 5% B, PB2 + 5% biochar. *, ***, significant at the 0.05, and 0.001 probability level, respectively.




Applying PB2 alone decreased soil pH in comparison with the control and the application of PB1 in both soils (Figs. 1*a* and 1*b*). Mineral fertilization decreased soil pH in both soils compared with the control (Figs. 1*a* and 1*b*).

Only amendment significantly influenced soil CEC in the Kamouraska clay soil (Table 3). Soil CEC increased over time in the St-Antoine sandy loam soil and was significantly influenced by amendment and incubation time (Table 4). Amending with PB only did not significantly affect soil CEC compared with the control in both soils (Tables 3 and 4). However, combining PB and 5% biochar increased the CEC of the St-Antoine sandy loam soil compared with the control (Table 4). In both soils, co-applying biochar and PB did not significantly affect soil CEC compared with PB only (Tables 3 and 4).

#### Soil extractable P, K, Mg, and Ca

Amendment and incubation time significantly influenced soil extractable P concentration in both soils (Tables 3 and 4). Soil extractable P concentration increased over the incubation period in both soils (Tables 3 and 4). Co-applying biochar and PB did not significantly affect soil extractable P concentration in comparison with the application of PB alone in both soils (Tables 3 and 4). In comparison with the control, the application of PB increased soil extractable P concentration in both soils (Tables 3 and 4) to the extent of their

**Table 3.** Effects of amendment and incubation time on soil pH, cation-exchange capacity (CEC), and extractable P, K, Mg, Ca, Mn, Cu, Fe, and Zn in Kamouraska clay soil.

| | pH | CEC (cmol kg$^{-1}$) | P (mg kg$^{-1}$) | K (mg kg$^{-1}$) | Mg (mg kg$^{-1}$) | Ca (mg kg$^{-1}$) | Mn (mg kg$^{-1}$) | Cu (mg kg$^{-1}$) | Fe (mg kg$^{-1}$) | Zn (mg kg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Amendment (*A*)** | | | | | | | | | | |
| Control | 5.38 ± 0.05 | 36.97 ± 1.02ab | 39.03 ± 0.57d | 122.82 ± 4.47d | 325 ± 4.27a | 2758 ± 36a | 79.66 ± 6.06b | 5.96 ± 0.29abc | 203 ± 4.19a | 10.48 ± 0.12a |
| Min | 5.21 ± 0.05 | 37.16 ± 1.14ab | 46.76 ± 1.13b | 138.09 ± 5.93c | 332 ± 5.35a | 2709 ± 39a | 88.21 ± 3.71a | 6.02 ± 0.32abc | 212 ± 5.58a | 10.67 ± 0.29a |
| PB1 | 5.35 ± 0.04 | 37.23 ± 0.96ab | 43.55 ± 0.85c | 120.81 ± 2.86d | 327 ± 6.03a | 2712 ± 57a | 83.96 ± 3.41ab | 6.31 ± 0.37a | 203 ± 5.94a | 10.66 ± 0.20a |
| PB1 + 2.5% B | 5.41 ± 0.05 | 37.96 ± 0.62ab | 43.07 ± 1.28c | 142.72 ± 4.03bc | 334 ± 7.68a | 2741 ± 33a | 80.65 ± 4.43b | 5.95 ± 0.33abc | 206 ± 5.30a | 10.52 ± 0.30a |
| PB1 + 5% B | 5.52 ± 0.03 | 38.38 ± 0.55ab | 43.77 ± 1.15c | 163.74 ± 3.10a | 330 ± 6.73a | 2714 ± 47a | 80.62 ± 3.97b | 5.76 ± 0.23bc | 204 ± 3.37a | 10.61 ± 0.38a |
| PB2 | 5.26 ± 0.03 | 36.88 ± 102b | 51.40 ± 1.59a | 119.34 ± 2.93d | 327 ± 5.77a | 2680 ± 29a | 81.65 ± 1.92b | 6.11 ± 0.19ab | 208 ± 2.90a | 10.80 ± 0.15a |
| PB2 + 2.5% B | 5.32 ± 0.02 | 38.01 ± 0.55ab | 51.47 ± 1.04a | 144.61 ± 4.64b | 331 ± 5.49a | 2745 ± 21a | 80.32 ± 5.06b | 6.09 ± 0.10ab | 208 ± 2.99a | 10.92 ± 0.31a |
| PB2 + 5% B | 5.36 ± 0.02 | 38.93 ± 0.74a | 51.55 ± 1.15a | 163.76 ± 4.12a | 334 ± 7.40a | 2724 ± 28a | 80.27 ± 2.68b | 5.68 ± 0.24c | 209 ± 3.51a | 10.91 ± 0.39a |
| **Incubation time (*T*, d)** | | | | | | | | | | |
| 14 | 5.84 ± 0.05 | 37.2 ± 0.95a | 43.83 ± 1.01d | 148.90 ± 3.38a | 364 ± 8.71a | 2734 ± 50b | 113.51 ± 7.69a | 6.52 ± 0.32a | 226 ± 8.90a | 12.16 ± 0.22a |
| 28 | 5.59 ± 0.07 | 37.3 ± 0.67a | 45.88 ± 1.27c | 145.84 ± 5.54a | 333 ± 7.33b | 2733 ± 33b | 84.72 ± 3.49b | 6.12 ± 0.24b | 208 ± 3.39b | 11.27 ± 0.37b |
| 56 | 5.33 ± 0.03 | 37.7 ± 0.55a | 46.69 ± 0.77bc | 139.22 ± 3.60b | 319 ± 4.05c | 2643 ± 24c | 74.64 ± 2.10c | 5.96 ± 0.22bc | 199 ± 2.58c | 10.04 ± 0.29d |
| 112 | 5.07 ± 0.02 | 38.0 ± 0.98a | 47.50 ± 1.09ab | 132.60 ± 3.71c | 304 ± 4.43d | 2554 ± 34c | 70.19 ± 3.24d | 5.81 ± 0.17c | 190 ± 2.73d | 9.37 ± 0.29e |
| 224 | 4.92 ± 0.02 | 38.1 ± 0.98a | 47.74 ± 1.32a | 130.88 ± 3.82c | 329 ± 5.94b | 2950 ± 40a | 66.51 ± 3.00e | 5.52 ± 0.23d | 211 ± 3.52b | 10.64 ± 0.17c |
| **Source of variation** | | | | | | | | | | |
| *A* | *** | * | *** | *** | NS | NS | *** | *** | NS | * |
| *T* | *** | NS | *** | *** | *** | *** | *** | *** | *** | *** |
| *A* × *T* | *** | NS | NS | NS | NS | NS | NS | NS | NS | NS |

**Note:** Values are the mean ± standard deviation of three replications. Means followed by different lowercase letters are significantly different (within amendment or incubation time) at $P < 0.05$ (Tukey's test). Mean comparison letters are not shown when the interaction between amendment and incubation time is significant. *, **, ***, significant at the 0.05, 0.01, and 0.001 probability levels, respectively; NS, not significant ($P > 0.05$); Control, unamended soil; Min, mineral fertilization; PB1, paper mill biosolids from thermomechanical pulping; PB1 + 2.5% B, PB1 + 2.5% biochar; PB1 + 5% B, PB1 + 5% biochar; PB2, paper mill biosolids from acid treatment and bleaching; PB2 + 2.5% B, PB2 + 2.5% biochar; PB2 + 5% B, PB2 + 5% biochar.





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**Table 4.** Effects of amendment and incubation time on soil pH, cation-exchange capacity (CEC), and extractable P, K, Mg, Ca, Mn, Cu, Fe, and Zn in St-Antoine sandy loam soil.

| | pH | CEC (cmol $kg^{-1}$) | P (mg $kg^{-1}$) | K (mg $kg^{-1}$) | Mg (mg $kg^{-1}$) | Ca (mg $kg^{-1}$) | Mn (mg $kg^{-1}$) | Cu (mg $kg^{-1}$) | Fe (mg $kg^{-1}$) | Zn (mg $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Amendment (*A*)** | | | | | | | | | | |
| Control | 5.80 ± 0.08 | 16.82 ± 0.72c | 34.40 ± 1.42d | 129.32 ± 7.15e | 250 ± 8.20ab | 1254 ± 40ab | 11.98 ± 1.03c | 3.28 ± 0.30ab | 393 ± 13.62 | 1.25 ± 0.13 |
| Min | 5.54 ± 0.06 | 17.13 ± 0.35bc | 44.96 ± 0.94b | 156.48 ± 4.04c | 254 ± 6.65ab | 1260 ± 21ab | 11.81 ± 0.93c | 3.18 ± 0.27bc | 393 ± 8.40 | 1.28 ± 0.14 |
| PB1 | 5.78 ± 0.05 | 17.26 ± 0.75bc | 39.54 ± 1.19c | 130.76 ± 4.35e | 249 ± 6.41ab | 1280 ± 31ab | 18.83 ± 0.42a | 3.61 ± 0.29a | 395 ± 13.59 | 1.49 ± 0.12 |
| PB1 + 2.5% B | 5.87 ± 0.06 | 17.64 ± 0.23abc | 39.79 ± 1.34c | 157.74 ± 3.31c | 247 ± 9.37ab | 1278 ± 29ab | 18.26 ± 0.91a | 3.25 ± 0.28b | 377 ± 7.55 | 1.47 ± 0.06 |
| PB1 + 5% B | 5.98 ± 0.04 | 18.17 ± 0.72ab | 39.60 ± 1.39c | 171.96 ± 4.73b | 241 ± 12.60b | 1221 ± 26b | 18.23 ± 0.51a | 3.09 ± 0.18bc | 371 ± 9.73 | 1.43 ± 0.10 |
| PB2 | 5.47 ± 0.05 | 17.17 ± 0.52bc | 51.19 ± 1.41a | 138.71 ± 4.61d | 257 ± 8.98a | 1312 ± 20a | 12.52 ± 0.46b | 3.38 ± 0.27ab | 408 ± 9.11 | 1.66 ± 0.09 |
| PB2 + 2.5% B | 5.54 ± 0.08 | 17.36 ± 0.60abc | 51.76 ± 2.49a | 158.72 ± 4.72c | 255 ± 12.27ab | 1298 ± 22a | 13.03 ± 0.45b | 3.12 ± 0.22bc | 398 ± 9.01 | 1.67 ± 0.03 |
| PB2 + 5% B | 5.63 ± 0.08 | 18.23 ± 0.93a | 50.33 ± 1.25a | 178.39 ± 7.77a | 245 ± 12,83ab | 1250 ± 38ab | 13.27 ± 0.54b | 2.88 ± 0.27c | 384 ± 7.72 | 1.61 ± 0.09 |
| **Incubation time (*T*, d)** | | | | | | | | | | |
| 14 | 5.65 ± 0.04 | 17.2 ± 0.59b | 40.39 ± 1.59c | 161.55 ± 7.55a | 256 ± 5.49a | 1323 ± 34a | 18.17 ± 0.70a | 3.40 ± 0.23a | 435 ± 11.29 | 1.84 ± 0.12 |
| 28 | 5.78 ± 0.08 | 17.0 ± 0.64b | 43.89 ± 1.07b | 163.21 ± 5.06a | 254 ± 14.35ab | 1307 ± 28ab | 14.23 ± 0.71c | 3.41 ± 0.30a | 392 ± 11.13 | 1.66 ± 0.11 |
| 56 | 5.77 ± 0.06 | 17.3 ± 0.45b | 44.51 ± 0.98ab | 154.79 ± 3.91b | 249 ± 11.05ab | 1252 ± 22c | 13.43 ± 0.65d | 3.27 ± 0.24ab | 374 ± 7.34 | 1.32 ± 0.13 |
| 112 | 5.76 ± 0.07 | 17.6 ± 0.73ab | 45.13 ± 1.49ab | 146.37 ± 3.76c | 243 ± 9.63b | 1197 ± 30d | 12.64 ± 0.74e | 3.13 ± 0.29b | 355 ± 10.69 | 1.14 ± 0.06 |
| 224 | 5.57 ± 0.06 | 18.3 ± 0.61a | 45.81 ± 2.01a | 137.86 ± 5.14d | 247 ± 7.80ab | 1267 ± 28bc | 15.24 ± 0.55b | 2.89 ± 0.23c | 394 ± 8.76 | 1.46 ± 0.07 |
| **Source of variation** | | | | | | | | | | |
| *A* | *** | *** | *** | *** | * | ** | *** | *** | *** | *** |
| *T* | *** | *** | *** | *** | ** | *** | *** | *** | *** | *** |
| *A* × *T* | *** | NS | NS | NS | NS | NS | NS | NS | *** | * |

**Note:** Values are the mean ± standard deviation of three replications. Means followed by different lowercase letters are significantly different (within amendment or incubation time) at $P < 0.05$ (Tukey's test). Mean comparison letters are not shown when the interaction between amendment and incubation time is significant. *, **, ***, significant at the 0.05, 0.01, and 0.001 probability level, respectively; NS, not significant ($P > 0.05$); Control, unamended soil; Min, mineral fertilization; PB1, paper mill biosolids from thermomechanical pulping; PB1 + 2.5% B, PB1 + 2.5% biochar; PB1 + 5% B, PB1 + 5% biochar; PB2, paper mill biosolids from acid treatment and bleaching; PB2 + 2.5% B, PB2 + 2.5% biochar; PB2 + 5% B, PB2 + 5% biochar.

initial $PO_4$-P and TP content (PB1, $PO_4$-P = 72 mg kg$^{-1}$, TP = 4.3 g kg$^{-1}$; and PB2, $PO_4$-P = 1051 mg kg$^{-1}$, TP = 7.4 g kg$^{-1}$). More specifically, mean soil extractable P concentration after 224 d of incubation was increased by between 12% and 49% by the addition of PB. In both soils, mineral fertilization increased soil extractable P concentration above the control more than PB1 but less than PB2 (Tables 3 and 4).

Amendment and incubation time significantly influenced soil extractable K concentration in both soils (Tables 3 and 4). Soil extractable K concentration declined over the incubation period in both soils (Tables 3 and 4). Co-applying biochar and PB significantly increased soil extractable K concentration in comparison with the application of PB alone in both soils, to the extent of the biochar rate (Tables 3 and 4). We noted that mean soil extractable K concentration after 224 d of incubation increased by between 14% and 36% in soils receiving biochar and PB compared with those amended with PB only. Soil extractable K concentration in PB-amended soils was similar to that of the control in the Kamouraska clay soil (Table 3). However, in the St-Antoine sandy loam soil, amending with PB2 alone significantly increased soil extractable K concentration in comparison with the control and the application of PB1 alone (Table 4). Mineral fertilization and amendment with 2.5% biochar and PB led to similar extractable K concentrations in both soils (Tables 3 and 4).

Only incubation time significantly influenced soil extractable Mg and Ca concentrations in the Kamouraska clay soil (Table 3). However, in the St-Antoine sandy loam soil, amendment and incubation time significantly influenced extractable Mg and Ca concentrations (Table 4). There was a decreasing trend in extractable Mg and Ca concentrations until day 112, and then an increase was observed at the end of incubation period in both soils. These variations in extractable Mg and Ca concentrations were more noticeable in the Kamouraska clay soil than in the St-Antoine sandy loam soil (Tables 3 and 4). Co-applying biochar and PB did not significantly affect soil extractable Mg and Ca concentrations in comparison with the application of PB alone in both soils (Tables 3 and 4). Application of PB and mineral fertilization did not significantly affect soil extractable Mg and Ca concentrations in comparison with the control in both soils (Tables 3 and 4).

#### Soil extractable Mn, Cu, Fe, and Zn

Amendment and incubation time significantly influenced soil extractable Mn, Cu, and Zn concentrations in both soils (Tables 3 and 4; Fig. 1*d*) and extractable Fe concentration only in the St-Antoine sandy loam soil (Fig. 1*c*). Only incubation time significantly influenced soil extractable Fe concentration in the Kamouraska clay soil (Table 3). There was significant interaction between amendment and incubation time on soil extractable Fe and Zn concentrations in the St-Antoine sandy loam soil (Figs. 1*c* and 1*d*). There was a decreasing trend in Mn concentration throughout the incubation period in the Kamouraska clay soil (Table 3) and until day 112 in the St-Antoine sandy loam soil, but an increase was observed at the end of incubation period (day 224) (Table 4). Soil extractable Cu concentration declined in both soils over time (Tables 3 and 4). Overall, soil extractable Fe and Zn concentrations decreased until day 112 and then increased at the end of incubation period (day 224) in both soils (Tables 3 and 4; Figs. 1*c* and 1*d*).

Co-applying biochar and PB had a similar effect on soil extractable Mn and Zn concentrations to application of PB alone in both soils (Tables 3 and 4; Fig. 1*d*). In comparison with PB alone, co-applying PB and 5% biochar significantly decreased soil extractable Cu concentration in both soils (Tables 3 and 4) and soil extractable Fe concentration only in the St-Antoine sandy loam soil (Table 4; Fig. 1*c*).

Application of PB did not significantly affect soil extractable Cu and Fe concentrations in comparison with the control in both soils (Tables 3 and 4; Fig. 1*c*), whereas it significantly increased soil extractable Mn and Zn concentrations in the St-Antoine sandy loam soil (Table 4; Fig. 1*d*) to the extent of their content in Mn and Zn (PB1, Mn = 1723 mg kg$^{-1}$, Zn = 32 mg kg$^{-1}$; PB2, Mn = 148 mg kg$^{-1}$, Zn = 104 mg kg$^{-1}$). We noted that mean soil extractable Mn and Zn concentrations after 224 d of incubation were increased by between 4% and 57% and between 18% and 33%, respectively, by the addition of PB in the St-Antoine sandy loam soil.

Mineral fertilization increased soil extractable Mn concentration in the Kamouraska clay soil (Table 3) but had no effect in the St-Antoine sandy loam soil (Table 4). Extractable Cu, Fe, and Zn concentrations in soils receiving mineral fertilizer were similar to concentrations in the unamended soil (Tables 3 and 4).

## Discussion

#### Effect on pH and CEC

Results confirmed our predictions that biochar co-applied with PB, especially at 5% application rate, would increase the pH of the soils used in this study, compared with the application of PB alone. The alkalinity of biochar may be associated with its surface organic functional groups such as phenolic, hydroxyl, and carboxyl groups that are capable of accepting protons (Yuan et al. 2011; Fidel et al. 2017) and can quickly buffer soil acidity when biochar is incorporated into acid soils (Yuan et al. 2011; Liang et al. 2017). Previously, we found that biochar co-applied with PB decreased soil $NH_4$-N concentration compared with the application of PB only and may have minimized the nitrification of $NH_4$-N released from the PB (Manirakiza et al. 2019). This suggests that biochar co-applied with PB may have limited soil acidification induced by the nitrification process (Czarnecki and Düring 2015). The increase in soil pH following biochar addition may also be caused by the presence of ash in the biochar (Glaser et al. 2002) that contain oxides, hydroxides, and carbonates of Ca, Mg, and K, which are easily dissolved and react with the soil, thereby increasing its pH (Ohno and Erich 1990; Demeyer et al. 2001). The ash content of the biochar used in this study was low (48 g $kg^{-1}$) and may have had little or no impact on the pH of the soils amended with PB and biochar. 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, whereas the increase was only by 0.1–0.2 units at 5% biochar in this study.

Despite high initial pH, the application of PB1 alone did not increase soil pH, probably because their decomposition may increase soil acidity. According to Bolan et al. (1991), the decomposition of organic residues results in the release of $H^+$ and thus in soil pH decrease. The decreasing soil pH observed over the incubation period was likely caused by the progressive mineralization of soil organic matter. This confirmed that the effects of the co-application of biochar and PB on soil pH depended also on incubation time. The significant interaction between amendment and incubation time on soil pH was possibly explained by the diverging trend at day 14 in mineral-fertilized Kamouraska clay soil and since day 28 in mineral-fertilized St-Antoine sandy loam soil and when PB2 was applied with or without biochar.

In this study, no increase in soil CEC was observed following the application of PB alone. This suggests that the effect of biochar was probably the main cause of the increase in soil CEC following co-application of 5% biochar and PB in the St-Antoine sandy loam soil. According to Liang et al. (2006), biochar increases soil CEC by any of three mechanisms: (1) a high charge density per unit surface area, which reflects a high degree of oxidation of soil organic matter, (2) a high surface area for cation adsorption sites, or (3) the combined effect of both mechanisms. The abundance of oxygen-containing functional groups on biochar surfaces, contributing to soil negative charges, can also increase soil CEC following biochar application (Zhu et al. 2017; Shaaban et al. 2018). Cheng et al. (2008) found that soil CEC increased over the incubation in biochar-amended soils because of oxidation of the biochar surfaces and (or) adsorption of organic acids by the biochar. Thus, the effect of biochar on soil CEC may be variable according to incubation time. Soil amendment with PB typically increases soil CEC (Camberato et al. 2006). In a study conducted in a forest soil, Kraske and Fernandez (1993) reported that an application of 40 Mg dry $ha^{-1}$ of PB increased soil CEC by 60%. In this study, the application of PB had no effect on soil CEC, likely because the rate of PB was too low. Indeed, the rate of PB was only 30 Mg wet $ha^{-1}$, 21.21 Mg dry $ha^{-1}$ for PB1, and 20.79 Mg dry $ha^{-1}$ for PB2.

**Effect on extractable P, K, Mg, and Ca**

In this study, applying PB increased soil extractable P concentrations compared with the unamended soil, probably due to the high extractable P content of PB as reported by other studies (Baziramakenga 2003; Camberato et al. 2006; Gagnon et al. 2010). This indicates that PB can efficiently supply P to the plants during the growing season (Gagnon et al. 2010). However, the application of PB2, with its higher $PO_4$-P content, resulted in higher soil extractable P concentration compared with mineral fertilization and could represent a risk of subsurface layer and water P contamination when applied repeatedly or at excessive rates (Gagnon et al. 2010).

Co-applying biochar and PB did not change soil extractable P concentration compared with the application of PB alone, possibly due to the low P content (0.4 g $kg^{-1}$) of the biochar used. Moreover, the increase in soil pH (0.06–0.2 units) due to biochar addition was probably too low to lead to a change in soil extractable P concentration. Increasing the pH of acidic soils may decrease P complexing with $Al^{3+}$ and $Fe^{3+}$ and thereby increase soil extractable P concentration (Xu et al. 2014; Glaser and Lehr 2019). Our results contrasted with those of Jiang et al. (2015) where the application of crop [rice (*Oryza sativa* L.), peanut (*Arachis hypogaea* L.), canola (*Brassica campestris* L.), and soybean (*Glycine max* L.)] straw-derived biochars increased the pH of two acidic soils by 1.31–3 units and significantly improved P mobilisation.

Although our biochar, generated from pine chip at 700 °C (Lévesque et al. 2018), contained substantial amounts of K (2500 mg $kg^{-1}$), Ca (6000 mg $kg^{-1}$), and Mg (1400 mg $kg^{-1}$), its co-application with PB increased only soil extractable K concentration. It is likely that a larger portion of the K in the biochar was in a bioavailable form compared with the Ca and Mg. Generally, biochars contain a large amount of water-soluble K, which can rapidly diffuse into the soil (Amonette and Joseph 2009; Limwikran et al. 2018). Zhao et al. (2016) found that more than 50% of the K in sawdust biochars prepared at between 500 and 900 °C existed as ions, whereas most of the Ca (65%) and Mg (60%) were bound in organic forms. Thus, biochars generated at high temperatures are rich in extractable K, whereas Mg and Ca extractability decreases with temperature because of mineral crystallization of amorphous P–Ca–Mg to form insoluble phases (Cao and Harris 2010; Zornoza et al. 2016). Our results showed that mineral fertilization and amending with 2.5% biochar and PB led to similar extractable K concentrations. This should encourage the use of this biochar, generated from pine chip at 700 °C, as a source of K.

The increase in soil extractable K concentrations observed in the St-Antoine sandy loam soil following application of PB2 was probably caused by the release of their K. The application of PB could also enhance the release of soil K by increasing soil acidification through nitrification and decomposition of organic residues

(Gagnon et al. 2003). According to McCauley et al. (2009), the decomposition of organic residues supplies the soil solution with chemicals that can serve as chelates and increase cation extractability. Even though the PB contained substantial amounts of Mg (PB1, Mg = 700 mg $kg^{-1}$; and PB2, Mg = 500 mg $kg^{-1}$) and Ca (PB1, Ca = 8000 mg $kg^{-1}$; and PB2, Ca = 2200 mg $kg^{-1}$), we found no increases in soil extractable Mg and Ca concentrations following PB application. According to Gagnon et al. (2010), this could be due to the forms in which Mg, Ca, and accompanying anions were present in the BP and their behaviour when they were released into the soil.

As expected, soil extractable K, Mg, and Ca concentrations varied with incubation time. The decrease observed throughout the incubation period for soil extractable K concentration and until day 112 for soil extractable Mg and Ca concentrations was probably caused by the fixation of K, Mg, and Ca by negatively charged soil mineral particles (Evangelou and Philips 2005; Huang 2005). However, the decrease in soil pH during the incubation period may have resulted in the increased solubility of the Mg and Ca, which could explain the increased soil extractable Mg and Ca concentrations observed at the end of the incubation period (Sharpley 1991; Curtin and Smillie 1995; Gagnon et al. 2003).

#### Effect on soil extractable Mn, Cu, Fe, and Zn

The decrease in soil extractable Cu concentration following the addition of 5% biochar to PB-amended soils was in agreement with other studies (Ahmad et al. 2014; Yang et al. 2016; Liang et al. 2017). According to Uchimiya et al. (2011), the electrostatic attraction between positively charged Cu and negatively charged biochar is the prevailing mechanism of Cu immobilization. Liang et al. (2017) reported a gradual decrease of soil Cu extractability when the proportion of biochar was increased in soils receiving the combination of biochar and compost. In contrast, Beesley et al. (2010) reported increased soil Cu mobilization following the application of hardwood-derived biochar, which was associated with the high dissolved organic carbon (DOC) content of the biochar used. This was likely because DOC may bind Cu resulting in the formation of soluble Cu-DOC complexes (Temminghoff et al. 1997; Amery et al. 2007).

Although the biochar contained substantial amounts of Mn (361 mg $kg^{-1}$), Fe (2309 mg $kg^{-1}$), and Zn (38 mg $kg^{-1}$), we found no increases in soil extractable Mn, Fe, and Zn concentrations following biochar addition to PB-amended soils. This indicates that the Mn, Fe, and Zn contained in the biochar were likely poorly extractable. According to Gunes et al. (2015), the oxidation process during high-temperature pyrolysis decreases the water solubility of these elements because of the occurrence of oxide or crystalline forms. Yuan et al. (2015) indicated that the high adsorption surface area and the formation of organometallic complexes could explain the low extractable contents of Mn, Fe, and Zn in biochars.

In this study, soil extractable Fe concentration decreased in the St-Antoine sandy loam soil following the co-application of PB with 5% biochar, probably due to the increase in soil pH. According to Ahmad et al. (2014), pH increase enhances the adsorption and complexation of metal cations on the biochar, which reduces their extractability. Berek et al. (2018) reported a decrease in soil extractable Fe concentration following the co-application of lac tree wood biochar and vermicompost due to the liming potential of the used biochar.

According to Beesley and Marmiroli (2011), sorption is one of the mechanisms by which Zn is retained by biochar. In this study, the addition of biochar to PB-amended soils did not decrease soil extractable Zn concentration, possibly due to the low Zn sorption capacity of pine chip biochar used. Pine-wood-derived biochars were reported to have low metal sorption capacity (Zhang et al. 2015; Jiang et al. 2016; Van Poucke et al. 2019), which is attributed to the low phosphate and carbonate levels of these type of biochars (Van Poucke et al. 2019). According to Xu et al. (2013), phosphate and carbonate originated from the feedstock play an important role in the sorption nature of biochar. The addition of biochar to PB-amended soil did not significantly decrease soil extractable Mn concentration. Heaney et al. (2018) suggested that Mn had a lower affinity to the biochar compared with Zn.

The increase in soil extractable Mn and Zn concentrations in the St-Antoine sandy loam soil following the application of PB could be explained by the release of Mn and Zn contained in the PB through its decomposition. Our results are consistent with those of Gagnon et al. (2010), who observed a linear increase in soil extractable Zn with PB rates. Similarly, Gagnon et al. (2003) reported that soil extractable Mn concentration increased with PB application rate. In this study, the effect of amendments on soil extractable Cu, Mn, Fe, and Zn concentrations was limited in the Kamouraska clay soil, probably because of its high initial CEC and higher adsorptive properties, as well as low PB decomposition in this soil.

As hypothesised, incubation time greatly affected the concentrations of soil extractable Cu, Mn, Fe, and Zn. The decrease observed throughout the incubation period for soil extractable Cu concentration and until day 112 for soil extractable Mn, Fe, and Zn concentrations was apparently caused by the reduction of the most labile forms of Cu, Mn, Fe, and Zn with time (Zhong et al. 2012; Fernández-Calviño et al. 2017) due to the transfer of exchangeable and soluble forms to more refractory forms (Zhong et al. 2012; Huang et al. 2015). Sayen et al. (2009) found that time reduced the amount of extractable Cu because of the redistribution of weakly bound Cu into strongly bound Cu. Increasing soil extractable Mn, Fe, and Zn concentrations after day 112 was likely caused by desorption associated with decreasing soil pH (Huang et al. 2014). The sharp decrease in soil extractable Fe concentration between days 14 and 28 in the St-Antoine sandy loam soil amended with PB2 and 5% biochar (Fig. 1*c*) resulted in a converging trend and may explain the significance of the interaction between amendment and incubation time. A slight diverging trend of soil extractable Zn concentration was observed at day 14 when the St-Antoine sandy loam soil was amended with PB1 and 5% biochar and may explain the significant interaction between amendment and incubation time.

## Conclusion

This study showed that co-applying pine chip biochar and PB increased soil pH in comparison with the application of PB alone in two acidic soils from Quebec, Canada, a clay (pH = 5.32) and sandy loam (pH = 5.89). Combined application of pine chip biochar and PB could be used to buffer the acidifying effect of PB. Our work suggests that a biochar application rate of 5% (60 Mg $ha^{-1}$) would be needed when PB is applied at rates (20–40 Mg $ha^{-1}$) commonly used in Quebec. Because of the positive effect on soil CEC, applying pine chip biochar with PB could improve the nutrient-retention capacity of sandy soils. Co-applying PB and biochar with high extractable K content, such as pine chip biochar, may be a good complement to PB fertilizing potential. Co-applying pine chip biochar and PB did not decrease the release of P from soil, as expected. Hence, co-application of pine chip biochar and PB with high extractable P content, such as PB2, could represent a risk if the proportion of PB in the combination is high. Combined application of PB and 5% pine chip biochar reduced the extractability of Cu and Fe in comparison with individual application of PB, but mainly in the sandy loam soil. Co-applying biochar and PB could improve metal sequestration and prevent metal toxicity, especially in sandy soils with low CEC. However, the lack of plants as a sink of the macro- and micronutrients presents limitations to ours results. Field trials are needed to further evaluate the benefits of the co-application of pine chip biochar and PB.

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