Soil Phosphorus Fractionation as Affected by Paper Mill Biosolids Applied to Soils of Contrasting Properties

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Industrial by-products such as paper mill biosolids (PBs) have been used as fertilizers and amendments in agriculture for many decades. However, their content of plant essential nutrients including phosphorus (P) varies largely with sources, and availability of these nutrients once applied to soil still remains unknown. Five PBs differing in their C/N ratio (12–47) were used in an incubation study to assess the P forms and availability from both PBs and PB-amended soils. Biosolids were added to three contrasting soils varying in texture and pH in 500-ml jars at the rate of 50 Mg wet ha^{-1}, supplying between 45 and 112 kg total P ha^{-1}. An unfertilized control and a mineral NP treatment (30 kg P ha^{-1}) were also included. Biosolids and soil P fractions were determined by a modified Hedley fractionation method following 2 and 16 weeks of incubation. Phosphorus forms in PBs varied across type of materials with labile P ranging from 20 to 72% and organic P (Po) ranging from 28 to 66% of total P. Soil incubated with PB showed changes in all P fractions due to amendment, soil type, and duration of incubation. Resin-P and labile P, the most available forms, were significantly higher with addition of high PB–P content. Soil labile P represented up to 50% of total P added by PB. Overall, most inorganic P (Pi) fractions and labile P further increased with incubation duration. Close relationships were established between resin-P and labile P content in PB and the increases of those fractions in incubated soils, notably after 2 weeks. The P recovery as labile P represented on average 34% of total P added or 68% in terms of mineral P. We concluded that PB could be used as an efficient source of P for fertilizing crops.

Keywords: phosphorus, paper mill biosolids, soil incubation, phosphorus fractions, phosphorus availability

INTRODUCTION

The non-renewable status of extractable phosphorus (P) on Earth (Cordell et al., 2009) has resulted in an increasing interest of alternative sources such as the use of biosolids in agriculture (Shu et al., 2016). Biosolids are by-products of industrial or urban wastewater treatment which are commonly used as fertilizer and soil amendment to improve crop productivity (Su et al., 2007). Biosolids application can positively enhance crop dry matter production and yield through their N availability

(Cogger et al., 2006; Al-Dhumri et al., 2013). Henry et al. (1994) confirmed the potential of biosolids to increase the productivity of many forests.

Some concerns about biosolids application, such as potential environment contamination, make its management a very important part when used in agriculture soils. Biosolids are often applied based on crop N requirements, which may lead to soil P accumulation and increase the risk of P loss to surface or groundwater (Kelling et al., 1977; Shober and Sims, 2003; Pierzynski and Gehl, 2005). The N/P ratios for nutrient crop uptake in field crops varied from 4.5 to 8.7 (Sadras, 2006), which are considerably higher than those found in municipal biosolids (2.7) but much closer to PB (5.7) (Miller et al., 2000; Charbonneau et al., 2001; Maguire et al., 2001). Moreover, biosolids properties and their treatment plant process may have a significant impact on their fertilizer value, which can affect soil P availability (Frossard et al., 1996; Maguire et al., 2001; Penn and Sims, 2002; Torri et al., 2017).

Many studies documented soil P status once biosolids are applied. Maguire et al. (2001) recommended testing biosolids for P availability rather than total P, since it was a more appropriate indicator for predicting extractable P from biosolids-amended soils. Conversely, biosolids with similar total P may vary widely in the amount of P measured in various extracts (O'Connor et al., 2004). Different methods, including water-extractable P, Olsen P, or Mehlich-3 P (Wang et al., 2004; Su et al., 2007; Shu et al., 2016), can be used to investigate the effect of biosolids on soil P availability. Ippolito et al. (2007) reported that characterizing fractions into labile and non-labile pools could be a typical method to predict P availability in biosolids-amended soils. To address this, soil P fractionation can serve to predict the availability of P in soil as well as the likelihood of its transport (Sui et al., 1999).

The pulp and paper industry constitutes a major component of the Canadian economy, and their activities generate huge amounts of organic residues from the treatment of derived wastewater. Most recent statistics indicate that 1.5 million dry Mg paper mill biosolids (PBs) are produced annually (Rashid et al., 2006), but a low percentage (<25%) is applied on cropland whereas the rest of the residues are burnt or landfilled (MDDELCC, 2016). Large volumes of PBs are also available in the United States (5.5 million dry Mg year^{-1}; Thacker, 2007) and Europe (11 million dry Mg year^{-1} including rejects and ash; Monte et al., 2009). Land application of PB as municipal biosolids can benefit crop growth by supplying N and P while improving soil physical properties (Cabral et al., 1998; Camberato et al., 2006). Better knowledge of nutrient contribution from PB including P might help promote their appropriate use in the field.

Studies conducted to characterize municipal biosolids indicated that labile P fraction composes a small proportion of total P but this does depend on sludge type (Frossard et al., 1996; Sui et al., 1999; Ajiboye et al., 2004; Shober et al., 2006). For example, addition of lime or metal salts during the wastewater treatment process to stabilize biosolids can reduce solubility of P (Frossard et al., 1996; Pierzynski and Gehl, 2005; Su et al., 2007; Torri et al., 2017). With PB, the

treatment of effluent generally consists of primary clarification to remove suspended solids followed by an activated secondary process in which microorganisms are used to reduce organic pollutants and biological oxygen demand (Nurmesniemi et al., 2007; Monte et al., 2009). To our knowledge, little is known about P forms in this particular material. When applied to soil, municipal biosolids were often reported to cause a net increase of relatively available Pi forms (H_2O, $NaHCO_3$, and NaOH) at the expense of more stable or recalcitrant forms (NaOH-Po, HCl-P, and residual P) (Sui et al., 1999; Kashem et al., 2004; Su et al., 2007; Alleoni et al., 2012). This transformation of NaOH-Po and residual P to more labile forms was also observed with PB after 6 years of application (Fan et al., 2010). All these studies, however, did not assess the P response of PB under different soil types and their possible interactions.

The objectives of this study were to (1) characterize the P forms in several PBs used in Canada and (2) determine the P forms after PB addition to soils with contrasting chemical properties after 2 (short-term) and 16 (typical duration of growing season) weeks under controlled conditions.

MATERIALS AND METHODS

Soils and Biosolids Characterization

The soils used for the incubation study were collected from the upper layer (0–15 cm) of three fields. Two soils came from near Quebec City, QC, Canada (47°N, 71°W): a Kamouraska silty clay (KAM; umbric Gleysol; FAO soil classification) from a cornfield and a St-Antoine sandy loam (StA; haplic Podzol) from a field under alfalfa/timothy pasture. The other soil came from near Lethbridge, AB, Canada (50°N, 113°W): a Chin fine sandy loam (CHIN; haplic Kastanozems) from a potato field. The soils were air-dried and sieved to 2 mm before incubation. Each soil was characterized in triplicate for particle size, pH, organic C, Mehlich-3 extractable elements, and P fractions (**Table 1**). The KAM and StA soils were selected to evaluate the response of PB in acidic soils, where P fixation occurs predominantly with Fe and Al oxides/hydroxides. The alkaline soil, CHIN, was selected to account for P fixation by Ca. According to critical P/Al or P/(Al + Fe) values, the KAM and StA soils had a greater capacity to retain P against losses into the environment (Pellerin et al., 2006; Wang et al., 2015).

Five different PBs were tested in this study: (1) mixed PB (primary and secondary treated sludge) from thermomechanical pulp (PB1); (2) mixed PB from bleached Kraft pulp with some municipal effluent (PB2); (3 and 4) mixed PB from bleached acid-treated Kraft pulp issued from different production times (PB3a and PB3b); and (5) de-inking sludge from recycled papers (PB4). These PBs have been previously used in field experiments (Gagnon et al., 2010, 2012b; Gagnon and Ziadi, 2012) and respected limits for trace metal contaminants (Camberato et al., 2006). Selected PBs differed largely in their properties, notably pH, total N and P, and C/N ratio (**Table 2**). PB2 and PB3b showed the highest concentrations in total N and P and the lowest C/N ratio.

TABLE 1 | Characteristics of selected soils used for the incubation study.

Attributes	Kamouraska (KAM)	Saint-Antoine (StA)	Chin (CHIN)
Sand (g kg^{-1})	302	683	554
Clay (g kg^{-1})	406	152	167
pH (1:2 soil to water)	5.32	5.89	7.51
Organic C (g kg^{-1})	30.2	16.3	14.3
Mehlich-3 P (mg kg^{-1})	38	36	119
Mehlich-3 Ca (mg kg^{-1})	2,551	1,023	2,511
Mehlich-3 Al (mg kg^{-1})	1,253	1,040	403
Mehlich-3 Fe (mg kg^{-1})	194	354	78
P fractions (mg kg^{-1})			
Resin-P	58	31	93
NaHCO$_3$-Pi	33	19	23
NaOH-Pi	118	59	20
HCl-P	415	116	227
ΣPi	624	225	363
NaHCO$_3$-Po	49	30	13
NaOH-Po	315	98	57
Residual-P	248	93	108
ΣPo	612	221	177
Σfraction P	1,236	446	540

TABLE 2 | Main properties of selected paper mill biosolids (PBs).

Attributes	PB1	PB2	PB3a	PB3b	PB4
pH$_{water}$ (1:2)	7.80	6.77	4.98	4.51	7.23
Moisture (g kg^{-1})	707	782	639	693	553
Total C (g kg^{-1})	315	450	446	485	281
Total N (g kg^{-1})	12.8	36.3	19.1	39.7	6.0
C/N ratio	25	12	23	12	47
Total P (g kg^{-1})	4.2	5.7	2.9	7.3	2.0
PO$_4$-P (mg kg^{-1})	72	344	177	1,051	2
Total Ca (g kg^{-1})	8	51	6	2	149
Total Al (g kg^{-1})	36.5	3.7	9.1	9.1	13.0
Total Fe (g kg^{-1})	3.1	1.9	1.0	1.4	1.6
(Fe + Al)$_{total}$ (mmol kg^{-1})	1,463	204	374	387	539
Total P added with 50 Mg wet PB ha^{-1} (kg ha^{-1})	62	62	52	112	45

Values on dry matter basis except moisture. Total C was determined by loss to ignition, whereas total major nutrients by wet acid digestion with H_2SO_4-H_2SeO_3 (Isaac and Johnson, 1976). The water-soluble PO_4^{3-} content was extracted from fresh material to a solution ratio of 1:5 by weight.

Incubation Study

Biosolids were mixed with 100 g of air-dried soil at a rate equivalent to 50 Mg wet ha^{-1} (4.17 g fresh material per jar considering a depth incorporation of 10 cm and a soil bulk density of 1.2 g cm^{-3}) and incubated in 500-ml Mason^{TM} glass jars. The PB supplied between 45 and 112 kg total P ha^{-1} (**Table 2**). Unamended controls containing soils only were prepared in a similar manner in order to estimate the contribution of soil-derived P. In addition, a mineral NP treatment [(30 kg KH$_2$PO$_4$-P ha^{-1} and 100 kg N ha^{-1} as NH$_4$NO$_3$ (35% N)] was added to evaluate the relative P contribution of each biosolids.

The experiment was laid out as a factorial of seven treatments (five PBs, NP, and the control) and three soils completely randomized in three replications. Distilled water was added to the soil–PB mixtures to adjust water-filled pore space to 60%. The jars were closed and incubated in the dark in a controlled environment chamber at 25°C for 16 weeks. Water loss was monitored twice a week and corrected if needed. At the same time, the soils were well aerated and carefully remixed before reclosing to maintain constant aerobic and mineralization conditions.

Soil Phosphorus Fractionation

Subsamples (5 g) of the soil–PB mixtures were collected after 2 and 16 weeks of incubation and analyzed for P fractions. The two sampling periods were chosen to simulate short-term (early root growth) and typical duration for a growing season in Canada. Soil samples 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 used in the Fan et al. (2010) study. Thus, a 0.5-g subsample of ground soil was weighed into 50- ml centrifuge tubes and sequentially extracted according to the following scheme:

(1) Resin-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. P was recovered from strips in 25 ml of 0.5 M HCl.
(2) NaHCO$_3$ (Pi and Po): 25 ml of 0.5 M NaHCO$_3$ at pH 8.5, shake for 16 h at 25°C, centrifuge, and collect supernatant.
(3) NaOH (Pi and Po): 25 ml of 0.1 M NaOH, shake for 16 h at 25°C, centrifuge, and collect supernatant.
(4) HCl (Pi): 25 ml of 1.0 M HCl, shake for 16 h at 25°C, centrifuge, and collect supernatant.
(5) Residual P: 10 ml of 0.9 M H$_2$SO$_4$ and 0.5 g of K$_2$S$_2$O$_8$, digestion at 121°C in an autoclave for 90 min.

The concentration of Pi in extracts and digests was determined by the ammonium molybdate–ascorbic acid 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 H$_2$SO$_4$–K$_2$S$_2$O$_8$ digestion and Pi. Total P in soils was also determined the same way as for residual P with 0.1 g of ground soil. This allowed evaluation of the P recovery from fractionation which varied from 83 to 103% (93 ± 5%). Additionally, the soil pH (1:2 soil:water) was determined on the air-dried 2-mm samples at the end of incubation.

Total Pi was the sum of resin-P, NaHCO$_3$-Pi, NaOH-Pi, and HCl-Pi, while 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). According to the criteria of

Bowman and Cole (1978) and Tiessen et al. (1984), the sum of resin-P and $NaHCO_3$-P was considered as labile P, NaOH-P as moderately labile P, and HCl-P and residual P as stable P.

Biosolids Phosphorus Fractionation

Paper mill biosolids P was also fractionated before application using the same method as described for soil. Since the method was developed for mineral soils, some modifications were made considering the organic nature of the material. Thus, fresh PB (0.5 g wet basis for P fractionation and 0.1 g wet basis for total P) was 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 M 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.

Data Analysis

All data for soil incubation were checked for normality with Shapiro–Wilk. Only NaOH-Pi was transformed based on the Box–Cox model to improve the normality of distribution. Treatment effects were evaluated as a factorial of 3×7 replicated three times using the MIXED procedure (SAS Institute Inc., 2004) with replicates and replicates $\times$ treatments as random effects, soil types and treatments as fixed effects, and incubation time as repeated effect. Main treatment effects and their interactions were tested using differences of least squares means. The NP treatment in the CHIN soil was omitted due to the unexpected negative total Pi recovery (-10%) at the end of incubation as compared with KAM (86%) and StA (91%) soils. As a consequence, this treatment was excluded from the statistical analysis. Statistical significance was defined as $P < 0.05$.

RESULTS AND DISCUSSION

Biosolids Phosphorus Fractions

Total P content in PB ranged from 1,535 to 6,904 mg kg^{-1}, with the PB3b having the highest concentration and the PB4 showing the lowest (Table 3). The P recovery from fractionation was high, varying between 93% and 101%, in agreement with other studies performed on organic materials (79–113%; Ajiboye et al., 2004; Turner and Leytem, 2004; Gagnon et al., 2012a).

Total Po, with the exception of PB1, accounted for a large part of total P (46–66%, Table 3). This contrasts with municipal biosolids in which Pi was dominant (>71%; Sui et al., 1999; Ajiboye et al., 2004; O'Connor et al., 2004; Su et al., 2007). In this study, PBs have been mostly subjected to a secondary biological treatment for further purification and stabilization before discharge to the water bodies. This treatment increases the microbial activity and could explain the high Po proportion in such materials, a tendency also observed when sewage sludge was treated by the activated process (Frossard et al., 1996).

The relative contribution of P in each fraction varied with the material (Table 3). Resin-P (Pi + H_2O-Po), the most readily available form, ranged from 2% in PB4 to 40% and 59% in PB3a and PB3b, respectively. Moreover, a significant part (around 40%) of Po was found in resin + H_2O and $NaHCO_3$ extracts for PB3a and PB3b. These fractions are considered mobile in the soil and biologically available (Turner and Leytem, 2004). Either PB3a and PB3b was treated with phosphoric acid to stimulate P degradation by microorganisms and reduce odor (Gagnon and Ziadi, 2012). Both materials came from the same source and were subjected to the same treatment process. Despite differences in total P, they were more related to each other than to other materials.

The labile P (resin + $NaHCO_3$), which is considered plant available, was the highest with PB2, PB3a, and PB3b (44–72%). It constituted, however, only 20–26% of total P in the other two materials. In counterpart, PB1 and PB4 contained 36–40% of their P in the stable (HCl + residual) fractions. This could be attributed to their high pH, which may contribute to the formation of recalcitrant Ca phosphate minerals (Torri et al., 2017) and to the high total Al and Fe contents (Table 2), which were found to result in materials having a low-availability P concentration (Krogstad et al., 2005; Torri et al., 2017). Khiari et al. (2020) reported that biosolids with a (Fe + Al)$_{total}$ >1,100 mmol kg^{-1} were classified as medium to low for their P bioavailability and were similar to a slow-release source of P for crops. Overall, the relative distribution of P forms in PBs indicated that P in this material could constitute a good source to crops, sometimes more efficient than many municipal biosolids and composts (Sharpley and Moyer, 2000; Ajiboye et al., 2004; Xu et al., 2012). To this end, Ebeling et al. (2016) found that municipal biosolids with a biological P removal process had consistently the highest soil test P values in opposition to biosolids treated with alum or $FeCl_2$.

Effect of Incubation on Soil pH

Variations in soil pH during incubation induced by mineralization of PB may have a large impact on the distribution and form of soil P fractions. In acidic soils, Fe and Al phosphates are more dominant, whereas in alkaline soils, Ca phosphate dominates. In this study, addition of PB4 due to its high Ca content (Table 2) induced a large increase in soil pH, 0.1 unit in the alkaline CHIN but 1.6–1.8 in the acidic KAM and StA (Table 4). On the opposite, PB3a and NP decreased the soil pH by an average of 0.2–0.3 units, while PB3b caused the largest drop in pH with 0.6 units. PB3b was the most acidifying material of all those tested (Table 2).

Effect of Incubation Time, Soil Type, and Biosolids on Soil Phosphorus Fractions

There were significant changes in the different P fractions with time during the incubation (Supplementary Table S1). From the beginning to week 16, there was a general increase in all Pi fractions, notably the labile forms (resin-P and $NaHCO_3$-Pi; Supplementary Table S2). This was made at the expense of Po and residual P fractions for StA and CHIN and $NaHCO_3$-Po

TABLE 3 | Phosphorus fractionation of paper mill biosolids (PBs) used in the incubation study.

Fractions	PB1	PB2	PB3a	PB3b	PB4
			$mg \cdot kg^{-1}$ **dry weight**		
Inorganic					
Resin	$577 \pm 45(13)$	$1,500 \pm 86(26)$	$810 \pm 78(29)$	$3,273 \pm 102(47)$	$8 \pm 4(1)$
$NaHCO_3$	$400 \pm 32(9)$	$729 \pm 30(13)$	$79 \pm 17(3)$	$196 \pm 5(3)$	$173 \pm 5(12)$
NaOH	$1,293 \pm 117(29)$	$153 \pm 52(3)$	$1 \pm 2(0)$	$0 \pm 0(0)$	$246 \pm 9(17)$
HCl	$894 \pm 26(20)$	$695 \pm 4(12)$	$37 \pm 4(1)$	$84 \pm 3(1)$	$228 \pm 12(16)$
Total Pi	$3,164 \pm 178(72)$	$3,077 \pm 78(54)$	$927 \pm 74(34)$	$3,554 \pm 107(51)$	$656 \pm 24(45)$
Organic					
Resin + H_2O	$66 \pm 22(2)$	$126 \pm 28(2)$	$303 \pm 32(11)$	$818 \pm 221(12)$	$28 \pm 4(2)$
$NaHCO_3$	$94 \pm 3(2)$	$172 \pm 30(3)$	$358 \pm 40(13)$	$708 \pm 37(10)$	$76 \pm 1(5)$
NaOH	$397 \pm 33(9)$	$1,617 \pm 73(28)$	$720 \pm 52(26)$	$1,180 \pm 115(17)$	$343 \pm 4(24)$
HCl	$48 \pm 6(1)$	$142 \pm 10(2)$	$102 \pm 48(4)$	$98 \pm 18(1)$	$144 \pm 33(10)$
Residual	$625 \pm 14(14)$	$604 \pm 66(11)$	$340 \pm 41(12)$	$594 \pm 48(9)$	$213 \pm 2(15)$
Total Po	$1,230 \pm 34(28)$	$2,661 \pm 33(46)$	$1,823 \pm 113(66)$	$3,397 \pm 215(49)$	$804 \pm 37(55)$
Total					
Σfraction P	$4,394 \pm 173$	$5,738 \pm 91$	$2,750 \pm 181$	$6,951 \pm 113$	$1,460 \pm 59$
Total P digestion	$4,754 \pm 99$	6031 ± 69	$2,838 \pm 121$	$6,904 \pm 156$	$1,535 \pm 107$
P recovery (%)	93	95	97	101	95

P recovery = (resin-Pi + $NaHCO_3$-Pi + NaOH-Pi + HCl-Pi + resin + H_2O-Po + $NaHCO_3$-Po + NaOH-Po + HCl-Po + residual P) × 100/total P in digestion. Values in parenthesis represent percentage of specific form P in the sum of fraction P.

TABLE 4 | Effect of paper mill biosolids (PBs) and mineral P fertilizer on the soil pH at the end of the 16-week incubation.

Treatment	KAM	StA	CHIN
PB1	5.17 ± 0.01	5.73 ± 0.07	7.54 ± 0.01
PB2	5.12 ± 0.02	5.79 ± 0.10	7.48 ± 0.03
PB3a	5.05 ± 0.01	5.42 ± 0.01	7.32 ± 0.04
PB3b	4.81 ± 0.00	5.01 ± 0.14	7.01 ± 0.03
PB4	6.82 ± 0.03	7.50 ± 0.01	7.71 ± 0.02
Mineral NP	5.07 ± 0.02	5.44 ± 0.10	7.43 ± 0.01
Control (0 NP)	5.23 ± 0.01	5.69 ± 0.13	7.61 ± 0.02
$LSD_{0.05}$	0.03	0.18	0.04

and residual P for KAM. Kashem et al. (2004) investigated the forms and distribution of P after 1, 4, and 16 weeks of incubation in a silty clay loam soil and reported that the amendment with municipal biosolids caused a net conversion of Po and residual forms toward H_2O-P, NaOH-Pi, and HCl-P fractions. Sui et al. (1999) and Su et al. (2007) also found a decrease in the most recalcitrant forms (HCl-P, NaOH-Po, and residual P) and a concomitant increase in labile forms (H_2O-P and $NaHCO_3$-Pi) after repeated applications of municipal biosolids. Fan et al. (2010) reported a large decrease in NaOH-Po and residual P after 6 years of continuous PB application, which was attributed to the mobility and/or mineralization of NaOH-Po and the transformation of recalcitrant P to more labile forms with time.

Soil type had a very significant effect ($P < 0.001$) on every soil P fraction (**Supplementary Table S1**). This was expected due to the significant variability in P distribution with the three soils selected in this study (**Table 1**). Globally, the greater P sorption capacity of KAM and StA soils made resin-P to be lower in these soils and NaOH-P associated with Al and Fe oxides to be higher

as compared with CHIN (**Supplementary Table S2**). However, there was a soil × treatment interaction for resin-P and labile P, meaning that these P fractions behave differently depending on which soil the different PBs have been incorporated in.
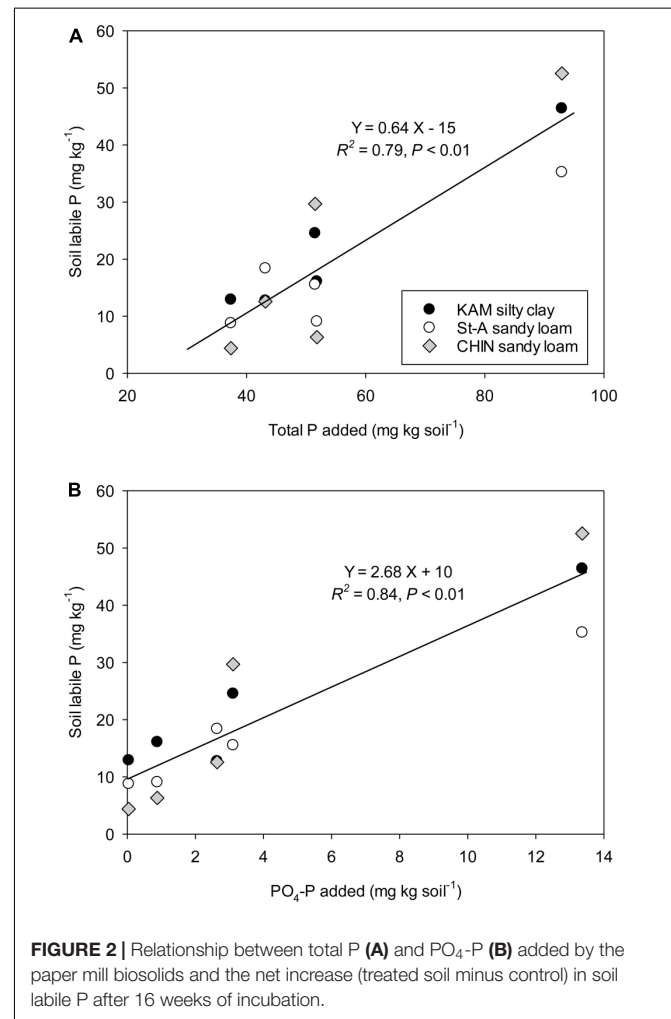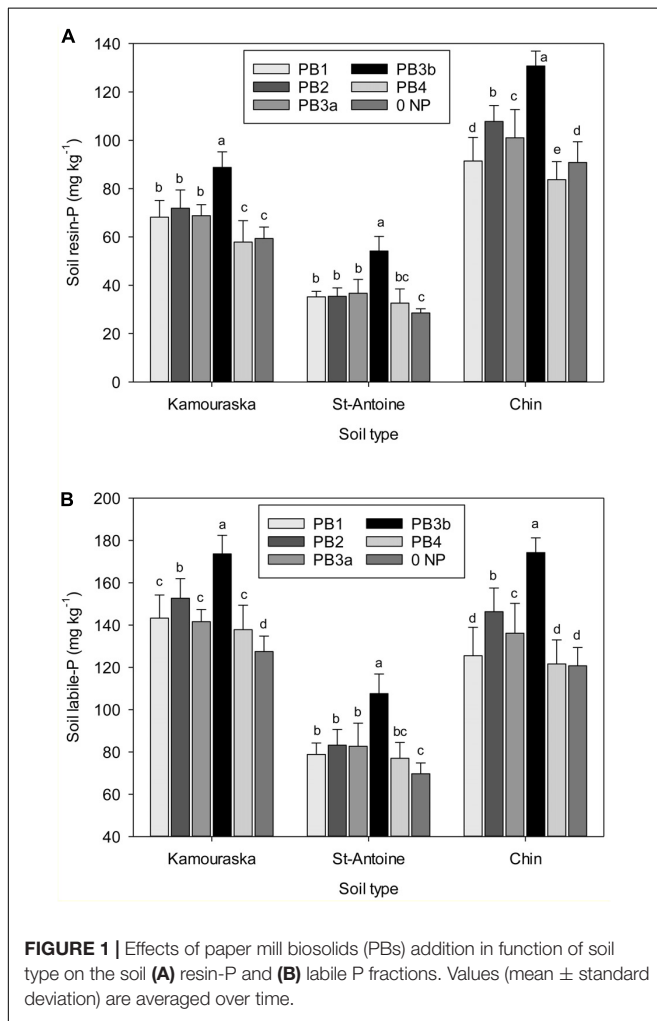
Application of PB was particularly important for soil resin-P, a freely available fraction, and labile P (**Supplementary Table S1**). The increases reached 26 to 40 mg kg^{-1} in resin-P and 39 to 51 mg kg^{-1} in labile P (**Figures 1A,B**). The strongest differences were noted for resin-P in CHIN soil. Such wider range has been already observed in a preceding study evaluating different composts (Gagnon et al., 2012a) and was attributed to the relatively low potential of this soil to fix added P. The Fe and Al oxides are the most important phosphate adsorbents in soil (Parfitt, 1979; Borggaard et al., 1990), and phosphate sorption increases with decreasing pH (Lopez-Hernandez and Burnham, 1974), which can mask the differences between PBs. Conversely, application of P in soils of temperate climate was responsible for the largest variations over the years in labile P (Negassa and Leinweber, 2009). To this end, Fan et al. (2010) obtained a linear increase in resin-P and a tendency ($P = 0.07$) for increase in $NaHCO_3$-Pi after 3 years of continuous application of 90 Mg wet PB ha^{-1} to a loamy soil.

In this study, PB3b caused the largest increase in P concentrations in all soils (**Table 5** and **Figure 1A**). This is expected with the supply of a high total P amount by this material (112 kg P ha^{-1}; **Table 2**). In terms of total P added, PB3b (42–55%) followed by PB2 and PB3a (26–49%) was an interesting source to increase soil labile P. Unfortunately, PB1 and PB4 were relatively inefficient at releasing P in the alkaline CHIN soil (**Figure 1B**). Moreover, PB4 induced a shift from NaOH-Po to $NaHCO_3$-Pi (**Table 5**). Accordingly, it appears that its very high Ca content (**Table 2**) and good liming potential (40% $CaCO_3$ equivalent; Gagnon and Ziadi, unpublished data) promoted soil

TABLE 5 | Effects of paper mill biosolids addition on selected soil P fractions averaged over soils and time (mg kg^{-1} dry basis).

	NaHCO$_3$-Pi	NaHCO$_3$-Po	NaOH-Pi	NaOH-Po	HCl-P	Total Pi
PB1	28 ± 5c	23 ± 14c	69 ± 40bc	160 ± 124b	256 ± 127ab	418 ± 171b
PB2	30 ± 7b	25 ± 15b	69 ± 43b	168 ± 128ab	254 ± 125ab	426 ± 170b
PB3a	27 ± 5c	25 ± 14b	65 ± 42d	168 ± 127ab	247 ± 127c	408 ± 169c
PB3b	35 ± 6a	26 ± 14a	72 ± 45a	173 ± 124a	258 ± 127a	455 ± 172a
PB4	31 ± 8b	23 ± 13c	65 ± 40d	148 ± 118c	252 ± 123abc	405 ± 162cd
Untreated control (0 NP)	24 ± 5d	23 ± 14bc	66 ± 41cd	162 ± 121b	249 ± 124bc	399 ± 172d

Total Pi = resin-P + NaHCO$_3$-Pi + NaOH-Pi + HCl-P. For each factor, means followed by the same lowercase letter are not different at P = 0.05.

FIGURE 1 | Effects of paper mill biosolids (PBs) addition in function of soil type on the soil (A) resin-P and (B) labile P fractions. Values (mean ± standard deviation) are averaged over time.

FIGURE 2 | Relationship between total P (A) and PO$_4$-P (B) added by the paper mill biosolids and the net increase (treated soil minus control) in soil labile P after 16 weeks of incubation.

pH increase (Table 4), which may have reduced the mobility of Al (Casséus et al., 2011).

Despite Po forming a large proportion of total P in some of these materials (Table 3), significant effects of PB were mostly detected on Pi fractions (Supplementary Table S1). This indicated that PB had a good potential for P mineralization in the studied soils. Increases in labile Pi were also observed with municipal biosolids even if these materials comprised Pi in less soluble forms (Sui et al., 1999). The net increase in labile P (soil labile P + PB minus soil labile P in 0 NP minus labile P applied with PB) was mainly negative, particularly for PB3a and PB3b (−11 and −21%, respectively). Negative values mean that PBs served more as a direct source of P fertilizer than soil P conditioner because they did not enhance the release of P from the soil.

Considering the application rate and the forms and distribution of P in the material, the PB in this study (excluding PB4 considered more as a soil conditioner) supplied 17 (6–38) kg resin-P ha^{-1} and 25 (9–55) kg labile P ha^{-1} after the early stage of application, based on the 2-week incubation data, and

a little bit more for the entire incubation (18 and 28 kg P ha^{-1}, respectively). This covers a large part of the P requirements for corn and small cereals (26–28 kg P ha^{-1}; CRAAQ, 2010) produced in eastern Canada in the low-P KAM and StA soils. The P availability at week 2 is important for early plant growth, particularly in temperate areas where the soil is usually cool at springtime (Grant et al., 2001). Even if this study did not include a crop test, the accompanying NP treatment can be used to assess the potential direct P contribution of PB sources by assuming that labile P measured in the NP treatment is considered to represent plant available P (Tiessen and Moir, 2008). In terms of mineral P, the P recovery as labile P represented on average 68%, with the lowest recovery with PB1 (48%) and the highest with PB3b (87%). Hence, PB could constitute an excellent source of P, more than the conventional treated sewage sludge in which application to the field indicated a much lower P availability than the commercial P fertilizer based on soil NaHCO$_3$-P extraction and corn plant P concentration (Tian et al., 2016).

Relationships Between Phosphorus Fractions in Biosolids and Soils

Soil resin-P and labile P increases over the control were closely related to total P added at both week 2 (R^2 = 0.79–0.83) and week 16 (R^2 = 0.76–0.79) of the incubation (**Figure 2A**). This indicates a high potential for PB to be a valuable source of P for crops. Su et al. (2007) also reported an increase in these fractions with municipal biosolids addition to a sandy forest soil. Soil labile P increases were also related to the amount of PO$_4$-P added (**Figure 2B**). Total P concentration and water-extractable P have been reported as the best indicators for predicting P release from composts and manures (Sharpley and Moyer, 2000; Zvomuya et al., 2006). In this study, a relationship could be established between PO$_4$-P concentration and pH of materials, all determined by water extraction (R^2 = 0.53). This indicates that total P and pH might be selected as controlling variables to estimate P contribution from PB.

When expressed on a total P basis, close relationships were obtained between net increases in soil resin-P and labile P and a proportion of these fractions in biosolids at both 2 and 16 weeks (**Supplementary Table S3**). There was also a negative correlation between soil resin-P and labile P and materials with the most recalcitrant (NaOH-P, HCl-P, and residual) P fractions. Besides the magnitude of labile P, which can be used for evaluating potential environmental impact (Sharpley and Moyer, 2000; Ajiboye et al., 2004) and plant P bioavailability (Zvomuya et al., 2006), the fate of P of the organic amendments once applied to soil has always been hard to predict. Despite several attempts, the biogeochemistry of the soil plays a role in the fixation of phosphate ions by Al and Fe oxides in acidic soil and by Ca ions in alkaline soil and causes a redistribution of the different P forms with time.

CONCLUSION

This study revealed that PB could potentially be an efficient P source for fertilizing crops based on our soil *P* test. These materials generally contained a high percentage of freely available resin-P and labile P and low Al and Fe contents, which enhanced the P availability in soil. The increases in soil labile P, which is considered plant available, may represent up to 50% of total P added and can even reach amounts obtained with the mineral P fertilizer. All soils can benefit from application of PB, at least in the short term for the development of young plants. However, the total P content and P forms varied largely, even within the same production plant. These wide variations could therefore translate into differences in PB response when applied in field and various beneficial P effects on crops.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/**Supplementary Material**.

AUTHOR CONTRIBUTIONS

XZ, a Ph.D. student under the supervision of NZ and ZH, did all the lab work, performed all calculations and statistical analyses, and wrote a first version of this manuscript. BG conducted the incubation study, validated statistical analyses, and contributed to the results and discussion. NZ initiated the study, supervised the Ph.D. student, and contributed to the whole manuscript. AC discussed and validated the statistical analyses and revised and commented on the manuscript. KA and ZH revised and commented on the manuscript.

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SUPPLEMENTARY MATERIAL

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