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ARTICLE

Soil carbohydrate and aggregation as affected by carbohydrate composition of paper mill biosolids[1]

Bernard Gagnon and Noura Ziadi

Abstract: Paper mill biosolids (PB) are recognized as a valuable source of carbon for the physical improvement of arable soils. However, little is known about the composition of carbohydrates of these materials and their breakdown in soil, which contributes to soil structural stability. The objectives of this study were to characterize the carbohydrates in PB and to determine under controlled conditions and in the field the soil carbohydrate content and water-stable aggregation. The field experiment consisted of PB applied every year (2000–2008) at 0, 30, and 60 Mg wet weight·ha^{-1} to annual row crops with soils collected after 3, 6, and 9 yr. The other experiment consisted of PB added at 50 Mg wet weight·ha^{-1} to two soils, a clay and a sandy loam, and incubated at 25 °C and 60% water-filled pore space for 16 wk. The PB differed in their content in galactose, mannose, and arabinose for total fraction and sum of carbohydrates for water-soluble fraction. In the field, repeated annual PB application increased most of soil total carbohydrates (sum and individuals) after 3 yr and the proportion of >1 mm stable aggregates. The incubation study confirmed results obtained in the field, where the PB richest in carbohydrates induced the highest increases in soil total carbohydrates in both soil types. Soil total and microbial (galactose and mannose)-derived carbohydrates were closely correlated with the percentage of large aggregates, while with water-soluble carbohydrates, they are highly correlated to the amount of microbial carbohydrates applied, thus further contributing to improve soil C quality.

Key words: carbohydrates, cluster analysis, deinking paper sludge, paper mill biosolids, soil aggregation, soil organic matter.

Résumé : Les biosolides papetiers (BP) constituent une source utile de carbone en vue de l'amélioration physique des sols arables. Cependant, on sait peu de chose sur la nature des hydrates de carbone qu'ils renferment et sur la façon dont ceux-ci se dégradent dans le sol pour contribuer à la stabilité de sa structure. Les auteurs voulaient caractériser les hydrates de carbone présents dans les BP puis en établir la concentration dans le sol, de même que celle des agrégats stables à l'eau dans des conditions contrôlées et sur le terrain. Lors de l'expérience sur le terrain, ils ont épandu annuellement (2000–2008) 0, 30 ou 60 Mg (poids humide) de BP par hectare sur des cultures annuelles sarclées et ont échantillonné le sol au bout de trois, six et neuf ans. L'autre expérience consistait à ajouter 50 Mg (poids humide) de BP par hectare à deux sols (argile, loam sablonneux) ensuite incubés à 25 °C et à emplir l'espace interstitiel d'eau à 60 % pendant 16 semaines. La concentration de galactose, de mannose et d'arabinose dans les BP varie à la fois au niveau de la proportion globale et de celui de la somme des hydrates de carbone présents dans la fraction hydrosoluble. Sur le terrain, l'application annuelle répétitive de BP accroît la concentration de la plupart des hydrates de carbone dans le sol (concentration individuelle et globale) au bout de trois ans, de même que la proportion d'agrégats stables de plus d'un millimètre. L'expérience d'incubation confirme les résultats obtenus sur le terrain, les BP plus riches en hydrates de carbone suscitant les hausses les plus marquées de la concentration d'hydrates de carbone dans les deux sols examinés. La concentration totale d'hydrates de carbone dans le sol et la concentration d'hydrates de carbone d'origine microbienne (galactose et mannose) sont étroitement corrélées à la proportion de gros agrégats, et avec les hydrates de carbone hydrosolubles, elles présentent une étroite corrélation avec la quantité d'hydrates de carbone d'origine microbienne appliquée, ce qui améliore encore plus la qualité du C présent dans le sol. [Traduit par la Rédaction]

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Mots-clés : hydrates de carbone, analyse typologique, boues de papier désencrées, biosolides papetiers, agrégation du sol, matière organique du sol.

Introduction

Paper mill biosolids (PB), an organic solid material generated by the wastewater treatment of pulp and paper mill effluent (Thompson et al. 2001), are recognized as a valuable source of carbon for restoring soil quality while providing beneficial nutrients to crops (N'Dayegamiye 2006, 2009; Gagnon et al. 2010) and diverting them away from landfill or incineration. On-site treatment of these PB often consists of primary sedimentation in a clarifier to remove suspended solids followed by a secondary biological treatment to reduce organic pollutants (Thompson et al. 2001; Nurmesniemi et al. 2007). Paper mill biosolids are thus heterogeneous in nature depending on the recovered paper being processed and the mixture of primary to secondary sludge (Monte et al. 2009), and contain a high proportion of labile C fractions as cellulose and hemicellulose (N'Dayegamiye and Watt 2000). However, less is known about the nature of the different carbohydrates that compose the PB, which may vary according to the mill operating process. McGovern et al. (1983) reported that total carbohydrates composed between 23.5% and 36% of effluent treated sludges in Wisconsin mills, with two-thirds consisting of glucose.

Soils under continuous arable row crops that include corn (*Zea mays* L.) and soybean (*Glycine max* (L.) Merr.) are subject to depletion in organic matter and deterioration in structural stability, compared with those used for grassland (Tisdall and Oades 1982; Karlen et al. 2006). Bowman et al. (1990) observed a rapid decline in soil organic C concentrations in the surface layer due to the conversion of virgin rangeland to arable farming. They also reported a decline in carbohydrate C that was proportionally greater than the decline in total organic C, which was interpreted as a decrease in soil organic C quality. Therefore, because it evolves only slowly over time, soil total organic C does not provide an adequate indication of the soil quality (Haynes 2005).

Neutral carbohydrates, a pool of labile organic C in soil, are viewed as an early indicator of changes in soil organic C due to management practices, particularly following the addition of organic amendments (Bolinder et al. 1999; Chantigny et al. 2000; Bissonnette et al. 2001). Soil carbohydrates are composed of polysaccharides of diverse sources: plant and microbial residues as well as root and microbial mucilage (Tisdall and Oades 1982; Oades 1984). They constitute on average 10% of the soil organic matter (Gunina and Kuzyakov 2015), but they play an essential role in soil by contributing to the maintenance and stimulation of microbial activities and functions, by recycling and sequestering C, and by acting as a precursor for soil aggregation and structural stability (Gunina and Kuzyakov 2015). Generally, microbial-derived carbohydrates (i.e., galactose and mannose) are mostly involved with clay particles in the formation of stable microaggregates <50 mm, whereas those of plant origin (i.e., xylose and arabinose) contribute to short-term changes in particulate organic matter and macroaggregation (Degens 1997; Puget et al. 1999; Jolivet et al. 2006; Samson et al. 2020).

Many studies have drawn links between land application of PB and improvement in soil organic C and water-stable aggregation (Zibilske et al. 2000; Bipfubusa et al. 2005; N'Dayegamiye 2006, 2009). By contrast, the effect of PB application on the dynamic of soil carbohydrates has been overlooked. Field application of organic amendments like manure and municipal biosolids was reported to increase total amounts and (or) different forms of carbohydrates (Metzger et al. 1987; Angers and N'Dayegamiye 1991; Albiach et al. 2001; García-Orenes et al. 2005; Xie et al. 2014). The decomposition of wood-derived residues is characterized for their part by the relatively rapid disappearance of soluble carbohydrates, followed by the labile fractions of hemicellulose and cellulose, whereas recalcitrant fractions such as lignin break down more slowly (Melillo et al. 1989; Thuriès et al. 2002). Chantigny et al. (2000) observed an increase of the different carbohydrate fractions during deinking paper sludge (DPS) decomposition in soil and a gradual conversion of plant-derived carbohydrates to microbial-derived carbohydrates with time. For their part, Bipfubusa et al. (2008) found an increase in total carbohydrate content of soil macroaggregates 2 yr after the last of three successive annual combined PB applications. Rasa et al. (2021) reported an increase in the pools of microbial-bound C, notably the proportion of fungi, in the soil amended with PB. Unfortunately, little studies have been conducted on the composition in carbohydrates of PB that differs according to organic materials (Martens and Frankenberger 1991; Xie et al. 2014), and their decomposition in the soil.

Therefore, the objectives of this study were to (*i*) characterize the carbohydrate composition of five different PB; (*ii*) determine the carbohydrate content in soils incubated with these PB; (*iii*) evaluate the effect of repeated PB applications on soil carbohydrates and water-stable aggregation under field conditions; and (*iv*) establish relationships between PB carbohydrates and soil properties.

Materials and Methods

Biosolids carbohydrate characterization

Five PB from different sources (PB1, PB2, PB3a, PB3b) including a DPS were chosen from previous studies conducted in eastern Canada (Gagnon et al. 2010, 2012; Gagnon and Ziadi 2012). Each material was kept frozen at −18 °C since its initial experimental use and thawed

Table 1. Main chemical properties of combined paper mill biosolids (PB) and deinking paper sludge (DPS) used in incubation and in the field (all data on dry matter basis except moisture).

	Incubation					Field		
Attribute	PB1	PB2	PB3a	PB3b	DPS	Average 2000–2002	Average 2003–2005	Average 2006–2008
pH (H_2O)	7.8	6.8	5.0	4.5	7.2	7.9 ± 0.2	5.2 ± 1.1	4.8 ± 0.7
Moisture ($g \cdot kg^{-1}$)	707	782	639	693	553	648 ± 52	680 ± 75	674 ± 30
Total C ($g \cdot kg^{-1}$)	315	450	446	485	281	297 ± 30	435 ± 3	441 ± 6
Soluble organic C ($g \cdot kg^{-1}$)	0.9	n.d.	2.1	2.9	13.4	1.7 ± 0.8	3.0 ± 1.8	2.9 ± 0.8
Total N ($g \cdot kg^{-1}$)	12.8	36.3	19.1	39.7	6.0	12.6 ± 1.8	21.4 ± 5.0	22.4 ± 7.6
C/N ratio	25	12	23	12	47	24 ± 1	21 ± 5	21 ± 6
Total P ($g \cdot kg^{-1}$)	4.2	5.7	2.9	7.3	2.0	4.2 ± 0.7	3.3 ± 0.3	3.7 ± 1.2
Application ($Mg\ DM \cdot ha^{-1}$)[a]	14.7	10.9	18.0	15.4	22.3	10.5 ± 1.6	9.6 ± 2.2	9.8 ± 0.9

Note: In the field study, PB1 was used in 2000–2002 and PB3a in 2003–2008. n.d., not determined.
[a]For an application rate of 50 Mg wet weight material·ha^{-1} in incubation and 30 Mg wet weight material·ha^{-1} in the field.

just before carbohydrate analysis and lab setting. Briefly, PB1 was produced from thermomechanical pulp, PB2 from bleached Kraft pulp with some municipal effluent, and PB3a and PB3b from acid-treated bleached Kraft pulp produced at a different time. All mills used either activated sludge (PB1, PB2, and DPS) or sequential aerobic biological reactor (PB3a and PB3b) as secondary wastewater treatment (Environnement Québec 2020). Chemical properties of the PB are given in Table 1. We expected that freezing would not cause a transformation of material composition as opposed to oven-drying samples (Ajiboye et al. 2004).

Total neutral carbohydrates in PB were determined in triplicate according to the procedure of Chantigny and Angers (2008). Briefly, 0.10 g (±0.001) of finely ground (<0.15 mm) material dried at 30 °C was presoaked with 8 mL of 12 $mol \cdot L^{-1}$ H_2SO_4 in 250 mL centrifuge bottles, gently mixed and left to stand on the bench for 2 h. Deionized water (184 mL) was then added to dilute the acid to 0.5 $mol \cdot L^{-1}$. After incubation at 85 °C for 24 h, the slurries were cooled to room temperature and centrifuged for 10 min at 10 000 $r \cdot min^{-1}$. The supernatant (20 mL) was decanted into a plastic vial and stored at −20 °C until analysis. Prior to analysis, samples were neutralized to pH 6.5–7.0 with 0.5 $mol \cdot L^{-1}$ NaOH, filtered on Whatman #934-AH, and then successively purified through a solid phase anion-exchange column and a solid phase cation-exchange column (Supelclean LC-SAX and LC-SCX, respectively; Supelco Inc., Bellefonte, PA, USA). The purified extracts were quantified for neutral carbohydrates (glucose, galactose, mannose, arabinose, xylose, fucose, and rhamnose) using high-performance anion-exchange chromatography with pulsed amperometry detection (Dionex model ICS-5000, Sunnyvale, CA, USA).

Soluble neutral carbohydrates were also extracted in triplicate using the hot water procedure (Chantigny and Angers 2008). This fraction contains the most labile carbohydrates. In this case, 0.10 g (±0.001) of finely ground (<0.15 mm) material was incubated with 30 mL distilled water in 50 mL centrifuge tubes at 85 °C for 24 h. After the incubation, the slurries were cooled to room temperature and centrifuged for 10 min at 10 000 $r \cdot min^{-1}$. Each hydrolysate was then transferred to new tubes with 1 part of 12 $mol \cdot L^{-1}$ H_2SO_4 to 23 parts of supernatant, incubated again at 85 °C for 24 h, cooled to room temperature and centrifuged. The supernatant (20 mL) was decanted into a plastic vial and stored at −20 °C until analysis. The procedures of neutralization, purification, and quantification followed the same as described for total neutral carbohydrates.

In addition to carbohydrates, the content in hemicellulose-, cellulose-, and lignin-like fractions was also determined on dried, ground PB samples (<1 mm) using the method of Van Soest (1963) as reported in Robin (1997). Hemicellulose is a complex carbohydrate polymer composed of xylose, mannose, galactose, glucose, and arabinose, whereas cellulose is essentially made up of glucose (Pérez et al. 2002). This step characterizes organic matter of materials, which can allow to predict their dynamic and stability once incorporated into the soil (Abiven et al. 2008). Extraction was done with the Ankom Filter bag technique for the determination of NDF (Ankom technology 2017*a*), ADF (Ankom technology 2017*b*), and ADL (Ankom technology 2020). The different fractions are obtained as follows:

(1) Hemicellulose = NDF–ADF

(2) Cellulose = ADF–ADL

(3) Lignin = ADL

Field study

The field trial was conducted over 9 yr, from 2000 to 2008 at Yamachiche (lat. 46°17'N, long. 72°48'W), QC, Canada, on a Chaloupe loam (Table 2) to evaluate the impact of PB applied alone or with liming by-products

Table 2. Selected characteristics of soils used in the field and in incubation studies.

Soil series	pH (H_2O)	Mehlich-3 P ($mg \cdot kg^{-1}$)	Total C ($g \cdot kg^{-1}$)	Sand ($g \cdot kg^{-1}$)	Clay ($g \cdot kg^{-1}$)	Texture	Soil classification
Field							
Chaloupe	6.2	157	20	417	130	Loam	Orthic Humic Gleysol
Incubation							
Kamouraska	5.3	38	30	302	406	Clay	Orthic Humic Gleysol
St. Antoine	5.9	36	16	683	152	Sandy loam	Orthic Humo-Ferric Podzol

Note: Soil series and classification from Agriculture and Agri-Food Canada (2017).

on crop yield and soil chemical properties (Gagnon and Ziadi 2012). All treatments were surface applied every year, at post-seeding of annual row crops (grain corn in 2000–2002, 2004, and 2006–2008, dry bean (*Phaseolus vulgaris* L.) in 2003, and soybean in 2005). The PB along with crop residues was incorporated (depth of 5–7 cm) before the following season by disk harrowing.

For this study, only treatments with an application rate of 0, 30, and 60 Mg PB·ha^{-1} (wet weight) were considered. The 30 Mg fresh material·ha^{-1} corresponded to the typical annual rate applied on cropland in Québec (Hébert 2016), and those reported in Ontario (15–30 Mg dry matter·ha^{-1}; Flemming et al. 2017). Supplemental inorganic N as Ca-NH_4NO_3 (45 kg N·ha^{-1} averaged over the years) was, however, added to the 30 Mg PB·ha^{-1} rate in 2004 and 2006–2008 to ensure adequate corn N nutrition. Plot size for each experimental unit was 3 m × 10 m, and experimental treatments were distributed within a randomized complete block design with four replicates. Among the five materials retained for carbohydrate characterization, PB1 was notably used in the 2000–2002 period, and PB3a was used in 2003–2008 (Table 1). The different choice was related to the PB availability from neighborhood mills and to a change for a more fertilizing material from 2003.

Soils were collected at random from each selected plot with a spade (composite of three cores) from the 0 to 10 cm layer after 3, 6, and 9 yr of PB application and sieved in the field to <4 mm. Samples were taken before dry bean seeding in spring 2003 and immediately after harvesting soybean and corn in October 2005 and 2008, respectively. Soil samples were air-dried, sieved to pass a 2 mm screen and then ground to <0.15 mm. The strong acid soil hydrolysis was performed as described for biosolids characterization except that 2.00 g (±0.001) was used in the extraction.

Water-stable aggregation was measured by wet sieving 10 g of field-moist soil through a series of sieves with decreasing openings (2, 1, 0.5, and 0.25 mm) by total immersion in water and gentle shaking for 10 min (Angers et al. 2008). The aggregate size classes were defined as >2 mm, 1–2 mm, 0.5–1 mm, 0.25–0.5 mm, and <0.25 mm and were expressed as a percentage of total initial soil (oven-dry basis) after correction for sand content. The mean weight diameter (mm) was calculated as:

$$\sum_{i=1}^{n} X_i W_i$$

where X_i is the mean diameter of each aggregate size class (mm) and W_i is the proportion of the total sample weight recovered in the corresponding size class.

Incubation study

Samples used were from a previous laboratory study evaluating the N and P release from several PB under controlled conditions (Gagnon and Ziadi 2021). Two texturally different soils were collected from fields located near Québec, QC, Canada (lat. 46°41-47′N, long. 71°08-28′W): a Kamouraska clay from a spring wheat field and a St. Antoine sandy loam from a field under alfalfa (*Medicago sativa* L.)/timothy (*Phleum pratense* L.) pasture (Table 2). Six treatments were used, which included the five materials (PB1, PB2, PB3a, PB3b, DPS) applied at 50 Mg wet weight·ha^{-1} and an unfertilized control (Table 1). We chose this rate because it could be applied to several crops without supplementary N (Gagnon and Ziadi 2021) and then allowed to better assess carbohydrate contribution from PB. Incubation took place for 16 wk in the dark in a controlled-environment chamber at 24.5 °C, 60% water-filled pore space, with periodic aeration using 500 mL glass jars.

Soils of all jars were collected at the end of incubation and treated in the same manner as those from the field study to determine the concentrations in total neutral carbohydrates. In addition, the hot-water soil hydrolysis was also performed as described for biosolids characterization with 2.00 g (±0.001) subsamples to determine the soluble neutral carbohydrates.

Statistical analysis

All data for soil studies were subjected to a Bartlett's test, and no transformation was necessary. Neutral carbohydrates were analyzed as a sum, as individuals or grouped as being from microbe- (galactose plus mannose) or plant (arabinose plus xylose)-derived origin (Oades 1984). Data on fucose and rhamnose were not reported in the soil analysis due to their lack of significance. Statistical significance was set at $p \leq 0.05$.

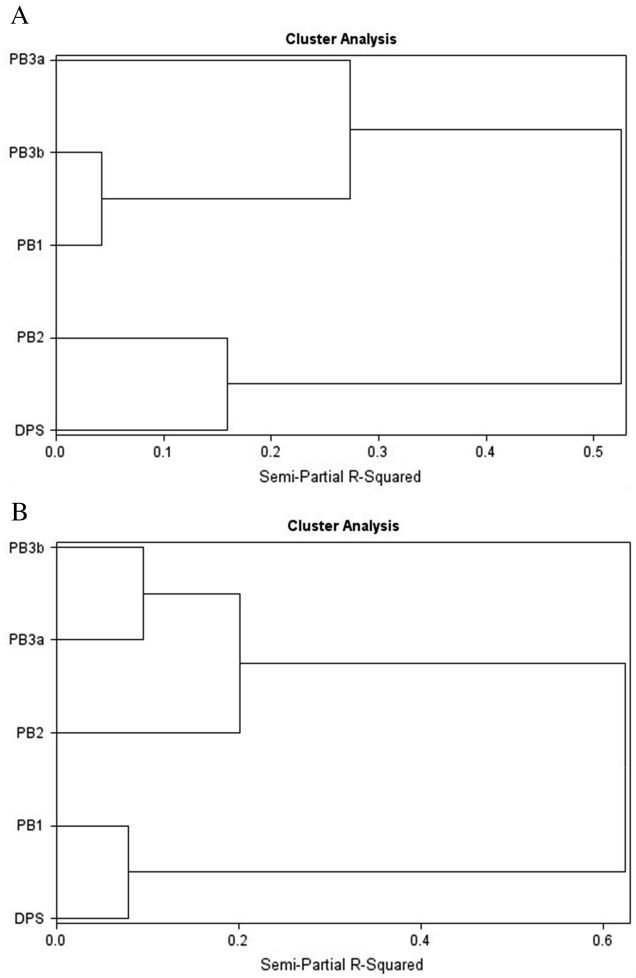
Material carbohydrates (individual and the sum) were submitted to a cluster analysis using the Ward's minimum variance method. Using cluster as a procedure of

statistical analysis allows to group materials similar in their composition and to relate this to the carbohydrate increases found in soil during incubation, even if properties of PB may vary from mill to mill. Results of clustering were subsequently submitted to a generalized linear model analysis of variance (SAS Institute 2010) to identify characteristics differing significantly among clusters. Total carbohydrates and soluble carbohydrates were analyzed separately. Other related variables not used in the cluster analysis, such as calculation of microbe- and plant-derived carbohydrates, percentage of total carbohydrates in total C, percentage of soluble carbohydrates in total carbohydrates and total C, and organic matter fractions (hemicellulose, cellulose, lignin), were also compared for each cluster.

Data from the field study were analyzed with treatments and years as fixed effects and replications as random effects, using the MIXED procedure (SAS Institute 2010) with a banded main diagonal covariance structure for carbohydrate composition and a compound symmetry covariance structure for aggregates. Main treatment effects were compared using the least significant difference (5%). Correlation analysis was used to establish links between soil total neutral carbohydrates and water-stable aggregation.

Treatment effects in the incubation study were evaluated as a factorial PB × soil using the MIXED procedure (SAS Institute 2010). Treatment means were compared using the least significant difference (5%) and single degree-of-freedom contrasts for comparison of material clusters between them and with the unamended control, and within each cluster. Regression analysis was performed to relate the content of carbohydrates in materials to that found in the amended soils at the end of incubation.

Fig. 1. Dendrogram for clustering of (A) total neutral carbohydrates and (B) soluble neutral carbohydrates of combined paper mill biosolids (PB) and deinking paper sludge (DPS). Material description is defined in Table 1.



Results and Discussion

Biosolids carbohydrate characterization

Cluster analysis identified two groups of PB for total carbohydrates. The first group comprised PB1, PB3a, and PB3b, and the second group PB2 and DPS (Fig. 1A). The first cluster separated from the other by a significantly higher content in galactose, mannose, and arabinose and a lower content in xylose (trend, $p = 0.07$), while having the same amounts of carbohydrates as a sum (Table 3). As a result, the carbohydrates of microbial origin (galactose and mannose) were also higher in the first group.

Glucose was the most abundant carbohydrate in the total composition (from 63% to 80%; Table 3), and with mannose and xylose formed 90% of total carbohydrates for cluster 1 and 97% for cluster 2 ($p = 0.010$). McGovern et al. (1983) reported that the composition of PB in total carbohydrates was quite constant between Wisconsin mills of Kraft, mechanical or recycled process, averaging about 65% glucose, 25% xylose, and 10% mannose. Our results agree for glucose, but a difference was noted for xylose and mannose that cannot be explained by the pulping process or wastewater treatment themselves. Possible explanation could be the tree species involved in the pulp and paper production. Softwood conifers (*Picea* and *Abies* spp.) are the main source of wood in the pulp and paper mills in the province of Quebec. However, hardwood such as quaking aspen (*Populus tremuloides* Michx.) may enter the paper-making chain depending on desired finished end-product, local wood supply, and type of recycled fibers. These species are composed of a larger proportion of xylose and a lower proportion of mannose and galactose than softwoods (Hakkila 1989).

Cluster analysis identified two groups of PB for water-soluble carbohydrates. The grouping, however, differed slightly from that for total carbohydrates. The first group comprised PB2, PB3a, and PB3b, and the second group PB1 and DPS (Fig. 1B). The separation of clusters was significant only for the sum of carbohydrates, with a trend

Table 3. Characterization of paper mill biosolids in total neutral carbohydrates according to clustering analysis.

	Cluster 1			Cluster 2			
Main attributes	PB1	PB3a	PB3b	PB2	DPS	*F* value	$P < F$
Glucose	121 ± 3 (63)	175 ± 26 (69)	122 ± 14 (65)	177 ± 32 (79)	157 ± 45 (80)	1.3	0.33
Galactose (G)	11.1 ± 0.6 (6)	8.4 ± 1.0 (3)	10.1 ± 1.1 (5)	2.2 ± 0.5 (1)	1.9 ± 0.5 (1)	59.1	0.005
Mannose (M)	33.0 ± 1.6 (17)	34.8 ± 4.3 (14)	25.8 ± 2.8 (14)	5.3 ± 0.6 (2)	8.6 ± 2.2 (4)	41.7	0.008
Arabinose (A)	5.5 ± 1.4 (3)	9.7 ± 1.0 (4)	7.3 ± 0.7 (4)	1.3 ± 0.3 (1)	0.6 ± 0.2 (0)	16.6	0.027
Xylose (X)	19.5 ± 1.2 (10)	24.0 ± 3.7 (9)	17.6 ± 2.2 (9)	34.2 ± 7.7 (15)	27.0 ± 8.3 (14)	7.9	0.07
Fucose	0.8 ± 0.5 (0)	0.6 ± 0.1 (0)	1.3 ± 0.2 (1)	0.4 ± 0.1 (0)	0.6 ± 0.1 (0)	2.0	0.25
Rhamnose	2.4 ± 0.3 (1)	2.0 ± 0.4 (1)	2.4 ± 0.6 (1)	2.8 ± 0.5 (1)	1.3 ± 0.6 (1)	0.1	0.73
Total carbohydrates	193 ± 1	254 ± 36	187 ± 21	223 ± 41	197 ± 56	0.0	0.97
Other related parameters							
Σ(G + M)	44.1 ± 2.1	43.3 ± 5.4	35.9 ± 3.8	7.5 ± 0.8	10.5 ± 2.7	82.0	0.003
Σ(A + X)	25.0 ± 1.1	33.7 ± 4.7	24.9 ± 2.5	35.5 ± 7.9	27.6 ± 8.1	0.6	0.50
Carbohydrates (% total C)	61	57	38	50	70	1.3	0.34
Hemicellulose + cellulose	327 ± 25	386 ± 9	324 ± 13	415 ± 23	285 ± 36	0.0	0.94
Lignin	488 ± 23	293 ± 7	348 ± 10	157 ± 7	203 ± 45	6.6	0.08

Note: Clustering analysis was made using single carbohydrates and their sum. Values in parenthesis indicate the percentage of each carbohydrate in total. All parameters are in $mg \cdot g^{-1}$ except when indicated. Galactose and mannose are assumed of microbial origin, whereas arabinose and xylose are of plant origin (Oades 1984).

Table 4. Characterization of paper mill biosolids in soluble neutral carbohydrates according to clustering analysis.

	Cluster 1			Cluster 2			
Attribute	PB2	PB3a	PB3b	PB1	DPS	*F* value	$P < F$
Glucose	1975 ± 635 (28)	2244 ± 1100 (23)	2413 ± 292 (26)	683 ± 129 (21)	1800 ± 830 (37)	4.7	0.12
Galactose (G)	1219 ± 442 (17)	1660 ± 829 (17)	2068 ± 237 (22)	649 ± 164 (20)	673 ± 286 (14)	9.7	0.05
Mannose (M)	885 ± 239 (12)	1431 ± 715 (15)	1359 ± 132 (15)	600 ± 118 (18)	592 ± 262 (12)	8.1	0.07
Arabinose (A)	534 ± 193 (7)	2550 ± 1209 (26)	1553 ± 165 (17)	447 ± 157 (14)	224 ± 40 (5)	2.6	0.21
Xylose (X)	910 ± 234 (13)	1021 ± 610 (10)	689 ± 64 (7)	443 ± 61 (13)	594 ± 233 (12)	6.6	0.08
Fucose	256 ± 82 (4)	216 ± 132 (2)	398 ± 61 (4)	84 ± 39 (3)	151 ± 87 (3)	5.2	0.11
Rhamnose	1346 ± 332 (19)	668 ± 430 (7)	756 ± 139 (8)	394 ± 174 (12)	787 ± 317 (16)	1.1	0.36
Soluble carbohydrates	7124 ± 2131	9791 ± 5020	9235 ± 1075	3300 ± 832	4823 ± 1976	15.2	0.030
Other related parameters							
Σ(G + M)	2104 ± 680	3091 ± 1542	3427 ± 367	1249 ± 282	1266 ± 548	9.9	0.05
Σ(A + X)	1443 ± 421	3572 ± 1817	2241 ± 227	890 ± 211	819 ± 199	3.8	0.15
Soluble (% total carbohydrates)	3.2	3.8	4.9	1.7	2.5	6.3	0.09
Soluble (% total C)	1.6	2.2	1.9	1.0	1.7	2.1	0.24

Note: Clustering analysis was made using single carbohydrates and their sum. Values in parenthesis indicate the percentage of each carbohydrate in total soluble. All parameters are in $\mu g \cdot g^{-1}$ except when indicated. Galactose and mannose are assumed of microbial origin, whereas arabinose and xylose are of plant origin (Oades 1984).

($p = 0.05$–0.07) for galactose and mannose, with higher values in cluster 1 (Table 4). The water-soluble carbohydrates formed between 1.7% and 4.9% of total carbohydrates but between 4% and 35% for those derived from microbes, including rhamnose and fucose. The carbohydrate fraction extractable with hot water has been found to be enriched in exocellular microbial polysaccharides (Haynes and Francis 1993; Gunina and Kuzyakov 2015). Results indicated that, contrarily to total fraction, the water-soluble fraction was composed of carbohydrates of various forms.

In this study, there was a trend ($p = 0.08$) for a lignin content twice as high in cluster 1 than in cluster 2, while the composition in hemicellulose and cellulose was similar (Table 3). Lignin, due to its polyphenolic complex structure, is recalcitrant to microbial decomposition (Bahri et al. 2008) and is considered as a precursor of soil humic substances (Robin 1997). According to

Table 5. Effect of repeated paper mill biosolids (PB) application in field on the concentrations of total neutral carbohydrates in the 0–10 cm layer of a loamy soil.

Treatments	Glucose (μg C·g^{-1})	Galactose (G) (μg C·g^{-1})	Mannose (M) (μg C·g^{-1})	Arabinose (A) (μg C·g^{-1})	Xylose (X) (μg C·g^{-1})	Total carbohydrates (mg C·g^{-1})	(G+M)/(A+X)
Unamended	939c	334b	296c	254b	381b	2.4b	1.2a
PB, 30 Mg·ha^{-1}	1586b	450a	472b	344ab	549a	3.7a	1.3a
PB, 60 Mg·ha^{-1}	2066a	527a	601a	410a	657a	4.3a	1.2a
Sampling date							
Spring 2003	1327b	332b	324b	215b	351b	2.7b	1.2b
Fall 2005	1029c	310b	360b	185b	285c	2.3b	1.6a
Fall 2008	2235a	669a	685a	608a	951a	5.3a	0.9c
	Analysis of variance (*F* value)						
Treatment	17.5***	11.2***	16.8***	4.2*	6.8*	10.6**	0.1
Year sampling	13***	29***	19***	29***	25***	17***	22***
Treatment × Year	2.7	1.4	2.2	1.3	2.2	1.7	2.0

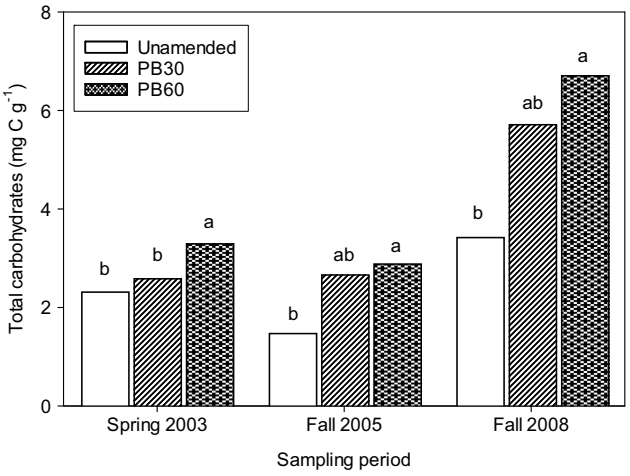
Note: PB1 was used in 2000–2002 and PB3a in 2003–2008. Statistical significance at 5%, 1%, and 0.1% was denoted by *, **, and ***, respectively. Means followed by the same letter within a treatment or a year are not statistically significant at $P = 0.05$ according to an LSD test.

Abiven et al. (2008), lignin has the greatest impact on soil aggregate stability, while the hemicellulose plus cellulose fraction contributes to long-lasting effect. Materials with a high lignin content decompose more slowly and their influence on aggregation is low (N'Dayegamiye 2006). We can then expect that PB of cluster 2 (PB2, DPS) could have the most positive effect on soil aggregation, at least in short term. Chantigny et al. (2000) reported that 30% of initial total carbohydrates in DPS was rapidly decomposed and then contributed to the formation of large (>1 mm) water-stable aggregates (Chantigny et al. 1999).

Soil carbohydrates under field study

Concentrations of total neutral carbohydrates were strongly affected by the repeated applications of PB (Table 5). Concentrations in all carbohydrates except arabinose were significantly increased by the 30 Mg PB·ha^{-1} rate. The application of 60 Mg PB·ha^{-1} also increased the concentrations in arabinose, and gave higher concentrations in glucose and mannose than the 30 Mg PB·ha^{-1}. These two carbohydrates composed of around 80% of total carbohydrates in the applied materials (Table 3). Relative to unamended control, the 60 Mg PB·ha^{-1} rate increased the concentrations of total neutral carbohydrates by 42% in spring 2003 and by 96% in fall 2005 and fall 2008 (Fig. 2), while the concentrations of individual carbohydrates were 1.6–2.7 times greater at the last sampling, in fall 2008 (data not shown). The ratio of galactose and mannose to arabinose and xylose was unaffected by treatments and varied from 0.9 to 1.6 depending on sampling dates (Table 5), meaning that both microbial and plant origin

Fig. 2. Effect of combined paper mill biosolids at 30 (PB30) and 60 (PB60) Mg wet weight·ha^{-1} on the concentration of total neutral carbohydrates in the 0–10 cm layer of a loamy soil after 3, 6, and 9 yr of annual applications under field conditions. PB1 was used in 2000–2002 and PB3a in 2003–2008.



carbohydrates contributed equally to the increase in soil total carbohydrates.

A positive effect of applying PB, including DPS, on soil carbohydrates was reported elsewhere under field studies. Bipfubusa et al. (2008) found a 29% increase in total carbohydrate content of soil large macroaggregates 2 yr after the last of three annual PB applications at 40 Mg wet weight·ha^{-1}. However, they did not evaluate the carbohydrate composition. Chantigny et al. (2000) reported increases in several measured carbohydrate

Table 6. Effect of repeated paper mill biosolids (PB) application in field on the water-stable aggregates in the 0–10 cm layer of a loamy soil.

	Soil aggregate size (% total soil)						
Treatments	>2 mm	1–2 mm	0.5–1 mm	0.25–0.5 mm	<0.25 mm	≥1 mm	Mean weight diameter (mm)
Unamended	34.1a	16.7a	11.0a	7.1a	30.9a	50.7b	1.76b
PB, 30 Mg·ha^{-1}	36.5a	17.5a	11.0a	6.4a	28.6ab	54.0ab	1.86ab
PB, 60 Mg·ha^{-1}	37.2a	19.5a	11.2a	6.5a	25.7b	56.7a	1.92a
Sampling date							
Spring 2003	45.0a	17.8a	7.3c	2.4b	27.5b	62.7a	2.16a
Fall 2005	32.4b	18.6a	14.8a	9.3a	24.8b	50.9b	1.75b
Fall 2008	30.4b	17.4a	11.1b	8.3a	32.8a	47.8b	1.63b
	Analysis of variance (*F* value)						
Treatment	1.5	1.4	0.1	0.7	3.1	4.0*	2.7
Year sampling	30***	2	96***	124***	8**	28***	36***
Treatment × Year	0.7	0.2	4.5*	0.4	0.4	0.8	0.7

Note: Difference was noted for the 0.5–1 mm size class in 2008 with a higher proportion in the 60 Mg PB·ha^{-1} amended plots (12.5%) than in the 30 Mg PB·ha^{-1} plots (10.9%) and the unamended control (9.8%). Statistical significance at 5%, 1%, and 0.1% was denoted by *, **, and ***, respectively. Means followed by the same letter within a treatment or a year are not statistically significant at $P = 0.05$ according to an LSD test.

Table 7. Effect of paper mill biosolids on the soil total neutral carbohydrates at the end of a 16 wk incubation.

Treatments	Glucose (μg C·g^{-1})	Galactose (G) (μg C·g^{-1})	Mannose (M) (μg C·g^{-1})	Arabinose (A) (μg C·g^{-1})	Xylose (X) (μg C·g^{-1})	Total carbohydrates (mg C·g^{-1})	(G + M)/(A + X)
Unamended (Un)	1409c	569b	632b	467bc	465c	4.0d	1.3a
Cluster 1							
PB1	2119b	669ab	846a	498abc	591b	5.2bc	1.4a
PB3a	2812a	740a	1014a	560ab	771a	6.4a	1.3a
PB3b	2254b	720a	881a	581a	633b	5.5ab	1.3a
Cluster 2							
PB2	1499c	624ab	658b	502abc	491c	4.2cd	1.3a
DPS	1402c	559b	602b	433c	448c	3.8d	1.3a
Soils							
Kamouraska	2187a	832a	952a	644a	602a	5.8a	1.4a
St. Antoine	1645b	462b	592b	370b	531b	3.9b	1.2b
	Analysis of variance (*F* value)						
Treatment	12.8***	2.7*	7.8***	2.4	15.0***	8.6***	0.8
Soil	17***	99***	55***	92***	7*	45***	55***
Treatment × Soil	0.6	0.9	0.5	0.8	2.0	0.8	0.8
Contrasts							
Cluster 1 vs. 2	39.7***	7.8*	26.4***	5.9*	42.9***	26.7***	1.6
Cluster 1 vs. Un	29.3***	7.4*	17.7***	4.0	30.5***	20.2***	1.4
Cluster 2 vs. Un	0.0	0.2	0.0	0.0	0.0	0.1	0.0
PB1 vs. PB3a/b	4.6*	1.2	2.0	3.0	8.3**	3.9	1.2
PB2 vs. DPS	0.2	1.0	0.4	1.8	0.8	0.6	0.4

Note: Galactose and mannose are assumed of microbial origin, whereas arabinose and xylose are of plant origin (Oades 1984). PB, combined paper mill biosolids; DPS, deinking paper sludge, applied at 50 Mg wet weight·ha^{-1}. Statistical significance at 5%, 1%, and 0.1% was denoted by *, **, and ***, respectively. Means followed by the same letter within a treatment or a soil are not statistically significant at $P = 0.05$ according to an LSD test.

Table 8. Effect of paper mill biosolids on the soil soluble neutral carbohydrates at the end of a 16 wk incubation.

Treatments	Glucose (μg C·g^{-1})	Galactose (μg C·g^{-1})	Mannose (μg C·g^{-1})	Arabinose (μg C·g^{-1})	Xylose (μg C·g^{-1})	Soluble carbohydrates (μg C·g^{-1})
Unamended (Un)	91b	50a	48a	32ab	31a	304b
Cluster 1						
PB2	114ab	50a	51a	30b	33a	327ab
PB3a	153a	69a	70a	49a	44a	457a
PB3b	122ab	63a	63a	43ab	41a	395ab
Cluster 2						
PB1	116ab	65a	60a	38ab	41a	378ab
DPS	154a	57a	62a	34ab	40a	400ab
Soils						
Kamouraska	135a	59a	62a	40a	38a	397a
St. Antoine	116a	59a	56a	36a	38a	356a
	Analysis of variance (*F* value)					
Treatment	2.1	1.0	1.0	1.7	0.9	1.2
Soil	2.0	0.0	1.0	0.6	0.0	1.0
Treatment × Soil	0.4	0.3	0.2	0.1	0.4	0.2
Contrasts						
Cluster 1 vs. 2	0.1	0.0	0.0	0.7	0.0	0.0
Cluster 1 vs. Un	3.7	1.2	1.9	1.4	1.4	2.1
Cluster 2 vs. Un	4.3*	1.2	1.5	0.3	1.5	1.7
PB2 vs. PB3a/b	1.4	2.7	2.6	5.9*	2.4	2.7
PB1 vs. DPS	2.8	0.6	0.0	0.3	0.0	0.1

Note: Galactose and mannose are assumed of microbial origin, whereas arabinose and xylose are of plant origin (Oades 1984). PB, combined paper mill biosolids; DPS, deinking paper sludge, applied at 50 Mg wet weight·ha^{-1}. Statistical significance at 5% was denoted by *. Means followed by the same letter within a treatment or a soil are not statistically significant at $P = 0.05$ according to an LSD test.

fractions of DPS-amended soils with a predominant contribution of microbial carbohydrates. Repeated PB application, even at low rates (20 Mg wet weight·ha^{-1}), may sustain soil physical properties longer and overcome the transient binding nature of decomposing freshly added labile C (N'Dayegamiye 2006).

Soil aggregation under field study

The water aggregate stability was affected by PB application. The proportion of aggregates ≥1 mm increased with the 60 Mg PB·ha^{-1} rate in the 0–10 cm soil layer over the course of the study (Table 6). Aggregate size between 1 and 5 mm is the most favorable for seedbed and plant growth (Braunack and Dexter 1989). At the opposite, repeated application of PB decreased the amount of microaggregates <0.25 mm while it did not impact the other size classes except 0.5–1 mm in fall 2008. On average, the mean weight diameter of aggregates increased from 1.76 mm in the untreated control to 1.92 mm in the plots receiving 60 Mg PB·ha^{-1} annually.

In this study, the soil had a degraded physical structure and was under intensive annual cropping (Haynes et al. 1991), even though minimum tillage was practised. Addition of PB, due to their high cellulose and labile C content, promoted a high mineralization rate (Bipfubusa et al. 2005) which significantly improved structural stability over the years. N'Dayegamiye (2006, 2009) reported that organic materials such as PB with a low C/N ratio and a low recalcitrant-like lignin fraction enhanced soil aggregation after several applications but their benefit effects varied with soil type, being more consistent on silt and clay loams than on sandy loam. Other studies observed increases in ≥1 mm size class aggregates with cumulative PB application (Zibilske et al. 2000; Price and Voroney 2007). Abiven et al. (2009) classified different organic products according to their magnitude and time-to-maximum effect on aggregate stability and found that sludge category, which comprised PB and DPS, had a long-term effect (>3 mo) with a strong magnitude.

Components of organic C, such as carbohydrates, are partially involved in the stabilization of soil into aggregates (Angers and Mehuys 1989). Those of microbial origin appear to be the most effective and active (Oades 1984; Haynes and Francis 1993; Degens 1997; Puget et al. 1999), although an accumulation of microbial carbohydrates probably only indicates greater

microbial decomposition of organic C (Degens 1997). In this study, significant correlations were found between total neutral carbohydrate content (sum and individual, $0.59 \leq r \leq 0.82$) and proportion of large water-stable aggregates measured in fall 2005, after 6 yr of repeated PB application. Additional years of amendment continued to increase soil total carbohydrates (Fig. 2) without further impacting soil macroaggregation.

Soil carbohydrates under incubation study

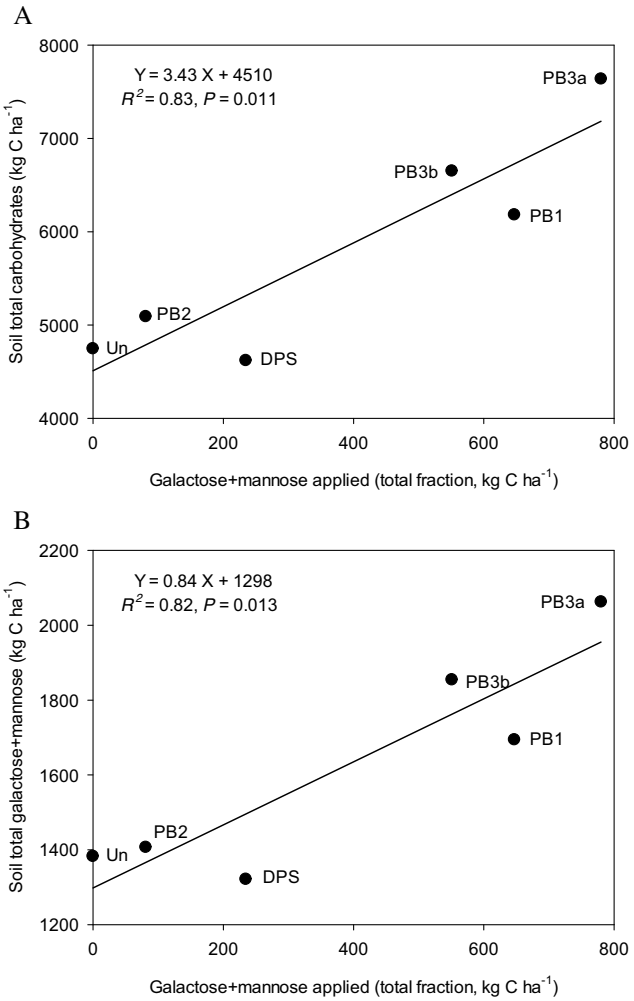
The different PB induced a significant effect on the soil total neutral carbohydrate content at the end of the 16 wk incubation (Table 7), with a supply of between 2.4 (PB2) to 4.6 (PB3a) Mg total carbohydrate-C·ha^{-1} at the application rate of 50 Mg wet weight·ha^{-1}. The Kamouraska clay soil had higher carbohydrate content as individual or sum than the St. Antoine sandy loam, but both soils responded similarly to PB application (no interaction of treatment × soil).

All PB of cluster 1 (PB1, PB3a, PB3b) increased soil total neutral carbohydrates, whereas those of cluster 2 (PB2, DPS) did not produce any effect compared with the unamended control (Table 7). Carbohydrates in the amended soils may originate from PB or be the product of the microbial activity promoted by PB addition. With a low (<15) or overly wide (>40) C/N ratio, microbial polysaccharides production from organic amendments may be restricted due, respectively, to a deficiency of organic C in substrate or a low microbial activity (Avnimelech and Cohen 1989). Under different conditions, Chantigny et al. (2000) reported a strong increase in several fractions of soil carbohydrates in a field study the next summer when 50–100 Mg dry weight·ha^{-1} of DPS (6.4–12.7 Mg total carbohydrate-C·ha^{-1}) were applied the preceding fall.

The increase in total carbohydrates for PB belonging to cluster 1 averaged 44% for the sum of carbohydrates, with 986 mg C·kg^{-1} more glucose relative to the control (+70%), 282 mg C·kg^{-1} more mannose (+45%), 200 mg C·kg^{-1} more xylose (+43%), 140 mg C kg^{-1} more galactose (+25%), and 79 mg C·kg^{-1} more arabinose (+17%). Results from the incubation study confirmed those obtained in the field. It was in line with the composition of PB (Table 3) and agrees with the relative carbohydrate abundance in soil composition observed by Chantigny et al. (2000) with DPS. The response when applying PB differed from that with manure in which the contribution of each individual carbohydrate is diverse (Angers and N'Dayegamiye 1991; Xie et al. 2014).

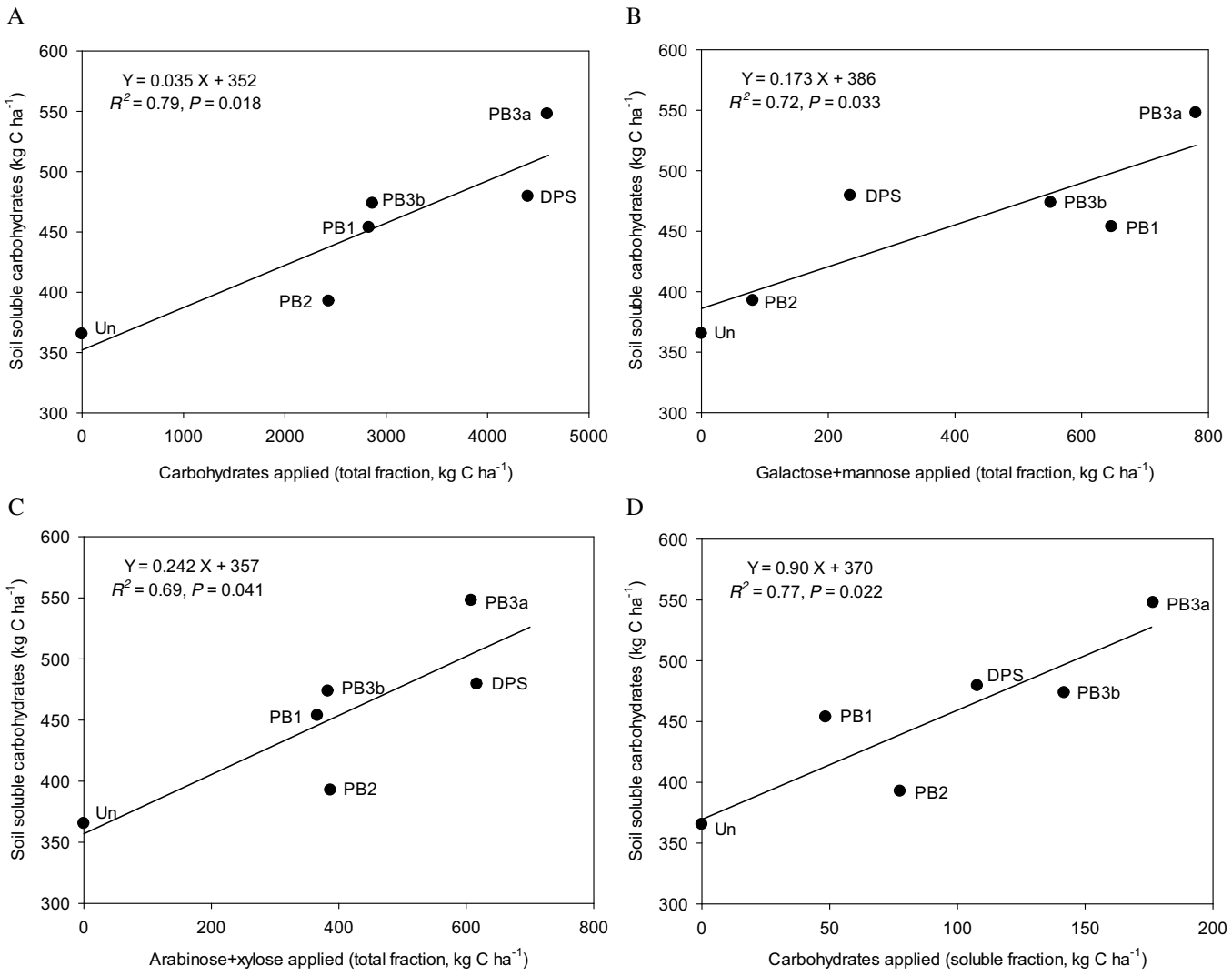
The ratio of galactose and mannose to arabinose and xylose is indicative of the predominance of microbial carbohydrates (>2) or plant carbohydrates (<0.5; Oades 1984). In this study, the ratio was higher in the Kamouraska clay than in the St. Antoine sandy loam but was unaffected by treatments (Table 7), which was also observed in the field. This may indicate greater microbial decomposition of organic C in the clay soil (Degens 1997).

Fig. 3. Relationship between amounts of microbial-derived carbohydrates applied and the concentrations of (A) total and (B) microbial neutral carbohydrates in the soil at the end of incubation (average over soil type). PB, combined paper mill biosolids; DPS, deinking paper sludge, applied at 50 Mg wet weight·ha^{-1}; Un, unamended control. Soil carbohydrates were converted in kg C·ha^{-1} by using a soil bulk density of 1.2 g·cm^{-3} and an incorporation depth of 10 cm.



Contrary to soil total neutral carbohydrates, the soil water-soluble neutral carbohydrates, as a sum or individual composition, were little affected by treatments, likely due to high variability (Table 8). Only PB3a increased the soluble fraction relative to unamended control due to an increase in glucose and arabinose. This fraction extracted by hot water represents 5–10% of total fraction (Gunina and Kuzyakov 2015). However, it decomposes rapidly during the first few days after material application and microbial replenishment (Abiven et al. 2008) and was particularly involved in the stabilization of soil aggregates (Metzger et al. 1987;

Fig. 4. Relationship between amounts of (A) total, (B) microbial-derived, (C) plant-derived, and (D) soluble carbohydrates applied and the concentrations of water-soluble neutral carbohydrates in the soil at the end of incubation (average over soil type). PB, combined paper mill biosolids; DPS, deinking paper sludge, applied at 50 Mg wet weight·ha^{-1}; Un, unamended control. Soil carbohydrates were converted in kg C·ha^{-1} by using a soil bulk density of 1.2 g·cm^{-3} and an incorporation depth of 10 cm.



Haynes and Francis 1993; Degens 1997). Since this fraction is low and very sensitive to changes in soil management (Degens 1997), reapplication should be advised to see any positive effects on soil quality.

Relationships between material carbohydrates and soil composition

The incubation study showed a close relationship between soil total neutral carbohydrate content and the amount of microbial (galactose + mannose) carbohydrates added by PB ($r^2 = 0.83$; Fig. 3A), which was not observed with the plant-derived (arabinose + xylose) ($r^2 = 0.15$) or total carbohydrates ($r^2 = 0.22$). In addition, the soil total microbial-derived carbohydrate content was also correlated with the amount of added galactose + mannose ($r^2 = 0.82$; Fig. 3B). Such links have never been reported before between material carbohydrates and soil composition once applied. With the positive link obtained in the field between the soil total ($r^2 = 0.59$) and microbial-derived ($r^2 = 0.64$) carbohydrates and the proportion of large water-stable aggregates, this indicated that the microbial carbohydrates would be an important contributor to the improvement of soil quality.

The soil water-soluble neutral carbohydrate fraction was relevant to soil aggregate stability, since this specific fraction generally associated with fungal development correlates better than the much larger acid-hydrolyzable fraction (Metzger et al. 1987). Despite a lack of significance for treatment effect, this fraction was closely related to the amount of total carbohydrates added (Fig. 4A) as well as the microbial-derived carbohydrates (Fig. 4B), plant-derived carbohydrates (Fig. 4C), and sum of soluble carbohydrates (Fig. 4D). This suggests that the

carbohydrates in the total fraction replenished those in soluble fraction once they were degraded.

Conclusion

The objectives of this study were to characterize the carbohydrate composition of PB, determine the carbohydrate concentration and composition in the soil once applied in a lab setting, evaluate the repeated application of some of these PB on the soil carbohydrates and water-stable aggregation in a field, and establish links between PB carbohydrates and soil quality.

Cluster analysis identified two groups of PB differing in their content in galactose, mannose, and arabinose for total fraction and sum of carbohydrates for water-soluble fraction. Under field conditions, a positive effect on the total fraction was found for most carbohydrates after 3 yr of repeated PB application to an annual row crop rotation, with a further increase throughout the entire 9 yr study. The incubation experiment confirmed the field results where the PB from the cluster most enriched in carbohydrates caused an increase in soil total carbohydrates content, mainly glucose, mannose, and xylose, in both soil types. The proportion of >1 mm water-stable aggregates was increased after 3, 6, and 9 yr of continuous applications in the field and was in relation with the soil total and microbial carbohydrate content. Relationships were also established between soil carbohydrate content, both as total or water soluble, and the microbial-origin carbohydrates applied, which contributed to this improvement in soil structural properties. The determination of PB in carbohydrate content from acid hydrolysis or water-soluble extraction could therefore be used as a proxy to assess the effect on soil C quality.

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References

Abiven, S., Menasseri, S., Angers, D.A., and Leterme, P. 2008. A model to predict soil aggregate stability dynamics following organic residue incorporation under field conditions. Soil Sci. Soc. Am. J. **72**: 119–125. doi:10.2136/sssaj2006.0018.

Abiven, S., Menasseri, S., and Chenu, C. 2009. The effects of organic inputs over time on soil aggregate stability – A literature analysis. Soil Biol. Biochem. **41**: 1–12. doi:10.1016/j.soilbio.2008.09.015.

Agriculture and Agri-Food Canada. 2017. Canadian soil information system. The national soil database. Soil survey reports. [Online]. Available from https://sis.agr.gc.ca/cansis/publications/surveys/index.html [16 Dec. 2021].

Ajiboye, B., Akinremi, O.O., and Racz, G.J. 2004. Laboratory characterization of phosphorus in fresh and oven-dried organic amendments. J. Environ. Qual. **33**: 1062–1069. doi:10.2134/jeq2004.1062. PMID:15224945.

Albiach, R., Canet, R., Pomares, F., and Ingelmo, F. 2001. Organic matter components and aggregate stability after the application of different amendments to a horticultural soil. Bioresour. Technol. **76**: 125–129. doi:10.1016/s0960-8524(00)00090-0. PMID:11131795.

Angers, D.A., Bullock, M.S., and Mehuys, G.R. 2008. Aggregate stability to water. Pages 811–820 in M.R. Carter and E.G. Gregorich, eds. Soil sampling and methods of analysis. 2nd ed. Can. Soc. Soil Sci., CRC Press, Boca Raton, FL, USA.

Angers, D.A., and Mehuys, G.R. 1989. Effects of cropping on carbohydrate content and water-stable aggregation of a clay soil. Can. J. Soil Sci. **69**: 373–380. doi:10.4141/cjss89-037.

Angers, D.A., and N'Dayegamiye, A. 1991. Effects of manure application on carbon, nitrogen, and carbohydrate contents of a silt loam and its particle-size fractions. Biol. Fertil. Soils **11**: 79–82. doi:10.1007/bf00335840.

Ankom Technology. 2017*a*. Neutral detergent fiber in feeds - Filter bag technique (for A2000 and A2000I; method 13). Available at: https://www.ankom.com/analytical-methods-support/fiber-analyzer-a2000 [1 June 2021].

Ankom Technology. 2017*b*. Acid detergent fiber in feeds - Filter bag technique (for A2000 and A2000I; method 12). [Online]. Available from https://www.ankom.com/analytical-methods-support/fiber-analyzer-a2000 [1 June 2021].

Ankom Technology. 2020. Method 8 – determining acid detergent lignin in beakers. [Online]. Available from https://www.ankom.com/analytical-methods-support/fiber-analyzer-a2000 [1 June 2021].

Avnimelech, Y., and Cohen, A. 1989. Use of organic manures for amendment of compacted clay soils. II. Effect of carbon to nitrogen ratio. Commun. Soil Sci. Plant Anal. **20**: 1635–1644. doi:10.1080/00103628909368172.

Bahri, H., Rasse, D.P., Rumpel, C., Dignac, M.-F., Bardoux, G., and Mariotti, A. 2008. Lignin degradation during a laboratory incubation followed by ^{13}C isotope analysis. Soil Biol. Biochem. **40**: 1916–1922. doi:10.1016/j.soilbio.2008.04.002.

Bipfubusa, M., Angers, D.A., N'Dayegamiye, A., and Antoun, H. 2008. Soil aggregation and biochemical properties following the application of fresh and composted organic amendments. Soil Sci. Soc. Am. J. **72**: 160–166. doi:10.2136/sssaj2007.0055.

Bipfubusa, M., N'Dayegamiye, A., and Antoun, H. 2005. Effets de boues mixtes de papetières fraîches et compostées sur l'agrégation du sol, l'inclusion et la minéralisation du C dans les macro-agrégats stables à l'eau. Can. J. Soil Sci. **85**: 47–55. doi:10.4141/s03-055.

Bissonnette, N., Angers, D.A., Simard, R.R., and Lafond, J. 2001. Interactive effects of management practices on water-stable aggregation and organic matter of a Humic Gleysol. Can. J. Soil Sci. **81**: 545–551. doi:10.4141/s00-078.

Bolinder, M.A., Angers, D.A., Gregorich, E.G., and Carter, M.R. 1999. The response of soil quality indicators to conservation management. Can. J. Soil Sci. **79**: 37–45. doi:10.4141/s97-099.

Bowman, R.A., Reeder, J.D., and Lober, R.W. 1990. Changes in soil properties in a Central Plains rangeland soil after 3, 20, and 60 years of cultivation. Soil Sci. **150**: 851–857. doi:10.1097/00010694-199012000-00004.

Braunack, M.V., and Dexter, A.R. 1989. Soil aggregation in the seedbed: a review. II. Effect of aggregate sizes on plant growth. Soil Tillage Res. **14**: 281–298. doi:10.1016/0167-1987(89)90014-7.

Chantigny, M.H., Angers, D.A., and Beauchamp, C.J. 1999. Aggregation and organic matter decomposition in soils amended with de-inking paper sludge. Soil Sci. Soc. Am. J. **63**: 1214–1221. doi:10.2136/sssaj1999.6351214x.

Chantigny, M.H., Angers, D.A., and Beauchamp, C.J. 2000. Decomposition of de-inking paper sludge in agricultural soils as characterized by carbohydrate analysis. Soil Biol. Biochem. **32**: 1561–1570. doi:10.1016/s0038-0717(00)00069-9.

Chantigny, M.H., and Angers, D.A. 2008. Carbohydrates. Pages 653–665 in M.R. Carter and E.G. Gregorich, eds. Soil sampling and methods of analysis. 2nd ed. Can. Soc. Soil Sci., CRC Press, Boca Raton, FL, USA.

Degens, B.P. 1997. Macro-aggregation of soils by biological bonding and binding mechanisms and the factors affecting these: a review. Aust. J. Soil Res. **35**: 431–459. doi:10.1071/s96016.

Environnement Québec. 2020. Bilan annuel de conformité environnementale: secteur des pâtes et papiers 2001-2013. [Online]. Available from https://collections.banq.qc.ca/ark:/52327/17310 [21 Jan. 2021].

Flemming, C.A., Pileggi, V., Chen, S., and Lee, S.S. 2017. Pathogen survey of pulp and paper mill biosolids compared with soils, composts, and sewage biosolids. J. Environ. Qual. **46**: 984–993. doi:10.2134/jeq2016.12.0467. PMID:28991979.

Gagnon, B., Ziadi, N., Côté, C., and Foisy, M. 2010. Environmental impact of repeated applications of combined paper mill biosolids in silage corn production. Can. J. Soil Sci. **90**: 215–227. doi:10.4141/cjss09055.

Gagnon, B., and Ziadi, N. 2012. Papermill biosolids and alkaline residuals affect crop yield and soil properties over nine years of continuous application. Can. J. Soil Sci. **92**: 917–930. doi:10.4141/cjss2012-026.

Gagnon, B., Ziadi, N., Chantigny, M.H., Bélanger, G., and Massé, D.I. 2012. Biosolids from treated swine manure and papermill residues affect corn fertilizer value. Agron. J. **104**: 483–492. doi:10.2134/agronj2011.0327.

Gagnon, B., and Ziadi, N. 2021. Nitrogen and phosphorus release from paper mill biosolids as affected by material source and soil type under controlled incubation. Can. J. Soil Sci. **101**: 103–112. doi:10.1139/cjss-2020-0055.

García-Orenes, F., Guerrero, C., Mataix-Solera, J., Navarro-Pedreño, J., Gómez, I., and Mataix-Beneyto, J. 2005. Factors controlling the aggregate stability and bulk density in two different degraded soils amended with biosolids. Soil Tillage Res. **82**: 65–76. doi:10.1016/j.still.2004.06.004.

Gunina, A., and Kuzyakov, Y. 2015. Sugars in soil and sweets for microorganisms: review of origin, content, composition and fate. Soil Biol. Biochem. **90**: 87–100. doi:10.1016/j.soilbio.2015.07.021.

Hakkila, P. 1989. Utilization of residual forest biomass. Springer-Verlag, Berlin, Germany.

Haynes, R.J. 2005. Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Adv. Agron. **85**: 221–268. doi:10.1016/s0065-2113(04)85005-3.

Haynes, R.J., and Francis, G.S. 1993. Changes in microbial biomass C, soil carbohydrate composition and aggregate stability induced by growth of selected crop and forage species under field conditions. J. Soil Sci. **44**: 665–675. doi:10.1111/j.1365-2389.1993.tb02331.x.

Haynes, R.J., Swift, R.S., and Stephen, R.C. 1991. Influence of mixed cropping rotations (pasture-arable) on organic matter content, water stable aggregation and clod porosity in a group of soils. Soil Tillage Res. **19**: 77–87. doi:10.1016/0167-1987(91)90111-a.

Hébert, M. 2016. Bilan 2015 du recyclage des matières résiduelles fertilisantes. Gouvernement du Québec, Ministère du Développement durable, de l'Environnement et de la Lutte contre les Changements Climatiques, Québec, QC, Canada. 30 pp. [Online]. Available from http://www.environnement.gouv.qc.ca/matieres/mat_res/fertilisantes/Bilan2015.pdf [16 Dec. 2021].

Jolivet, C., Angers, D.A., Chantigny, M.H., Andreux, F., and Arrouays, D. 2006. Carbohydrate dynamics in particle-size fractions of sandy spodosols following forest conversion to maize cropping. Soil Biol. Biochem. **38**: 2834–2842. doi:10.1016/j.soilbio.2006.04.039.

Karlen, D.L., Hurley, E.G., Andrews, S.S., Cambardella, C.A., Meek, D.W., Duffy, M.D., et al. 2006. Crop rotation effects on soil quality at three northern Corn/Soybean Belt locations. Agron. J. **98**: 484–495. doi:10.2134/agronj2005.0098.

Martens, D.A., and Frankenberger, W.T., Jr. 1991. Determination of saccharides in biological materials by high-performance anion-exchange chromatography with pulsed amperometric detection. J. Chromatogr. **546**: 297–309. doi:10.1016/s0021-9673(01)93027-4.

McGovern, J.N., Berbee, J.G., Bockheim, J.G., and Baker, A.J. 1983. Characteristics of combined effluent treatment sludges from several types of pulp and paper mills. Tappi J. (march) 115–118. [Online]. Available from https://www.fpl.fs.fed.us/documnts/pdf1983/mcgov83a.pdf [21 Jan. 2021].

Melillo, J.M., Aber, J.D., Linkins, A.E., Ricca, A., Fry, B., and Nadelhoffer, K.J. 1989. Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. Plant Soil **115**: 189–198. doi:10.1007/bf02202587.

Metzger, L., Levanon, D., and Mingelgrin, U. 1987. The effect of sewage sludge on soil structural stability: microbiological aspects. Soil Sci. Soc. Am. J. **51**: 346–351. doi:10.2136/sssaj1987.03615995005100020016x.

Monte, M.C., Fuente, E., Blanco, A., and Negro, C. 2009. Waste management from pulp and paper production in the European Union. Waste Manag. **29**: 293–308. doi:10.1016/j.wasman.2008.02.002. PMID:18406123.

N'Dayegamiye, A., and Watt, S. 2000. Changes in soil organic matter and humic substances after paper mill sludges application to corn. in 10th Proceeding International Meeting IHSS. 24–28 July 2000, Toulouse, France. pp. 1009–1013.

N'Dayegamiye, A. 2006. Mixed paper mill sludge effects on corn yield, nitrogen efficiency, and soil properties. Agron. J. **98**: 1471–1478. doi:10.2134/agronj2005.0339.

N'Dayegamiye, A. 2009. Soil properties and crop yields in response to mixed paper mill sludges, dairy cattle manure, and inorganic fertilizer application. Agron. J. **101**: 826–835. doi:10.2134/agronj2008.0170x.

Nurmesniemi, H., Pöykiö, R., and Keiski, R.L. 2007. A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto Mills. Waste Manag. **27**: 1939–1948. doi:10.1016/j.wasman.2006.07.017. PMID:16987647.

Oades, J.M. 1984. Soil organic matter and structural stability: mechanisms and implications for management. Plant Soil **76**: 319–337. doi:10.1007/bf02205590.

Pérez, J., Muñoz-Dorado, J., de la Rubia, T., and Martínez, J. 2002. Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. Int. Microbiol. **5**: 53–63. doi:10.1007/s10123-002-0062-3. PMID:12180781.

Price, G.W., and Voroney, R.P. 2007. Papermill biosolids effect on soil physical and chemical properties. J. Environ. Qual. **36**: 1704–1714. doi:10.2134/jeq2007.0043.

Puget, P., Angers, D.A., and Chenu, C. 1999. Nature of carbohydrates associated with water-stable aggregates of two cultivated soils. Soil Biol. Biochem. **31**: 55–63. doi:10.1016/s0038-0717(98)00103-5.

Rasa, K., Pennanen, T., Peltoniemi, K., Velmala, S., Fritze, H., Kaseva, J., et al. 2021. Pulp and paper mill sludges decrease soil erodibility. J. Environ. Qual. **50**: 172–184. doi:10.1002/jeq2.20170. PMID:33084047.

Robin, D. 1997. Intérêt de la caractérisation biochimique pour l'évaluation de la proportion de matière organique stable après décomposition dans le sol et la classification des produits organominéraux. Agronomie **17**: 157–171.

Samson, M.-E., Chantigny, M.H., Vanasse, A., Menasseri-Aubry, S., Royer, I., and Angers, D.A. 2020. Management practices differently affect particulate and mineral-associated organic matter and their precursors in arable soils. Soil Biol. Biochem. **148**: 107867. doi:10.1016/j.soilbio.2020.107867.

SAS Institute. 2010. SAS OnlineDoc. Version 12.1. SAS Institute Inc., Cary, NC, USA.

Thompson, G., Swain, J., Kay, M., and Forster, C.F. 2001. The treatment of pulp and paper mill effluent: a review. Bioresour. Technol. **77**: 275–286. doi:10.1016/s0960-8524(00)00060-2. PMID:11272013.

Thuriès, L., Pansu, M., Larré-Larrouy, M.-C., and Feller, C. 2002. Biochemical composition and mineralization kinetics of organic inputs in a sandy soil. Soil. Biol. Biochem. **34**: 239–250. doi:10.1016/s0038-0717(01)00178-x.

Tisdall, J.M., and Oades, J.M. 1982. Organic matter and water-stable aggregates in soils. J. Soil Sci. **33**: 141–163. doi:10.1111/j.1365-2389.1982.tb01755.x.

Van Soest, P.J. 1963. Use of detergents in the analysis of fibrous feeds. I. Preparation of fiber residues of low nitrogen content. J. Assoc. Off. Anal. Chem. **46**: 825–829. doi:10.1093/jaoac/46.5.825.

Xie, H., Li, J., Zhu, P., Peng, C., Wang, J., He, H., et al. 2014. Long-term manure amendments enhance neutral sugar accumulation in bulk soil and particulate organic matter in a Mollisol. Soil Biol. Biochem. **78**: 45–53. doi:10.1016/j.soilbio.2014.07.009.

Zibilske, L.M., Clapham, W.M., and Rourke, R.V. 2000. Multiple applications of paper mill sludge in an agricultural system: soil effects. J. Environ. Qual. **29**: 1975–1981. doi:10.2134/jeq2000.00472425002900060034x.