Investigating the use of paper mill residuals as agricultural soil amendments in Thunder Bay, Ontario

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Abstract

This study investigates the repurposing of pulp and paper mill residuals as soil amendments for agriculture around Thunder Bay, Ontario, Canada. Two pulp and paper mill residuals, wood ash (WA) and pulp and paper mill mixed biosolids (PPMS), were applied to agricultural soils as a liming agent and organic amendment, respectively, to improve soils and plant productivity. To determine the suitability of soils in the area to receive these materials under Ontario's Nutrient Management Act and O.Reg. 267/03, soils from 17 farms in the Thunder Bay area were collected and analyzed to establish heavy metal and fertility ranges. Soils were then collected from three farms in the area for a greenhouse pot experiment. The pot experiment was designed to compare the effects of adding PPMS and WA separately and in combination with and without the addition of supplementary mineral fertilizers in accordance to O.Reg 267/03, the legislation regulating the land application of these materials in Ontario. The addition of PPMS at recommended rates significantly increased grass yield, soil organic matter (SOM) concentrations, nutrient availability, pH, and soil health scores, demonstrating the benefits that land application of PPMS can offer to area growers. In soils that require a pH adjustment and could benefit from additional organic matter, the results showed applying WA and PPMS together is more beneficial when either are applied alone. Results indicate that the application of WA and PPMS in the ratio of 1:3 (by mass) had the greatest benefit. The benefits observed were immediate but may not be realized in the year of application in the field due to weather constraints that may constrain the solubility of inorganics and the decomposition and solubility of organic materials.

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Introduction

Soil degradation is the decline in soil quality, which includes physical, chemical and/or biological properties through natural or anthropogenic factors (FAO, 2020). Soil degradation can occur naturally (e.g., rainfall or wind), but is substantially increased because of land management, including the continuous use of land for agriculture. Crop monoculture, as an example, is responsible for structural deterioration, loss of organic matter, and soil acidification (Lalande et al., 2009). To keep agricultural soils productive, amendments can be applied to enhance properties important to soil health and crop production. There are commercial options for amending soils, such as mineral fertilizers, but most commercial options are expensive and can have a negative effect on the environment (Gu et al., 2023). Non-agricultural source materials (NASM) are defined by the Ontario Ministry of Agriculture, Food and Agribusiness (OMAFA) as waste materials from a non-agricultural source that provide beneficial use when land applied. Beneficial use can include an increase in soil pH, moisture, organic matter, and nutrients (NPK) and can be used as an alternative to synthetic commercial products when applied to soil. The land application of NASM is regulated at the provincial level in Canada to protect water quality and environmental and human health (Camberato et al., 2006).

The pulp and papermill industry generates residuals from their processes that can be land applied as NASM to enhance soil quality and plant productivity. More than 35% of the wood chips that enter a paper mill become waste residuals (Cherian & Siddiqua, 2019). These waste residuals are typically disposed of in landfills, but paper industries are under increasing pressure to find alternative endpoints for their waste products because of stringent environmental regulations and lack of space to landfill. The concentrated dumping of papermill waste has the potential to create toxic levels of organic and non-organic materials, including heavy metals, which may be leached into surrounding soils and waterways (Pöykiö et al., 2016). This has led to research to identify uses for such waste products, one of which is NASM.

A survey of Canadian papermills found that 50% of wood ash (WA) produced is landfilled with only 20-25% being used as NASM (Cherian & Siddiqua, 2019). Wood ash is produced as the result of biomass combustion processes to create energy for paper production. There are two types of WA, bottom ash which is recovered from the bottom of the boiler and fly ash, which is recovered from the flue. The resulting wood ash can be used as a substitute for agricultural liming products which increase soil pH. Additionally, it also has a high water-holding capacity and contains a significant amount of plant nutrients (Ram & Masto, 2014). With more than 80% of WA being composed of particles <1.0mm coupled with its low density, it can be challenging to distribute to farms (Demeyer et al., 2001). The possibility of mixing WA with other residuals, such as papermill biosolids, is therefore attractive from a transportation efficiency perspective.

Papermill biosolids share chemical characteristics with livestock manure and have been land applied as early as the 1950s (Turner et al., 2022). Papermill biosolids, or paper sludges, are high in organic matter and nutrients while being low in trace metals and organic pollutants (Ziadi et al., 2013). These biosolids are recovered from papermill wastewater treatment processes and are separated into primary and secondary sludge (Scott & Smith, 1995). It has been reported that of every 1 tonne of paper produced ~40-50 kg of paper mill biosolids are generated and of this 70% is primary and 30% is secondary (Bajpai, 2015). Primary sludge is created by the process of sedimentation. Solids precipitate to the bottom of large settling tanks, or clarifiers, and are then removed for the dewatering process through a system of pumps (Scott & Smith, 1995). Secondary sludge is the result of biological processes which assist in further purifying wastewaters. Microorganisms are used to flocculate and break down wastes into carbon dioxide and water with the remaining solids being removed to be combined with primary sludge for the dewatering process (Scott & Smith, 1995). Primary sludge alone has lower potential as a soil amendment because it is generally low in key nutrients but high in carbon (C). This can lead to nitrogen (N) immobilization in soils, which can negatively affect plant growth. Maintaining a

C/N ratio of 20-30:1 in soils has been shown to prevent N immobilization (Munroe, 2018; Sims, 1990). Camberato et al. (2006) reported an average concentration of 2.7 g kg^{-1} of N in primary sludge. Primary sludge is often combined with secondary sludge to facilitate the dewatering process as secondary sludge tends to take more energy to dewater alone. This material is referred to as pulp and papermill mixed solids (PPMS). In the same survey, Camberato et al. (2006) reported the average N concentrations in secondary sludge as 23.3 g kg^{-1}. Therefore, the combination of primary and secondary sludge may be optimal for spreading when land applying these materials.

Wood ash

Chemical characteristics of fly ash

Acidic soils are defined as soils with a pH of 5.5 or lower (Bojórquez-Quintal et al., 2017). Approximately 30% of global top soils are acidic, which includes 50% of agricultural cropland (Yang et al., 2018). Acidic soils can restrict plant growth in several ways. Aluminum (Al), which can be toxic to plants, is more soluble at acidic pHs (Zheng, 2010). The increased Al concentration inhibits root growth which can lead to a deficiency in phosphorus (P), an essential nutrient for plant growth (Zheng, 2010). The Al will also compete for absorption sites, which can cause a decreased root uptake of calcium (Ca) and magnesium (Mg), also essential nutrients (Berkelaar, 2001). Acidic soils can negatively affect microbial-mediated processes by disrupting the signals sent to microorganisms from the potential host plant (Ferguson et al., 2013). An example is that low pH soils will decrease legume nodulation, which decreases N fixation and available ammonia. For these reasons, finding an appropriate and cost-effective soil neutralizer is important to farmers.

Wood ash can be land-applied to agricultural soils as a lime substitute to increase soil pH (Turner et al. 2022). The chemical properties of the ash depend on the source material and the combustion process but universally it is highly alkaline (Table 1). Cherian & Siddiqua (2019) reported an average pH of 11 and range between 8 and 13. These findings are consistent with what is reported in

The Canadian Wood Ash Chemistry database (Table 1). When compared to commercial liming products, fly ash is often viewed as a valuable substitute.

Table 1. Summarized results from selected studies of the pH of pulp and papermill fly ash.

Reference	pH
The Canadian Wood Ash Chemistry database	11.2 (8.1-13.8)
Gagnon & Ziadi (2020a)	12.7
Pöykiö et al. (2016)	12.8
Backer et al. (2016)	8.3
Allaire et al. (2015)	7.3
Grau et al. (2015)	12.6
Glaser et al. (2015)	10.3
Nurmesniemi et al. (2012)	12.8
Serafimova et al. (2011)	12.6
Major et al. (2010)	9.2
Lalande et al. (2009)	9.0
Cabral et al. (2008)	12.8
Patterson et al. (2004)	13.0

Wood ash contains hydroxide and carbonate salts, primarily calcium carbonate ($CaCO_3$), which are responsible for the neutralizing effect in the soil (Basu et al., 2009). The $CaCO_3$ in WA will dissolve in the soil to release calcium from the carbonate molecule. This creates unstable carbonic acid (H_2CO_3) molecules that will then break up into water (H_2O) and carbon dioxide (CO_2) (Hyatt et al., 1958). The pH of WA is influenced primarily by the combustion temperature, with temperatures <500°C having a positive effect on carbonate content (Demeyer et al., 2001). Gagnon & Ziadi (2020a) found that applications of WA as low as 12 t ha^{-1} increased soil pH by 20.14% over the control. Wood ash has also been shown to increase pH more rapidly than liming materials due to the high solubility of hydroxide and carbonate salts in soil making it an ideal alternative to commercial liming agents (Demeyer et al., 2001).

As well as increasing the pH of soils, WA also contains a variety of essential plant nutrients, such as P and K. This characteristic gives it an advantage over commercial lime, which doesn't contain these elements. Although the properties of WA are influenced by the manufacturing and combustion processes of the individual mill, all WA has phosphorus (P), potassium (K), magnesium (Mg), as well as calcium (Ca) (Table 2). In a field study by Gagnon & Ziadi (2020a), 20 t ha^{-1} of WA increased extractable P (28.95%), K (41.44%), Ca (26.31%) and Mg (10.71%). Due to the high alkalinity and Ca concentrations of WA, there is typically a rapid release of nutrients after application (Cherian & Siddiqua, 2019). Wood ash has an almost negligible amount of N and is therefore often used in combination with an N fertilizer but the addition of PPMS alongside the ash has the potential to alleviate this need due to a higher N content in the PPMS (Basu et al., 2009; Camberato et al., 2006).

Table 2. Summarized results from selected studies on total macronutrient concentrations in wood ash (phosphorous (P), potassium (K), calcium (Ca), and magnesium (Mg)).

	Nutrients			
Reference	P %	K %	Ca %	Mg %
The Canadian Wood Ash Chemistry database	0.61 (0.19-1.06)	3.70 (1.17-9.66)	17.08 (4.77-40.25)	1.48(0.64-2.94)
Gagnon & Ziadi (2020a)	0.73	2.41	12.8	1.26
Nurmesniemi et al. (2012)	0.8,1.0	0.6, 1.0	9.4, 17.3	NR[a]
Serafimova et al. (2011)	0.72	2.39	52.0	1.32
Lalande et al. (2009)	NR	2.1	17	1.1

Cabral et al. (2008)	0.53	2.73	28.1	2.71
Patterson et al. (2004)	0.6	3.4	21.1	1.9
Etiegni et al. (1991)	1.36	4.17	33.14	2.24

[a] No reported value

Metal content

One concern when applying NASM is the concentrations of heavy metals that accumulate during processing. Ontario regulates the concentration of metals in NASM products under two categories (CM1 & CM2), which are determined by concentration of metals (Table 3). Typically, WA does not exceed any of the regulatory limits for heavy metal concentration (Table 4). The temperature at which ash is generated affects the concentration of metals (Cherian & Siddiqua, 2019). The increase in pH, caused by the application of WA, may lower plant uptake of heavy metals such as Cd, Cr, Cu and Zn (Basu et al., 2009). The bioavailability of heavy metals was reported by Pöykiö et al. (2005) to be in the following order: Cd>Cu>Zn>Ni>Pb>Cr. The composition in fly ash is directly related to its source and should be evaluated on an individual basis. However, higher concentrations of fly ash mean higher levels of heavy metals added to the soils therefore the metal contents of ash should be taken into consideration when land applying WA (Mishra et al., 2007).

Table 3. Standards for regulated metals in non-agricultural source materials of non-aqueous material (Source: Schedule 5 of the Regulation).

Parameter	CM1 (mg kg^{-1} dry weight)	CM2 (mg kg^{-1} dry weight)
Arsenic	13	170
Cadmium	3	34
Cobalt	34	340
Chromium	210	2800
Copper	100	1700
Lead	150	1100
Mercury	0.8	11
Molybdenum	5	94
Nickel	62	420
Selenium	2	34
Zinc	500	4200

Table 4. Summarized results from selected studies on heavy metal concentrations in wood ash.

Parameter (mg/kg)	Reference: The Canadian Wood Ash Chemistry database	Pöykiö et al. (2016)	Nurmesniemi et al. (2012)	Cabral et al. (2008)	Serafimova et al. (2011)	Augusto et al. (2008)
Arsenic (As)	10.3 (0.6-27.9)	13.0	14	NR	11.3	≅10
Cadmium (Cd)	11.1 (2.3-24.6)	2.9	3.3	4.7	1.11	≅3
Cobalt (Co)	10.3 (4.8-20.1)	6.6	NR	NR	NR	≅10
Chromium (Cr)	32.9 (15.0-67.9)	66.9	74	24.1	23	≅35
Copper (Cu)	80.8 (35.0-144.6)	63.6	72	25.8	129	≅70
Lead (Pb)	21.1 (3.3-61.3)	28.7	31	44.3	99.7	≅70
Mercury (Hg)	N/A	0.03	0.1	NR	NR	NR
Molybdenum (Mo)	7.5 (2.9-36.9)	3.8	NR	NR	NR	≅10
Nickel (Ni)	36.5 (10.3-184.4)	32.4	33	97.4	16.1	≅20
Selenium (Se)	7.0 (0.7-20.0)	3.1	NR	NR	NR	≅5
Zinc (Zn)	1167.5 (250.2-2661.5)	295.3	320	68.9	133	≅300

Crop productivity

Studies have shown that land application of WA increases crop productivity (Biederman & Harpole 2013; Patterson et al., 2004; Jones et al., 2012). There have been yield increases of many crop species such as corn (*Zea mays* L.), grasses (*Dactyli glomerata* L., *Lolium multiflorum* Lam. & *Phleum pratense* L.), soybean (*Glycine max* (L.) Merr.), and barley (*Hordeum vulgare* L.) (Patterson et al., 2004; Husk & Major 2010; Jones et al., 2012; Allaire et al., 2015; Agegnehu et al., 2016; Backer et al., 2016; Arif et al., 2017;). Patterson et al. (2004) observed applications up to 25 t ha^{-1} positively impacted plant growth of barley or canola crops, with yield increases of 50 and 124% respectively. This effect was thought to have been the result of the increased soil pH and nutrients available to plants. An increase in biomass was reported for concentrations as high as 50 t ha^{-1} in a study by Jones et al. (2012).

Pulp and papermill biosolids

Chemical characteristics of mixed pulp and papermill biosolids (sludge)

A common issue with primary biosolids (sludge) is its high C/N ratio, which results in N immobilization. A summary of 22 studies showed a range of C/N ratios based on the type of biosolids, with primary biosolids having the widest C/N ratio (111:1-943:1), secondary biosolids with C/N ranging from 8:1-50:1 and mixed biosolids close to the optimal C/N with a range of 13:1-31:1 (Faubert et al., 2016). The C/N ratio will depend on the ratio of primary to secondary biosolids, as well as pulp and papermill operations but a mixed pulp and papermill biosolid (PPMS) typically will have a low C/N ratio (Table 5). A study by N'Dayegamiye (2006) compared the application of mineral fertilizer to two organic waste materials (manure and PPMS). The results of this study showed that PPMS promoted an increase in N mineralization accompanied by increased crop yield, which was comparable to the commercial fertilizer.

Table 5. Summarized results from selected studies of the carbon-nitrogen (C/N) ratio of mixed pulp and papermill biosolids.

Reference	C/N Ratio
Abdullah et al. (2015)	30.61
O'Brien et al. (2002)	84.9
Gagnon et al. (2013)	31 & 14
Gagnon & Ziadi (2020b)	25, 12, 23 & 12
Gagnon et al. (2010)	14.67
Gagnon & Ziadi (2012)	24
Abdi et al. (2016)	21
Manirakiza et al. (2019)	24.1 & 13.3

During the wastewater treatment process, N-P-K fertilizers are added to encourage microflora growth, which is a key part of the secondary treatment process (N'Dayegamiye et al., 2003). These nutrients are then carried over into the resulting biosolids (Table 6). PPMS has shown to significantly increase macronutrient levels in agricultural soils. Ziadi & Nyiraneza (2013) reported an increase in total plant N (22.12-46.90%), P (24-52%), Ca (29.41-52.94%) and Mg (26.65-46.65%) in barley. To avoid toxic levels of nutrients, pulp and papermill biosolids are recommended to be applied at low rates (Gagnon et al., 2003; Simard, 2001).

Table 6. Summarized results from selected studies of macronutrients found in mixed pulp and papermill biosolids. (phosphorous (P), potassium (K), calcium (Ca), and magnesium (Mg))

	Nutrients			
Reference	P %	K %	Ca %	Mg %
Abdullah et al. (2015)	0.18	0.12	0.66	0.61
O'Brien et al. (2002)	<0.01	0.02	7.63	0.04
Gagnon et al. (2013)	0.58	0.33 & 0.15	0.70 & 0.11	0.03 & 0.12
Gagnon & Ziadi (2012)	0.42	0.24	0.8	0.07
Abdi et al. (2016)	<0.01	0.06	0.67	NR
Feldkirchner et al. (2003)	0.25 & 0.28	0.05 & 0.03	6.77 & 21.79	0.29 & 0.47
Gagnon et al. (2010)	0.55	0.18	4.5	2.9
Manirakiza et al. (2019)	<0.01	0.25 & 0.1	0.8 & 0.22	0.07 & 0.05

Metal Content

The concentration of heavy metals in the PPMS is highly dependent on mill processes and differs widely between sources (Table 7). Both short and long-term studies have looked at the effects of heavy metals from PPMS on soils. A six-month study by Rosazlin et al. (2010) examined heavy metal leaching from applications of PPMS and found that the heavy metal content increased with increased rates of PPMS applied but, the total concentration of metals leached was relatively small (<1% of total metal content in PPMS). In long-term studies of metal contamination of crop plants growing in PPMS amended soils, the risk of toxicity is lower than when city sewage is applied to agricultural soils (Gagnon & Ziadi, 2021). The land application of PPMS is a safe alternative to landfilling in regard to heavy metal contamination; however, the concentration of heavy metals should still be monitored to prevent soil toxicity.

Table 7. Summarized results from selected studies of metal concentrations found in mixed pulp and papermill biosolids.

Parameter ($mg\ kg^{-1}$)	Reference					
	Abdullah et al. (2015)	O'Brien et al. (2002)	Gagnon et al. (2013)	Gagnon et al. (2010)	Gagnon & Ziadi (2012)	Pervaiz & Sain (2015)
Arsenic (As)	NR	NR	NR	NR	NR	<1
Cadmium (Cd)	2.34	0.0	0.7 & 0.8	5.3	0.4	<1
Cobalt (Co)	NR	NR	NR	NR	NR	1.5-2.5
Chromium (Cr)	20.58	0.4	NR	NR	NR	5.2-12
Copper (Cu)	130.38	5	8 & 7	13.67	9	250-310
Lead (Pb)	126.5	5	NR	NR	NR	8.3-10
Mercury (Hg)	NR	NR	NR	NR	NR	0.57-0.87
Molybdenum (Mo)	NR	NR	1.6 & 1.0	2.5	1.4	2.5-3.8
Nickel (Ni)	21.56	0.4	NR	NR	NR	2.9-5.6
Selenium (Se)	NR	NR	NR	NR	NR	<1
Zinc (Zn)	314.63	31	48 & 67	162.67	38	130-250

Crop productivity

Papermill biosolids have been applied to agricultural soils to increase nutrient content and enhance soil properties for decades. N'Dayegamiye (2006), compared the effect of application rates of PPMS with or without N fertilizer on corn yields and found that crop productivity when PPMS was applied at a rate of 60 t ha^{-1} was similar to the fertilizer only treatment. When lower concentrations of PPMS were applied an N supplement was required to see optimal plant yields. In another study measuring corn yields, PPMS application alone at high rates (60-90 t ha^{-1}) had a similar or greater effect on plant growth compared to N fertilizer applied alone at 0.18 t ha^{-1} (N'Dayegamiye et al., 2003). Simard (2001) reported yields of corn and cabbage (*Brassica oleracea* var *capitata* L.) increasing (150-360%) with increasing PPMS concentrations with strong residual effects in the third year where no PPMS was applied. Pulp and papermill biosolids have a significant positive effect on crop yields with or without N supplements, however, these effects depend on PPMS composition and soil conditions.

Co-applying Wood Ash and Pulp and Papermill Biosolids

Individual land application of WA and PPMS can benefit agricultural soils by improving chemical and physical characteristics. Studies have shown that, in combination, the residuals have a larger impact on plant growth and soil health than when used separately (Manirakiza et al., 2020; Gagnon & Ziadi, 2012; Manirakiza et al., 2019). Due to the rapid mineralization of nutrients, PMSB has to be continuously applied to soils to be effective. As a result of this continuous application, nutrient leaching can be accelerated and can contribute to a higher loss of N (Manirakiza et al., 2019). Co-application of PPMS and WA is therefore important because of the high content of stable C in WA which can increase soil organic matter which prevents leaching (Manirakiza et al., 2019). A study by Manirakiza et al. (2020) found when WA and PPMS are co-applied there was a significant increase in soil pH as well as extractable K concentrations. This study also suggests that the co-application of these papermill residuals also has the potential to prevent metal toxicity by improving metal sequestration. Gagnon & Ziadi (2012) reported soil P availability improved with the co-application of WA (at 3 Mg ha^{-1}) and PPMS (at 30 Mg ha^{-1}). When papermill biosolids and WA are co-applied to acidic and nutrient deficient agricultural soils the potential to increase soil fertility and crop productivity is increased.

The application of WA and PPMS to soil, either individually or together, has the potential to improve agricultural sustainability, promote environmental quality, and increase crop productivity. Locally in the Thunder Bay area, farmers have been applying WA but uptake on PPMS has been limited, despite the benefits realized in other areas of Canada. The objectives of this project were to: 1. examine the fertility and metal concentrations in a range of soils in agricultural production in the Thunder Bay area to determine if WA or PPMS could be applied within the regulatory framework, and if the soils in the area could benefit from the application of WA and/or PPMS, 2. determine the effect of applying WA and PPMS to soils at rates prescribed within the regulatory framework from three agricultural areas on the yield of a pasture mixture of forages, and soil properties in a greenhouse trial, 3. determine an optimal ratio of WA to PPMS that maximizes yield and enhances soil fertility to improve transportation efficiencies of these NASMs. I hypothesize that the application of WA and PPMS will increase yield and improve soil properties, and that the effects will be similar to mineral fertilizer.

Materials and Methods

Local Metal and Nutrient Range

To determine the local range of heavy metals and fertility indicators in agricultural soils, soil samples were collected from 87 fields at 17 farms in the Thunder Bay area in the Spring of 2020. Metal concentrations were measured in soil samples collected from 47 fields at 17 farms. Soil nutrient concentrations were measured in soil samples collected from 87 fields at 17 farms across the Thunder Bay area. Soil samples were collected from the top 0-15 cm using an auger. Sampling followed the OMAFA soil sampling protocol and analysis protocol (Ontario.ca/document/sampling-and-analysis-protocol/sampling-methods, 2021), which involves zig-zagging across the field to collect 20 cores within 5 ha, with two additional cores in each additional hectare. Cores were composited into one sample for each field when the field was less than 10 ha. If the field was larger than 10 ha, the sampling approach just described is repeated. Samples were kept cool until they were returned to the lab where they were air-dried before being sieved to 2 mm. A subsample was sent to A&L Laboratories in London, ON, which is an OMAFA accredited laboratory, for determination of the concentrations of ten regulated metals and soil fertility. Carbon and nitrogen concentrations were determined by flash combustion on an Elementar Vario-Cube in the Lakehead University Instrumental Laboratory after pulverizing the sample to pass through a 53 um sieve using a Spex ball mill.

Soil Description

The soil used for the pot trial was collected from 3 local farms in May, 2021. Soils were collected from a field in a farm in Murillo (N 48° 27’ 0.24” W 89° 25’ 47.564”), a field in a farm in Slate River Valley, herein referred to as Slate River, (N 48° 18’ 21.606” W 89° 27’ 32.51”) and field in a farm located in South Gillies (N 48° 14’ 18.8880” W 89° 43’ 50.4372”). The Murillo and Slate River soils were characterized as loams and South Gillies soil was characterized as a clay loam (Table 8). Initial soil properties are shown in Table 8.

Table 8. Initial soil characteristics of soils used in the pot experiment.

Parameter	Murillo	Slate River	South Gillies
Organic Matter (%)	6.4	5.2	8.2
pH	6.7	6.9	5.7
Bulk Density (g cm^{-3})	1.03	1.15	1.02
Soil Texture (%)			
Sand	46	32	22
Silt	36	43	27
Clay	17	26	40
C:N ratio	13.69	11.21	12.08
Phosphorus (P) (mg kg^{-1})	5	46	8
Potassium (K) (mg kg^{-1})	61	117	133
Calcium (Ca) (mg kg^{-1})	2800	1880	1480
Magnesium (Mg) (mg kg^{-1})	458	411	406

Pulp and Papermill Biosolids and Wood Ash

The PPMS and WA used in this experiment were obtained from the Resolute Forest Products paper mill in Thunder Bay, ON. The PPMS contained on average a C:N ratio of 23:1. The total nutrient concentration for the PPMS was 2266.67 mg kg^{-1} P, 760 mg kg^{-1} K, 4180 mg kg^{-1} Ca, 755.67 mg kg^{-1} Mg. The wood ash had a pH of 12.7 and total nutrient concentrations of 5760 mg kg^{-1} P, 28800 mg kg^{-1} K, 96400 mg kg^{-1} Ca, 8990 mg kg^{-1} Mg. Metal concentrations of both residuals are shown in Table 9.

Table 9. Metal concentrations of paper mill biosolids (PPMS) and wood ash (WA) used in pot experiment.

Metal	Concentration in PPMS (mg kg^{-1})	Concentration in WA (mg kg^{-1})
Arsenic	0.55	<0.7
Cadmium	2.48	6.7
Chromium	10.8	45
Cobalt	0.55	4.5
Copper	11.17	42
Lead	1.19	6.7
Mercury	0.041	0.19
Molybdenum	0.89	1.6
Nickel	4.3	24
Selenium	<0.2	0.41
Zinc	180.33	700

Pot experiment

Soils were sieved field moist to 6 mm prior to being potted. The pots used for this experiment were 1L Tricorn™ beakers, which measured 145 mm H x 115 mm O.D. At the bottom of each pot, 4x7 mm holes were drilled for drainage. The amount of soil added to the pots was calculated based on a target volume of 750 cm^3 using the bulk density of the soil collected from each site (Table 8). The moisture content of the soils was determined by weighing a representative field moist sample and then reweighing after drying to a constant weight at 105°C. The target wet weights for each pot were 969.31 g, 1096.14 g, and 987.8 8g for Murillo, Slate River, and South Gillies, respectively.

Crop characteristics

The grass mixture used in this study was based on common forage crops used in the Thunder Bay area. The mixture consisted of 50% timothy (*Phleum pratense)*, 40% coated alfalfa (*Medicago sativa*) and 10% coated double cut red clover (*Trifolium pratense*). The seeds were supplied by Speare Seeds and mixed in the lab. Pots were seeded at a rate of 20 kg ha^{-1}.

Rates of nutrient application and treatments

The maximum allowable application rate of NASM to soils in Ontario is 20 wet tonnes ha^{-1}, provided the application does not exceed the maximum allowable metal addition to soils prescribed by O. Reg. 267/03 or result in the application of NPK in excess of the crop requirements. The nutrient calculator in OMAFA's Agrisuite calculator (https://agrisuite.omafra.gov.on.ca/) was used to determine rates of WA and PPMS addition using soil pH and the concentrations of NPK in the soils, the PPMS and the WA. If the target nutrient requirements were not met with application of the papermill residuals, N was applied as ammonium sulphate 20-0-0-24S and urea 46-0-0, P was applied as TSP 0-45-0 and K was applied as MOP 0-0-62 to satisfy the crop requirements for growth. Soils from Murillo and South Gillies were able to achieve the N target with biosolids alone and did not require mineral N fertilizer. The soil from Slate River was able to achieve the P target with biosolids alone and did not require mineral P fertilizer.

The PPMS met the beneficial use criteria with its organic matter concentration and was applied to the soils collected from the three farms. Only the soil collected from Farm 3 in South Gillies required WA, which meets the beneficial use criteria as a liming amendment to increase soil pH.

The treatments were designed to represent scenarios in decision making around nutrient management and for all farms included: 1. no mineral fertilizer and no NASM (control), 2. mineral fertilizer only, 3. biosolids only, and 4. biosolids with mineral fertilizer. The fertilizer recommendations for the soil from South Gillies included a pH adjustment, which was met through the application of WA. Mixtures of WA and PPMS were prepared in ratios of 1:1, 1:3, and 1:4 (WA:PPMS) by weight for application to soils from South Gillies, which reflected ratios that made logistic sense for transportation from the mill to farmer's fields. Treatments for the soil from South Gillies included those mentioned above, plus the ratios applied with and without mineral fertilizer. The PPMS and WA were mixed with the soil prior to potting to emulate the incorporation of these materials into the soil, which is required as part of O.Reg. 267/03.

Table 10. Recommended nutrient additions.

Nutrient	Murillo	Slate River Valley	South Gillies
Nitrogen	75 kg N ha^{-1}	75 kg N ha^{-1}	75 kg N ha^{-1}
Phosphorus	110 kg P ha^{-1}	20 kg P ha^{-1}	90 kg P ha^{-1}
Potassium	40 kg K ha^{-1}	20 kg K ha^{-1}	20 kg K ha^{-1}

After seeding and nutrient application, pots from each farm were arranged in a randomized block design in the Lakehead University greenhouse. Each treatment was replicated four times and pots were repositioned once monthly using a random number generator. The pots were watered every 3 days but monitored daily for moisture stress.

Table 11. Maximum application rates of regulated metals according to O. Reg. 267/03.

Metal	Maximum addition to soil (kg ha^{-1} 5 y^{-1})
Arsenic (As)	1.4
Boron (B)	5*
Cadmium (Cd)	0.27

Chromium (Cr)	23.3
Cobalt (Co)	2.7
Copper (Cu)	13.6
Lead (Pb)	9
Molybdenum (Mo)	0.8
Nickel (Ni)	3.56
Selenium (Se)	0.27
Zinc (Zn)	33

*5 year maximum based on 1 kg ha^{-1} yr^{-1}

Laboratory analyses

The grasses were harvested after 105 days by clipping the aboveground biomass with scissors. The biomass was placed in a pre-weighed and labelled paper bag and weighed before drying to a constant weight at 60°C in a drying oven. The biomass was weighed after drying and the dry weight was used to calculate yield (g m^{-2}) using the surface area of the pots. The amount of biomass harvested from each plot did not meet the minimum weight required for the forage analysis package at A&L Laboratories and replicates were composited for the chemical analyses. Chemical analyses included the determination of protein (%), fibres (%), energy (Mcal kg^{-1}), minerals (%; Ca, Cu, P, K, S, Mg, An, Fe, Co, Mn, Na), and the relative feed value (calculation).

Before the soils were subsampled for analyses, the pots were weighed and the height of soil in the pot was measured to calculate bulk density. The soil from each pot was then transferred to a plastic bag where it was mixed to homogenize the soil. A subsample of the soil was dried at 105°C to calculate the soil moisture content. Soils were air dried before further analyses.

A sample of soil (approximately two cups) from each pot was sent to A&L Laboratories in London for determination of soil fertility parameters which included pH, organic matter by loss on ignition, and concentrations of P, K, Ca, and Mg. Total C and N concentrations were determined by flash combustion on an Elementar Vario Cube in the LUIL after grinding to pass through a 53 um sieve using a Spex ball mill. Aggregate stability, a measurement of the resistance of the soil structure to external forces (mechanical and physio-chemical), was determined using an Eijkelkamp wet sieving apparatus (Eijkelkamp Agrisearch Equipment 08.12. Giesbeek, Netherlands) following the method of Kemper and Rosenau (1986).

Soil biological activity was investigated using the Solvita burst CO_2-C (BURST) and Solvita labile amino N (SLAN) test methods (Solvita, 2019a; Solvita, 2019b). The BURST test measures potential carbon mineralization over 24h and SLAN is an indicator of available nitrogen. For BURST, a 30-cc scoop of soil subsample was transferred to a 50 mL plastic beaker. Nine mL of distilled water was added to the beaker, which was placed inside a 475 mL jar. A Solvita BURST paddle was inserted into each beaker and the jars were immediately sealed and transferred to an incubator where they were left undisturbed for 24 h at 22°C. A Solvita digital colorimeter reader was used to record the CO_2 evolved and expressed as mg CO_2-C kg^{-1} soil. For SLAN, a 4 g subsample was weighed into a 50 mL beaker. Ten mL of 2N NaOH was added to the beaker, which was placed in a 250 mL jar with a SLAN paddle. The jar was sealed immediately and transferred to an incubator where they were left undisturbed for 24 h at 22°C. A Solvita digital colorimeter reader was used to record the NH3-N evolved and expressed as mg NH_3-N kg^{-1} soil. Permanganate oxidizable carbon (POXC) is considered to be a labile fraction of C that is readily available for microbial decomposition (Weil et al., 2003). We quantified the POXC fraction using the methodology outlined in Weil et al., (2003). Absorbance at 550 nm was measured using a Biotek 800 TS plate reader.

Soil health scores were calculated using scoring functions developed by Chahal et al. (2023) for soil textural groups. We checked for outliers using the Tukey's inner fences interquartile range technique (Hoaglin, 2003), and using the soil texture data, grouped the observations into textural groups, as outlined in the Comprehensive Assessment of Soil Health (Moebius-Clune et al., 2016; Chahal et al., 2023). We used cumulative normal distributions as the scoring functions for BURST, SLAN, and SOM, with the means and standard deviations reported by Chahal et al. (2023) for our textural classes. This approach assigns a score ranging from 0-100. To calculate a SH score out of 100, we assigned an equal weighting of the scores for BURST, SLAN and SOM and took the average of these three scores for the final score. Soil health scores were interpreted as very low (<40), low (40-55), medium (55-70), high (0-85), and very high (>85) following the approach of Moebius-Clune et al. (2016)

Statistical Analysis

All analyses were performed using SPSS (version 29.0.2.0, IBM). Descriptive statistics, including mean and range, were computed for soil samples collected from farms in the Thunder Bay area using SPSS's descriptive statistics function. The data satisfied the assumptions required for analysis of variance (ANOVA), so no transformations were necessary. A two-way ANOVA was employed to evaluate the effects of site and treatment (control, mineral fertilizer, biosolids, and a combination of biosolids and fertilizer) on yield and soil parameters. When an interaction between site and treatment was present, a one-way ANOVA was conducted to assess the effect of treatment at each individual site. Post-hoc comparisons were carried out using the Tukey-Kramer least significant difference test with an alpha level of 0.05.

For South Gillies, a one-way ANOVA was used to assess the impact of soil amendment treatments, which included WA and PPMS, both separately and in combination. Significant treatment effects were further analyzed using orthogonal contrasts (Snedecor & Cochran, 1989) to explore the effects of different amendment types and their combinations on the measured parameters (Table 12).

Table 12. Orthogonal contrasts examining the effects of nutrient amendments on response variables (C=control, F=mineral fertilizer, WA=wood ash, PPMS=paper mill biosolids).

Question	Contrast
L1: Does the application of soil amendments affect the response variable?	[C]-1/11*[F+WA+WA&F+PPMS+PPMS&F+1:1+1:1&F+1:4+1:4&F+1:3+1:3&F]
L2: Does the response to mineral fertilizer differ from all other amendments or combinations?	[F]-1/10*[WA+WA&F+PPMS+PPMS&F+1:1+1:1&F+1:4+1:4&F+1:3+1:3&F]
L3: Does the response differ when wood ash amendment treatments	[WA+1:1+1:4+1:3]-[WA&F+1:1&F+1:4&F+1:3F]

are applied with mineral fertilizer versus without?	
L4: Does the response differ when papermill biosolid amendment treatments are applied with mineral fertilizer versus without?	[PPMS+1:1+1:4+1:3]-[PPMS&F+1:1&F+1:4&F+1:3F]
L5: Does the response differ between wood ash only and papermill biosolid only amendments?	[WA+WA&F]-[PPMS+PPMS&F]
L6: Does the response differ between wood ash only and wood ash applied in combination with papermill biosolids?	[WA+WA&F]-1/3*[1:1+ 1:1&F+1:4+1:4&F+1:3+1:3&F]
L7: Does the response differ between papermill biosolid only and papermill biosolids applied in combination with wood ash?	[PPMS+PPS&F]-1/3*[1:1+ 1:1&F+1:4+1:4&F+1:3+1:3&F]
L8: Does the response differ between the 1:1 (WA:PPMS) and 1:3 (WA:PPMS) applications?	[1:1+1:1&F]-[1:3+1:3&F]
L9: Does the response differ between the 1:1 (WA:PPMS) and 1:4 (WA:PPMS) applications?	[1:1+1:1&F]-[1:4+1:4&F]
L10: Does the response differ between the 1:3 (WA:PPMS) and 1:4 (WA:PPMS) applications?	[1:3+1:3&F]- [1:4+1:4&F]

Results

Local Metal and Nutrient Range

Metal concentrations from the 17 sampled farms were highly variable. Metal concentration exceedances for cadmium (1 farm), cobalt (3 farms) and nickel (10 farms) were evident in some soils.

Table 13. Metal concentration data for Thunder Bay regional agricultural soils.

Regulated Metal	Average (ug g^{-1})	Range (ug g^{-1})
Arsenic (As)	4.78	1 - 11
Cadmium (Cd)	0.94	0.22 - 2.8
Chromium (Cr)	44.70	35.22 - 52.85
Cobalt (Co)	16.36	11.79 - 24.39
Copper (Cu)	29.98	16.54 - 88
Lead (Pb)	11.13	1 - 16
Mercury (Hg)	0.16	0.1 - 0.22
Molybdenum (Mo)	2.32	1.1 - 4.9
Nickel (Ni)	32.37	24.18 - 55.75
*Selenium (Se)	BDL	BDL
Zinc (Zn)	108.60	46.62 - 214.8

*Selenium below detectable limit on all farms (<1 ug/g)

Table 14. Fertility data for Thunder Bay region agricultural soils.

Parameter	Average	Range	Median
Organic matter (%)	8.4	4.1 - 16.2	7.3
pH	5.8	5.2 - 7.1	5.8
P (ppm)	16.2	3 - 231	9
K (ppm)	116.7	9 - 546	99.5
Mg (ppm)	385.7	93 - 1100	353.5
Ca (ppm)	1804.0	620 - 5570	1625
Na (ppm)	23.9	8 - 84	20

Effects of Soil Amendments on Vegetation

There was significant interaction between site and treatment for dry matter yield ($F=2.53$, $p=0.03$) and the relative N efficiency coefficient ($F=24.330$, $p<0.001$). There was no significant effect of treatments on yield in Murillo ($F=2.776$, $p=0.087$), where the average yield was 2.0 Mg ha^{-1} but there was in Slate River ($F=2.242$, $p=0.003$) and South Gillies ($F=7.556$, $p=0.004$). In the Slate River soil, yield was highest when PB was applied with fertilizers, and in South Gillies the application of all amendments increased yield (Figure 1). Of note, there was no significant difference in yield among the sites when no amendments were incorporated ($F=3.673$, $p=0.068$) and for the treatments that received mineral fertilizers alone ($F=2.165$, $p=0.171$). There were significant differences among the sites for the pots where PB was applied alone ($F=31.153$, $p<0.001$) and with mineral fertilizers ($F=21.629$, $p<0.001$), with the Murillo soil having a significantly lower yield than South Gillies and Slate River. With regards to the relative N efficiency coefficient, which was estimated by the dry matter yield per unit of N applied, the soils from Slate River that received PB alone had the highest relative N efficiency coefficient (50.3 kg DM kg N^{-1}) compared to the fertilizers alone treatment (22.7 kg DM kg N^{-1}) and the PB+mineral fertilizers (28.3 kg DM kg N^{-1}) ($F=53.887$, $p<0.001$). In the Murillo soil, the mineral fertilizers treatment had a higher relative N efficiency coefficient (21.7 kg DM kg N^{-}1) compared to the PB alone treatment (9.9 kg DM kg N^{-1}) ($F=4.235$, $p=0.051$). There was no effect of treatment on the relative N efficiency coefficient in South Gillies (26.7 kg DM kg N^{-1}) ($F=2.256$, $p=0.161$). The relative N efficiency coefficients were comparable between South Gillies (26.7 kg DM kg N^{-1}) and Slate River (25.8 kg DM kg N^{-1}) but were notably lower for Murillo (15.7 kg DM kg N^{-1}).

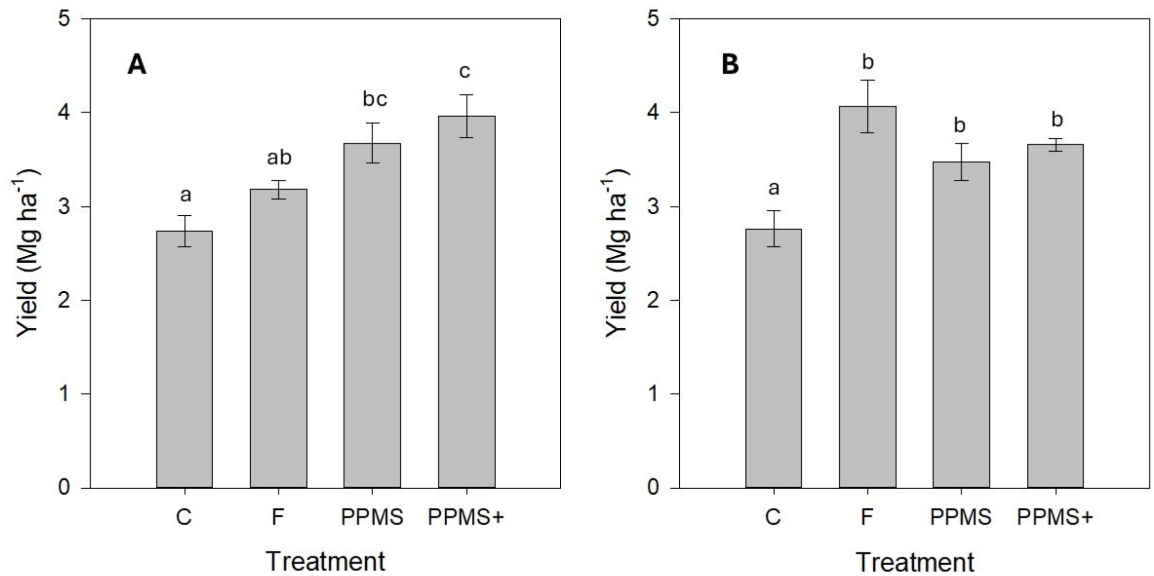

Figure 1. Biomass yield in the treatments applied to A) Slate River and B) South Gillies. Bars are means (n=4) ± standard error. Different lower-case letters indicate significant differences. (C=control, F=mineral fertilizer, PPMS=paper mill biosolids, PPMS+=paper mill biosolids+mineral fertilizer)

In the South Gilllies soil, which has WA treatments and mixtures of PPMS and WA, there was a significant effect of adding amendments on yield (F=3.258, p=0.004), but there was no effect on the relative N use efficiency coefficient (F=1.102, p=0.389), which averaged 28.2 kg DM kg N^{-1}. The linear contrasts showed that the application of any amendment increased yield (L1, Figure 2A). Applying PPMS with WA increased yield more than applying PPMS alone (L7, Figure 2B), and the ratios in the mixture did not differ from one another.

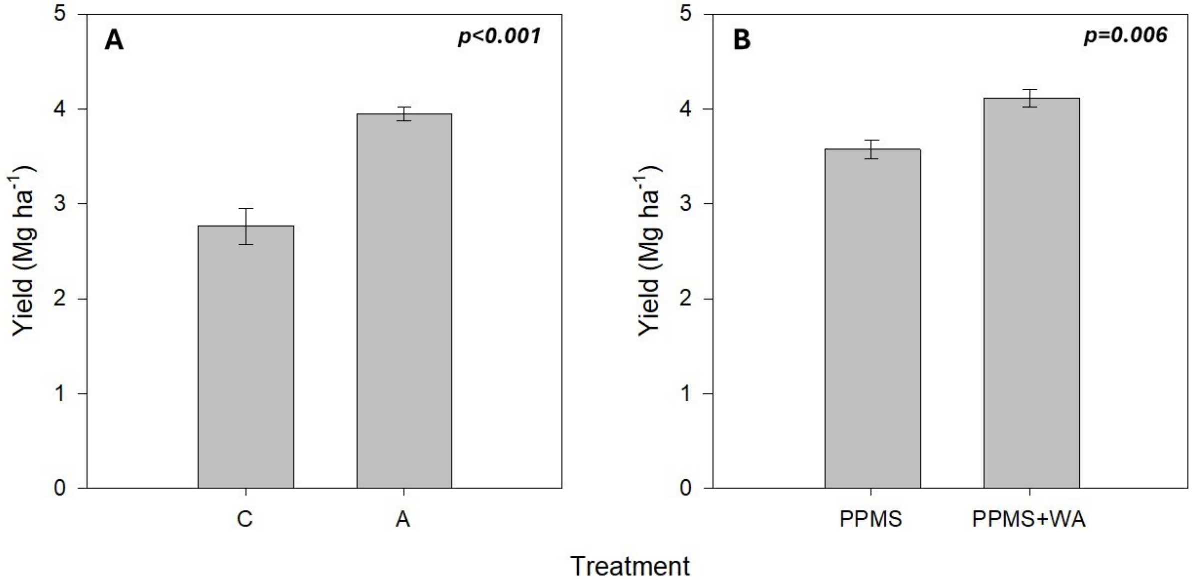

Figure 2. Dry matter yield in A) the control vs soils receiving nutrient amendments (L1) and B) soil receiving PB and mixtures of PB and WA (L7). Bars are means (n=4) ± standard error. (C=control, A=amendment, PPMS=paper mill biosolids, PPMS+WA=paper mill biosolids+wood ash)

Effects of Soil Amendments on Soil Properties and Soil Health

In the pot trial, comparing the effects of amendments by site, there was no effect of amendment treatment on soil health score, but scores differed by the site (Table 10). The mean soil scores were, Slate River:91, Murillo:66 and South Gillies:79.

Table 15. Two-way analysis of variance results evaluating the effects of site and nutrient amendment treatment on soil health score, soil health indicators, and other physical and chemical properties of the soils in the greenhouse experiment.

	Treatment		Site		Treatment*Site	
Parameter	*F*	*P*	*F*	*p*	*F*	*p*
Soil Health Score	0.928	0.437	72.709	***<0.001***	0.975	0.456
BURST	0.382	0.767	5.357	***0.009***	1.38	0.249

SLAN	1.515	0.227	85.223	<0.001	2.489	***0.041***
SOM	3.78	0.019	275.298	<0.001	3.927	***0.004***
POXC	1.8	0.165	1.363	0.256	1.363	0.256
WAS	1.819	0.161	48.186	<0.001	2.991	***0.018***
Bulk Density	3.682	0.021	286.505	<0.001	3.243	***0.012***
pH	35.487	<0.001	404.854	<0.001	5.898	***<0.001***
CEC	1.57	0.212	43.143	***<0.001***	1.832	0.120
C	6.599	0.001	622.82	<0.001	5.621	***<0.001***
N	5.069	0.005	1643.612	<0.001	4.267	***0.002***
C:N	7.437	<0.001	627.985	<0.001	3.024	***0.017***
P	5.217	***0.004***	2147.395	***<0.001***	0.508	0.798
K	10.431	***<0.001***	93.478	***<0.001***	2.279	0.058
Ca	0.829	0.487	36.098	***<0.001***	0.889	0.513
Mg	0.399	0.754	189.386	***<0.001***	1.588	0.179

Similar to the SH scores, BURST only differed by site (Table 10). Soil from South Gillies had the lowest BURST rate (90.7 mg C-CO_2 kg^{-1} d^{-1}) compared to Slate River (114.8 mg C-CO_2 kg^{-1} d^{-1}) and Murillo (112.6 mg C-CO_2 kg^{-1} d^{-1}). There was interaction between site and treatment for SLAN, SOM, and WAS (Table 10). There was no effect of treatment on SLAN in Murillo, which had an average value of 220.6 mg N-NH_3 kg^{-1} d^{-1} but rates of SLAN were highest in the PPMS+fertilizers treatment in Slate River (Figure 3A) and lowest in the PPMS+ treatment in South Gillies (Figure 3B). There was no effect of treatment on SOM concentration in Slate River (53.9 g kg^{-1}) but the application of PPMS increased SOM concentration for both Murillo and South Gillies (Table 11 and Figure 3C-D). There was no effect of treatment on WAS in South Gillies, which had an average value of 47%, but the Slate River and Murillo soils that received mineral fertilizers alone had the lowest WAS and in Murillo, the application of PPMS increased WAS (Figure 3 E-F). The concentration of POXC did not differ between sites or treatments (Table 10) and averaged 700.5 mg kg^{-1}.

Table 16. One-way analysis of variance results evaluating the effects of nutrient amendment treatment by site on soil health indicators, and other physical and chemical properties of the soils in the greenhouse experiment.

	Slate River		Murillo		South Gillies	
Parameter	*F*	*p*	*F*	*p*	*F*	*p*
SLAN	18.215	***<0.001***	1.171	0.361	4.006	***0.034***
SOM	2.242	0.136	6.581	***0.007***	3.865	***0.038***
WAS	14.98	***<0.001***	4.689	0.036	1.067	0.399
Bulk Density	7.719	***0.004***	2.524	0.107	2.476	0.111
pH	26.615	***<0.001***	6.692	***0.007***	56.09	***<0.001***
C	1.727	0.214	7.764	***0.004***	5.923	***0.01***
N	1.727	0.214	5	***0.018***	4.816	***0.02***
C:N	0.892	0.473	3.02	0.072	9.239	***0.002***

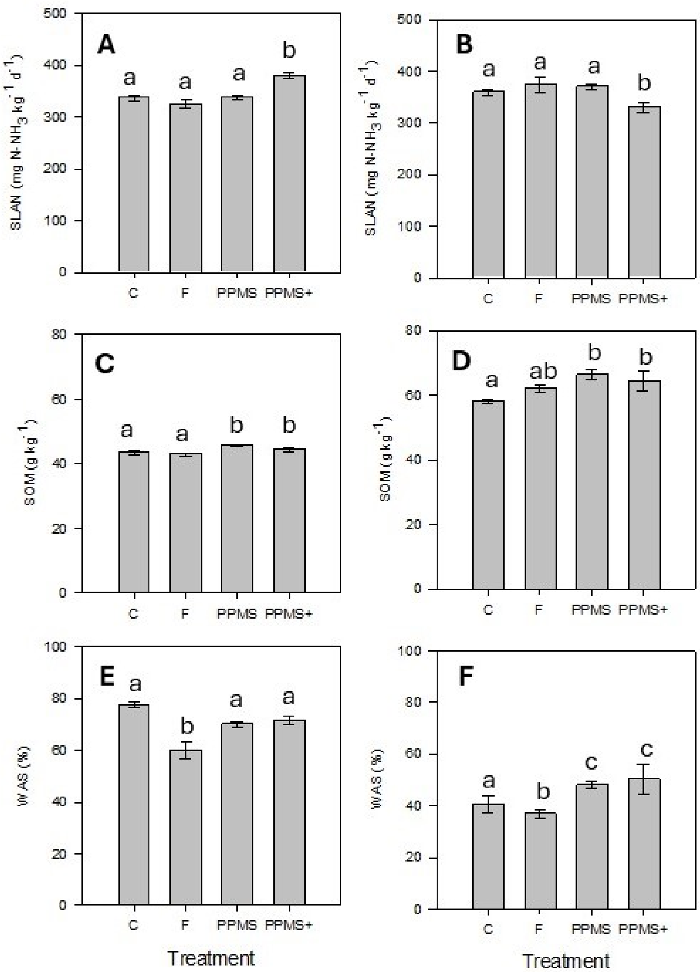

Figure 3. The effects of nutrient amendment treatments on A) SLAN in Slate River, B) SLAN in South Gillies, C) SOM in Murillo, D) SOM in South Gillies, E) WAS in Slate River, and F) WAS in Murillo. Bars are means (n=4) ± standard error. Different lower-case letters indicate significant differences. (C=control, F=mineral fertilizer, PPMS=paper mill biosolids, PPMS+=paper mill biosolids+mineral fertilizer)

There was no significant interaction between site and nutrient treatment on the concentrations of P, K, Ca and Mg (Table 10). There was no effect of nutrient amendment treatment on concentrations of Ca and Mg and between sites, Slate River (2210 mg Ca kg^{-1}, 526 mg Mg kg^{-1})>Murillo (1823 mg Ca kg^{-1}, 402 mg Mg kg^{-1})>South Gillies (1656 mg Ca kg^{-1}, 300 mg Mg kg^{-1}). There was a significant effect of site and treatment for P and K. PPMS+ had the highest concentration of P and the treatments with mineral fertilizers had the highest concentration of K (Figure 4). The lowest concentrations of P and K were in the Murillo soil (4.6 mg kg-

^{1}, 62.5 mg kg^{-1}) and the highest concentrations were in Slate River (58.9 mg kg^{-1}, 1171 mg kg^{-1}). Concentrations in South Gillies were lower in South Gillies (13.4 mg kg^{-1}) compared to Slate River but similar for K (111.6 mg kg^{-1}).

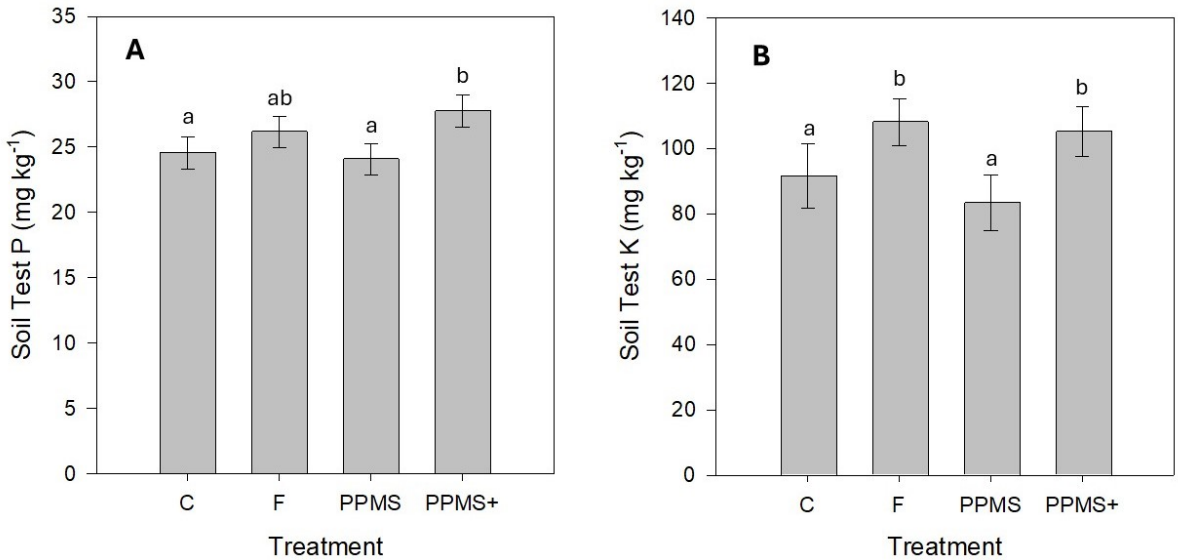

Figure 4. The effects of nutrient amendment treatments on A) soil test P and B) soil test K. Bars are means (n=4) ± standard error. Different lower-case letters indicate significant differences. (C=control, F=mineral fertilizer, PPMS=paper mill biosolids, PPMS+=paper mill biosolids+mineral fertilizer)

There was significant interaction between site and treatment for bulk density, pH, C, N and C:N ratio (Table 10). There was only an effect of treatment on bulk density in Slate River (Table 11), where PPMS+ increased bulk density, though the increase was small (Figure 5A). There was no effect of treatment on C or N concentrations, or on the C:N ratio, in Slate River (Table 11). The application of mineral fertilizers to soils from South Gillies and Murillo lowered the soil pH (Figure 6A) and the application of PPMS alone increased soil pH in Murillo (Figure 6B). The application of PPMS+ in South Gillies increased soil carbon and nitrogen concentrations (Figure 6C, E) as well as the C:N ratio (Figure 5B), though marginally. In the Murillo soil, the application of PPMS increased soil carbon and nitrogen concentrations (Figure 6D, F) but there was no effect on the C:N ratio (Table 11).

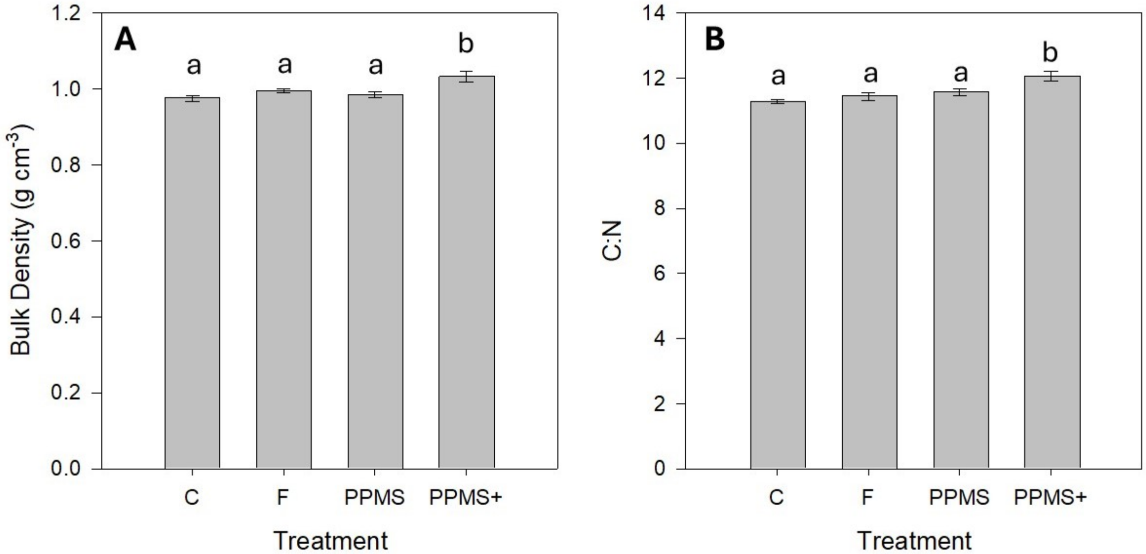

Figure 5. The effect of nutrient amendment treatments on A) bulk density in SR and B) the C:N ratio in South Gillies. Bars are means (n=4) ± standard error. Different lower-case letters indicate significant differences. (C=control, F=mineral fertilizer, PPMS=paper mill biosolids, PPMS+=paper mill biosolids+mineral fertilizer)

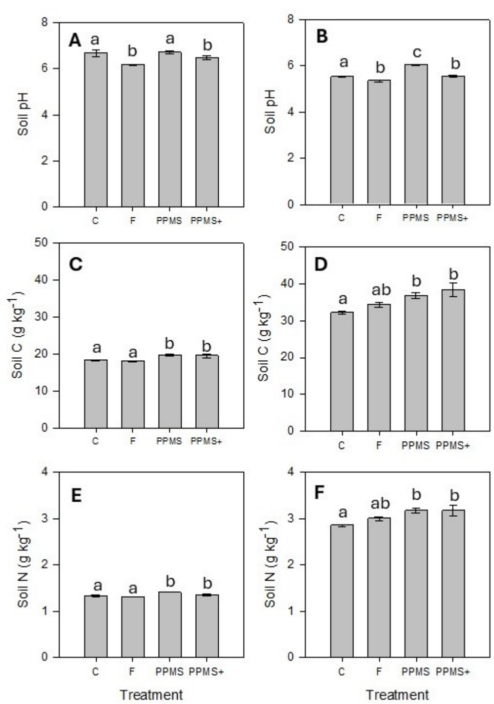

Figure 6. The effect of nutrient amendment treatments on soil pH in A) South Gillies and B) Murillo, soil C concentrations in C) South Gillies and D) Murillo, and soil nitrogen concentrations in E) South Gillies and F) Murillo. Bars are means (n=4)

± standard error. Different lower-case letters indicate significant differences. (C=control, F=mineral fertilizer, PPMS=paper mill biosolids, PPMS+=paper mill biosolids+mineral fertilizer)

There was an effect of treatment on the soil health score, BURST, SLAN, SOM, POXC, but not WAS (63%) in the pot trial experiment for the South Gillies soil with the expanded set of treatments that included WA (Table 14). Applying any amendment improved the soil health score by two points, the application of the papermill residuals increased the score by four points, adding fertilizers to WA or PPMS when applied alone had no effect on soil health score (L3, p=0.267; L4, p=0.368), applying PPMS alone increased the score more than applying WA alone, the mixtures of WA and PPMS increased the score by five points relative to when WA was applied alone and by 10 points relative to when PPMS was applied alone (Figure 10). In terms of the effectiveness of increasing the soil health score, the ratio of 1:4 (WA:PPMS) was four to five points lower than the other mixtures (Figure 7), which did not differ from each other (L8, p=0.382).

Table 17. One-way analysis of variance results evaluating the effects of nutrient amendment treatment on soil health scores, soil health indicators, and other soil properties in the greenhouse experiment that included WA application for pH adjustment. (SH score=soil health score, BURST=Solivita CO2 burst test, SLAN=Solvita Labile Amino Nitrogen, SOM=soil organic matter, POXC=permanganate oxidizable carbon, WAS=water stable aggregate, C=carbon, N=nitrogen, C:N=carbon to nitrogen ratio, P=phosphorous, K=potassium, Ca=calcium, Mg=magnesium, CEC=cation exchange capacity)

Parameter	F	Sig
SH score	6.941	<0.001
BURST	7.117	<0.001
SLAN	3.114	0.005
SOM	5.353	<0.001
POXC	3.738	0.001

WAS	1.580	0.147
pH	11.485	<0.001
Bulk Density	4.762	<0.001
C	12.242	<0.001
N	14.004	<0.001
C:N	6.187	<0.001
P	12.960	<0.001
K	12.038	<0.001
Mg	2.380	0.025
Ca	1.543	0.159
CEC	1.420	0.206

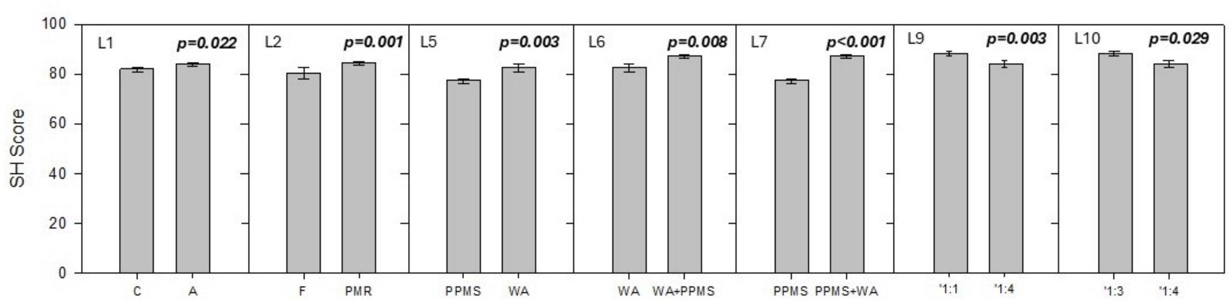

Figure 7. Orthogonal contrasts (means and standard error of the mean) for soil health score (C, control; A, amendment; F, mineral fertilizers; PMR, pulp and papermill residuals; PPMS, pulp and papermill biosolids; WA, wood ash; 1:1, WA:PPMS; 1:3, WA:PPMS; 1:4, WA:PPMS).

Adding any amendment increased BURST (L1, Figure 8A). The effect was greater when the PMR were applied instead of mineral fertilizers (L2) and when the PMR were applied as mixtures, as opposed to being applied singularly (L6-7).

Combinations of WA and PPMS increased SLAN slightly compared to when WA was applied alone (L6, $p<0.001$) and a mixture of WA:PPMS of 1:3 had higher SLAN than 1:1 (L8, $p=0.002$). Soils that received PPMS had higher SOM concentrations than those that received WA (L5, Figure 8B) and SOM concentrations were higher when WA and PPMS were applied alone (L6-7) compared to when the PMR were applied as mixtures. The mixture of 1:3 had higher SOM concentrations than mixtures of 1:1 and 1:4 (L8-10). The application of any amendment resulted in lower concentrations of POXC than the control, which received no amendments (L1). The concentration of POXC was higher when PPMS was applied alone compared to when WA was applied alone (L5, Figure 8C). Mixtures of WA and PPMS in the ratios of 1:3 and 1:4 had higher concentrations of POXC than 1:1 (L8-9) and the 1:4 mixture had slightly higher concentrations than the 1:3 (L10).

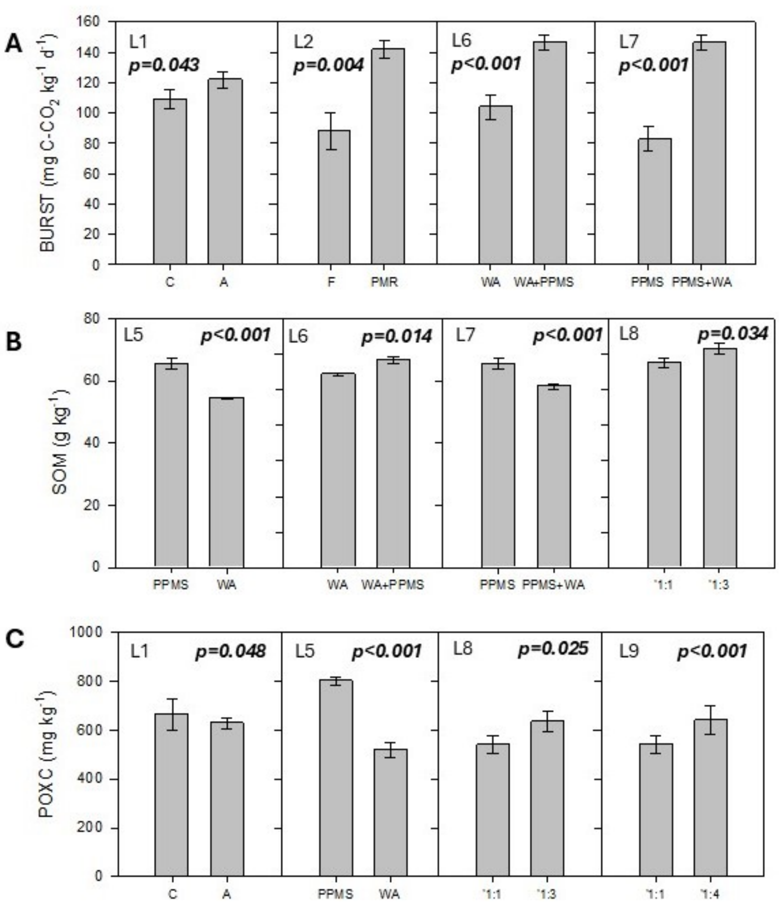

Figure 8. Orthogonal contrasts (means and standard error of the mean) for A) BURST, B) SOM, and C) POXC (C, control; A, amendment; F, mineral fertilizers; PMR, pulp and papermill residuals; PPMS, pulp and papermill biosolids; WA, wood ash; 1:1, WA:PPMS; 1:3, WA:PPMS; 1:4, WA:PPMS).

There was a significant effect of treatment on soil pH, bulk density, concentrations of C and N, P, K, Mg and the C:N, and no effect on CEC (19.3 Meq 100 g^{-1}) or concentrations of Ca (1739 mg kg^{-1}) (Table 14). Amending soils increased the concentrations of C, P, and K, and the C:N ratio (L1, Figure 9). The pH, and concentrations of P and K were higher when the papermill residuals were applied compared to the mineral fertilizers (L2, Figure 10). The pH and concentration of K was also higher when the WA and PPMS were applied without supplemental fertilizers (L3-4, Figure 10). When comparing the application of WA to PPMS, applying PPMS increased soil pH, bulk density, C, N, C:N ratio compared to WA but the application of WA resulted in higher concentrations of P, K and Mg (L5, Figure 11). For Mg ($p=0.002$), mean concentration for the PPMS treatment was 284 mg kg^{-1} and for WA it was 333 mg kg^{-1}. Compared to when WA was applied alone, applying mixtures of WA and PPMS increased soil pH, C, N, C:N ratio and decreased the bulk density of the soil (L6, Figure 11). Applying PPMS alone, compared to the mixtures of WA and PPMS, resulted in higher pH, bulk density, C, N, C:N ratio , but lower concentrations of P, K, and Mg (L7, Figure 11). For Mg ($p=0.021$), mean concentration for the PPMS alone treatment was 284 mg kg^{-1} and for the mixtures it was 325 mg kg^{-1}. In terms of the mixtures, 1:3 had higher concentrations of C, N, P and K compared to 1:1 (L8, Figure 12), 1:4 had higher bulk density, C:N ratio (11.3 vs 11.6, $p=0.007$) and P concentrations, but lower N and Mg concentrations than 1:1 (L9, Figure 12), and 1:3 had lower bulk density and P concentration and higher concentrations of C, N and K compared to 1:4 (L10, Figure 12).

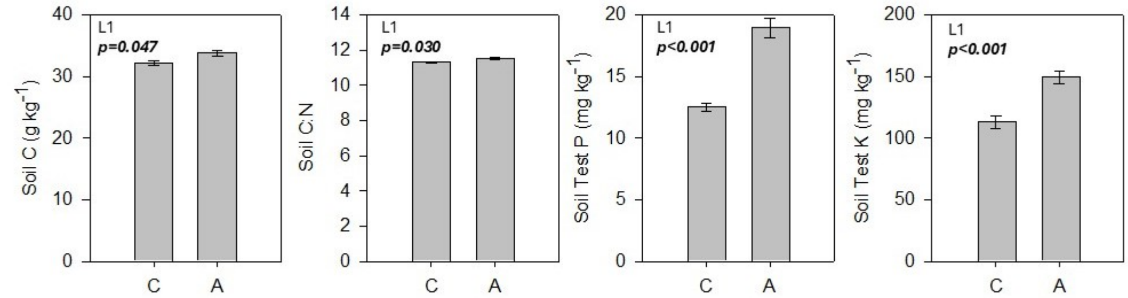

Figure 9. Orthogonal contrast (means and standard error of the mean) for soil C, C:N, soil test P and soil test C (C, control; A, amendment).

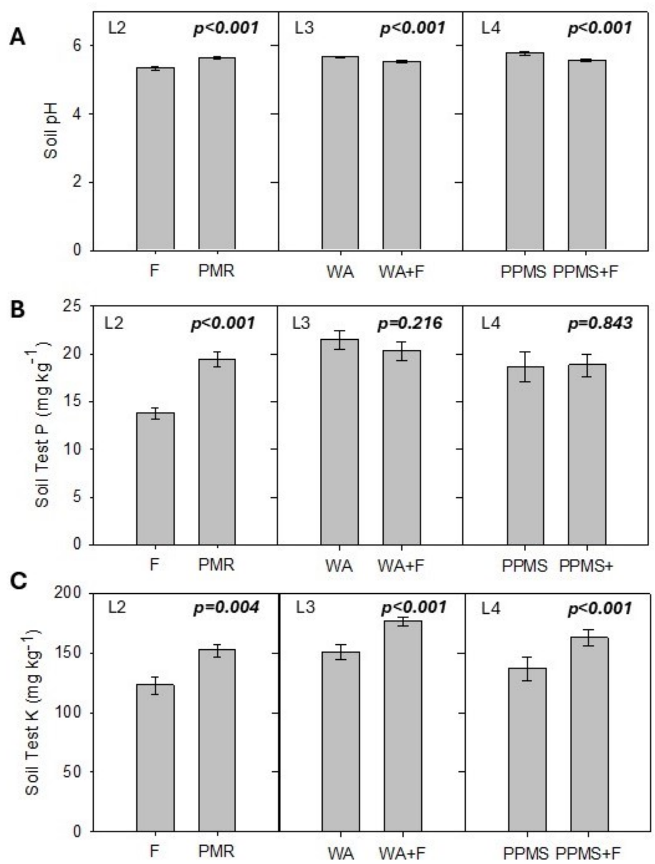

Figure 10. Orthogonal contrasts (means and standard error of the mean) for A: soil pH, B: soil test P, and C: soil test K. (F, mineral fertilizers; PMR, pulp and papermill residuals; PPMS, pulp and papermill biosolids; WA, wood ash).

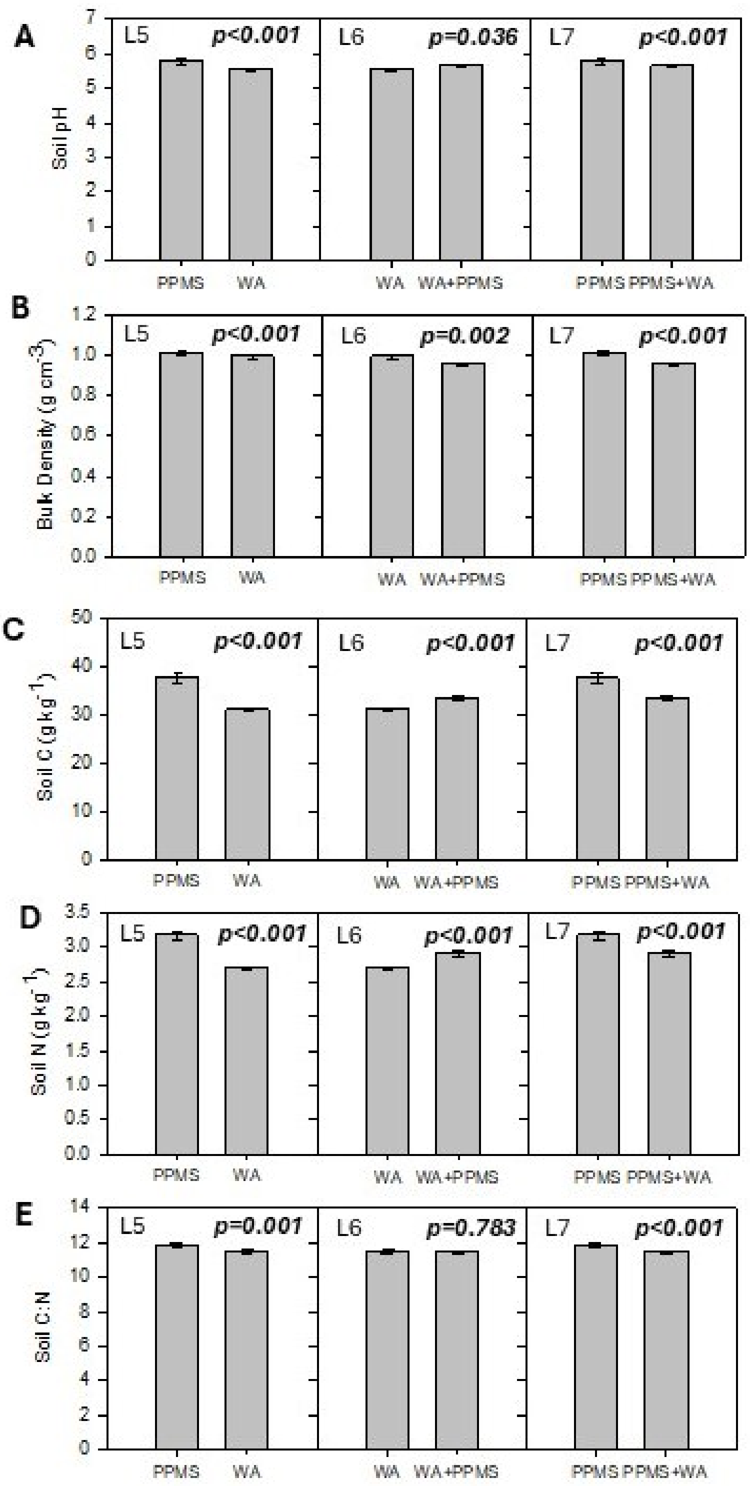

Figure 11. Orthogonal contrasts (means and standard error of the mean) for A) soil pH, B) bulk density, C) soil C. D) soil N, and E) C:N ratio (PPMS, pulp and papermill biosolids; WA, wood ash).

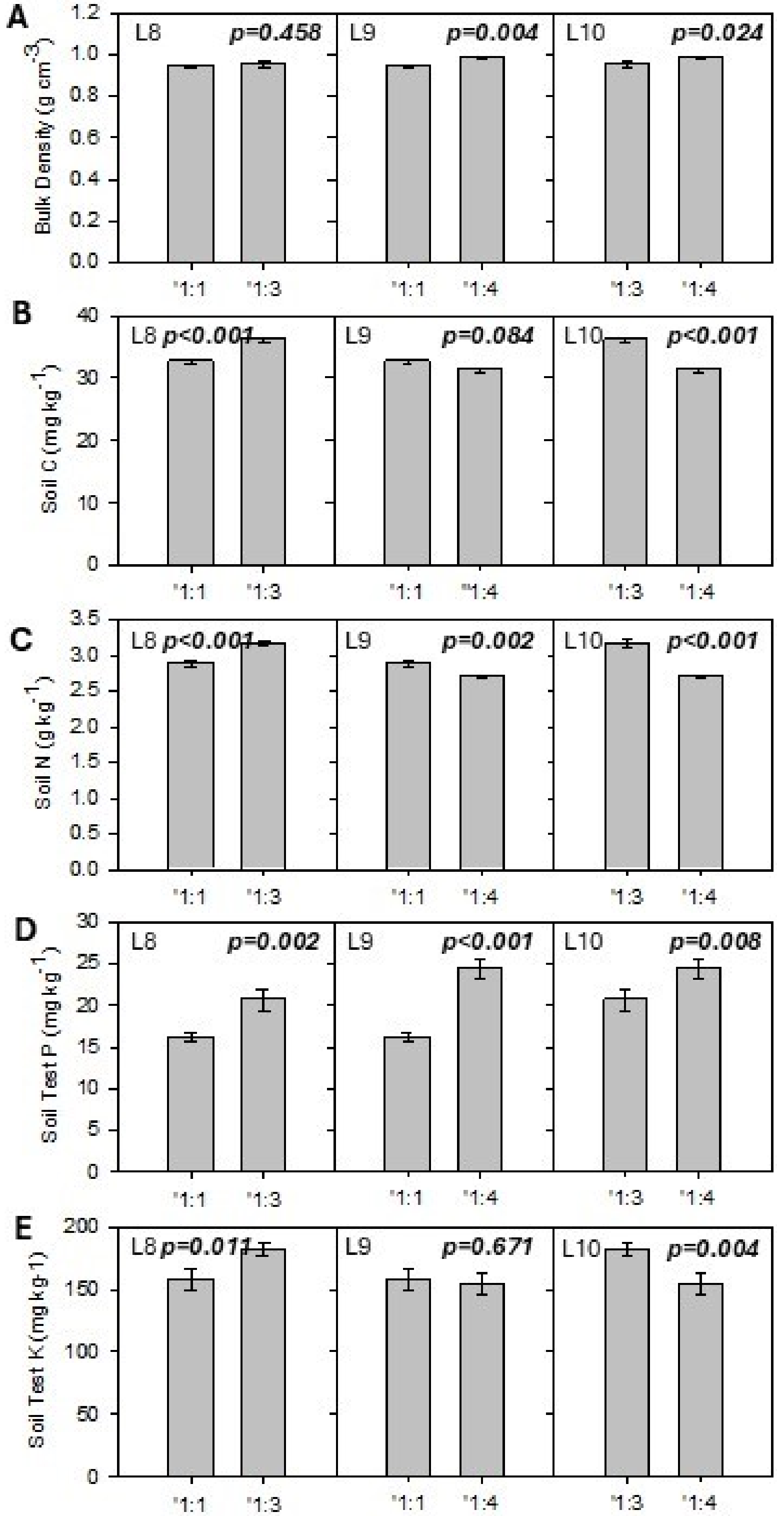

Figure 12. Orthogonal contrasts (means and standard error of the mean) for A) bulk density, B) soil C, C) soil N, D) soil test P, and E) soil test K (PPMS, pulp and papermill biosolids; WA, wood ash; 1:1, WA:PPMS; 1:3, WA:PPMS; 1:4, WA:PPMS).

Discussion

Practicality of Paper Biosolids and Wood Ash Combinations as Soil Amendments in Northwestern Ontario

Data collected from local farms in the Thunder Bay area indicates that the use of paper biosolids and wood ash as a NASM would be possible within the regulations and beneficial for crops and soils. The metal concentrations in these soils would allow for the application of the paper mill residuals. As expected, the soils tested showed some variability in soil characteristics, which is to be expected with a diverse range of soil types in the region caused by historic glacial activity (Figure 16). Soil groups identified in the region include Brunisols, which are moderately to highly acidic with little to no organic-mineral surface layer, organic –rich Mesisol, Luvisol which are typically neutral or alkaline due to the presence of calcium carbonate as well as Podzol which is sandy and acidic. There were exceedances in the nickel concentrations in the majority of soils tested as well as cobalt (Table 13). The source of metal exceedances are taken into consideration when an application for the use of NASM is presented to the government for approval. Both cobalt and nickel have been mined in the area around Thunder Bay so the presence in the soils is not unexpected.

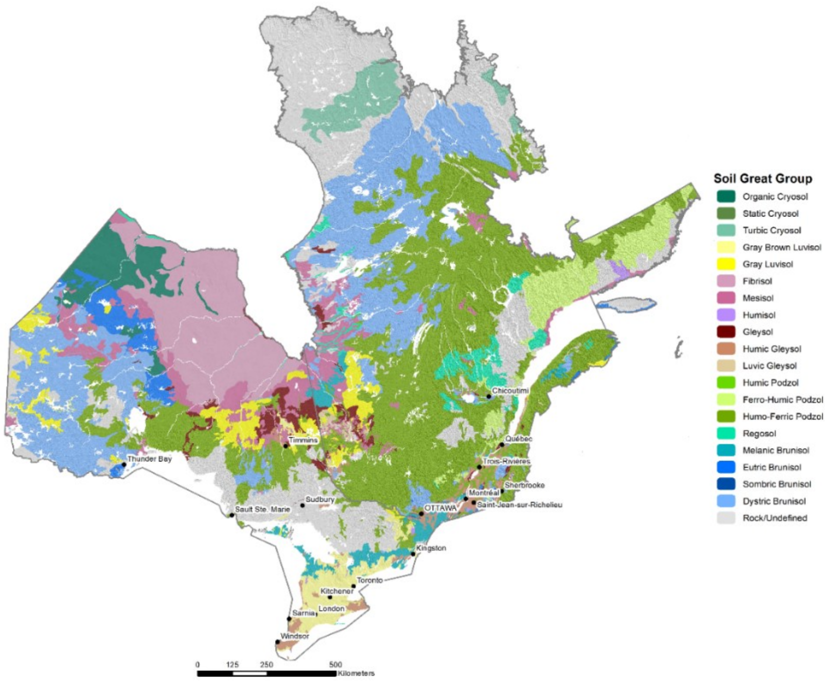

Figure 13. Distribution of Soil Great Groups in Ontario and Quebec. Thunder Bay area showing Dystric Brunisol dominating the west with areas of Gray Luvisol. In the north-east Humo-Ferric Podzol dominates with areas of Mesisol. Eutric Brunisol can be found on the southern end of the region.

Soil fertility data of the local farms indicated that the addition of PPMS and WA of varying combinations have potential to be beneficial (Table 14). As a liming product, wood ash would only be utilized at farms with acidic soils. Of the samples, 70% were below the optimal pH for agricultural soils of 6.0-7.5 (Table 18). The addition of organic material, like PB, before SOM depletion occurs is good practice to maintain healthy soils. As organic matter decomposes, stores of nutrients are slowly released into the surrounding soil. Therefore, adding organic materials to soils creates a time capsule of nutrients that depletes slowly over time. Organic matter is also positively associated with soil stability, water retention, soil texture, and microbial colonies that live within the soil (Michael 2021). The soil data from the farms show that PB/WA combinations have potential benefits that can be utilized locally to improve soil quality.

Table 18. pH of farms in Thunder Bay surrounding area

	pH	# of samples
Optimal pH	Between 6.0 and 7.5	26
Soils requiring pH adjustment	Between 5.7 and 5.9	34
	5.6	13
	5.5 and below	14

Benefits of Land Application of Papermill Residuals to Agricultural Soils

In the greenhouse experiments, temperature and moisture are not considered to be factors limiting decomposition and plant growth, and the observations may be considered potential outcomes of land application of papermill residuals (PMR). Dry matter yields were comparable across the sites and consistent with field studies (Arfaoui et al., 2001; Jefferson & Larson, 2014; Bremer et al., 2023). There was no realized benefit of any amendment to yield in the Murillo soil, which was surprising given that the concentrations of P and K in the soil were very low, but yields were higher with application of mineral fertilizers compared to other treatments. One possibility is that moisture was limiting in the pots for this soil, which inhibited decomposition and the release of nutrients. Though the soil moisture was monitored and adjusted regularly and there was no apparent stress to plant growth, there may have been insufficient moisture within and around the PPMS to optimize decomposition and nutrient release. This could also be because of the soil properties. This soil had more compaction in the experiment that the soils from the other sites. There was no difference among sites for yield when mineral fertilizers were applied, and when they were not, but yields were lower for Murillo when PPMS was applied and the relative N efficiency coefficient was lower, suggesting that PPMS was limiting growth.

The Slate River soil was the only site where supplemental N fertilizer was required because the maximum rate of application was limited by the concentration of P in the soil. Dry matter yield did not differ between the PPMS and mineral fertilizer treatments, and yield in the PPMS treatments did not differ significantly from one another. For the South Gillies soil, all amendments increased yield and there was no difference among those treatments. This is interpreted to indicate that PPMS can meet the crop's nutrient requirements for growth when conditions aren't limiting decomposition and could represent an economic opportunity for growers. Locally, the PMR are provided and transported to area farms free of charge to the grower, though the grower does require a NASM plan and must have access to a manure spreader to land apply the materials. Land applying PMR would decrease the application of mineral fertilizers, which continue to increase in cost.

The South Gillies soil was the only one that required the application of WA to increase pH to an optimal level for plant growth. There were clear benefits to applying the WA and PPMS together on yield and the ratio of the mixture did not make any difference to dry matter yield. There was also no difference in yield when supplemental fertilizers were applied to optimize plant available nutrient concentrations, again suggesting that area growers, and especially those that could benefit from increasing the pH of their soil, could increase their yields by applying PMR. The benefits of applying PMR were further realized in the soil itself, where increases in soil health scores and indicators occurred rapidly.

Soil health scores were classified as medium for the field trial and for the Murillo soil, high in South Gillies and very high in Slate River. These observations are within the range of soil health scores reported by Benalcazar et al., (2022) for soils in the area, acknowledging that they measured a broader suite of indicators. In the greenhouse trial where WA and PPMS were applied alone and in combination, there were significant improvements to soil health. The incorporation of PMR to the soil increased the soil health score into the very high range and the greatest benefits were seen when PPMS and WA were applied together in the ratio of either 1:1 or 1:3 (WA:PPMS). This suggests that, alongside yield, soil function could be rapidly improved through the application of PMR; if weather conditions were optimal and beyond what is achievable with mineral fertilizers alone. These benefits are likely to be most immediate in soils that are acidic and require the application of liming materials to optimize yield.

In their review of the effects of land application of PPMS, Turner et al. (2022) reported increases in CEC, pH, aggregate stability, organic matter/organic carbon, and nutrients, and decreases in bulk density with PPMS application. In the experiments here, there was no effect of PPMS on CEC and limited effects on pH, aggregate stability, organic matter/organic carbon and bulk density. Application of mineral fertilizer lowered pH and WAS in the greenhouse experiments, while PPMS did tend to increase concentrations of SOM, but did not lower bulk density. The application of PMR generally led to increases in soil test P and K, with limited effects on Ca and Mg. Rates of PMR application in this study were considerably lower (9 Mg ha^{-1}), compared to the studies included in the Turner et al. (2022)'s review (20-225 Mg ha^{-1}) and applications of PMR on an annual basis to the soils in our area would likely lead to benefits similar to, or beyond, what is reported here and more in line with Turner et al. (2022). There are five-year maximum rates of application of 10 regulated metals in Ontario, but based on the concentrations of these metals in the PMRs produced locally, metal concentrations would not limit annual application. The unknown is the weather and the availability and timing of soil moisture to promote the decomposition and availability of nutrients required to optimize growth and yield.

There are well established benefits to land applying PMR on crop yield and soil properties in the literature, but the vast majority of these studies have applied PMR at rates that far exceed the maximum annual rate of application in Ontario, which is 20 Mg ha^{-1} wet weight. Concerns persist around the concentrations of heavy metals and other toxins like dioxins and furans. The rates of application in this study were limited by the concentrations of plant available

N and P in the PMR, and the amount of metals applied is actually lower than the standard error of the background concentrations of metals in the soils. Despite the lower application rates of PMR, I still observed benefits, most notably for yield, and these benefits exceeded those observed for mineral fertilizers. Land applying PMR to agricultural soils in the Thunder Bay area could minimize or eliminate the need to mineral fertilizers and conventional liming materials. Diverting these materials from the landfill would have economic benefits to the PMR generator and the growers, and could improve soils, which has environmental benefits to society.

These results confirm that the addition of PPMS as a soil amendment increases crop yield. The Slate River and South Gillies plant yield was higher than the control with the addition of biosolids. This also corroborates previous results from others that support the increase in yield after PPMS additions (N'Dayegamiye, 2006; Gagnon et al., 2003;). Crop yield increases are attributed to the changes to overall soil health resulting from the addition of PPMS.

Conclusion

Pulp and papermill residuals are utilized as agricultural soil additives internationally with positive responses. Previous studies have indicated that the simultaneous addition of PPMS and a liming agent (including wood ash) have a positive impact on soil properties and crop yield. There was a significant increase in yield and of available plant nutrients with the application of pulp and papermill residuals in this study. These findings indicate that papermill residuals can be as effective as commercial fertilizers and may offer advantages for soil health that go beyond the capabilities of conventional fertilizers. From a transportation perspective the low density of wood ash makes shipping the material difficult. To combat this the creation of a combination of mixed pulp and papermill biosolids and wood ash, possibly in the ratio of 1:3 (WA:PPMS) would potentially alleviate this issue. This study demonstrates that the land application of PMR is not only beneficial for soils, it also has the potential to out-perform conventional fertilizers, and at rates much lower than are typically reported in the literature.

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