

Net nitrogen mineralization enhanced with the addition of nitrogen-rich particulate organic matter



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ABSTRACT

Particulate organic matter (POM) is a labile fraction of soil organic matter (SOM) that can contribute to nitrogen (N) mineralization. We added native and non-native POM to soils with contrasting properties and assessed net N mineralization during a 28 days incubation study. Soils (0–15 cm depth) for this study were a clay soil with a 3-year history of corn (*Zea mays* L.), a loam soil with a 2-year history of alfalfa (*Medicago sativa* L.) and sandy-loam and silty-clay-loam soils that were cropped in the previous 5 years with a corn-soybean (*Glycine max* L.) – corn-forage-forage [45% alfalfa + 55% timothy (*Phleum pratense* L.)] and corn-soybean-forage-forage rotation, respectively. The POM was separated by size fractionation (>53 μm) from coarsely sieved (>6 mm) soil. The N concentration in POM followed the order loam > silty-clay-loam > clay > sandy-loam, whereas the acid unhydrolyzable fraction, a proxy for the lignin concentration, was the reverse. Compared to soil only, addition of N-rich POM from the loam soil increased net N mineralization in the clay soil and gave similar net N mineralization in the other soils, while addition of N-poor POM from the sandy-loam soil resulted in lower net N mineralization in the loam and silty-clay-loam soils. Multiple stepwise regression analysis showed that net N mineralized due to POM addition was related to the N concentration in the POM (partial R² = 0.54) and the initial soil mineral N concentration (partial R² = 0.33), suggesting that N mineralized from POM was related more to POM chemical composition than soil properties. We propose that information on POM chemistry in conjunction with soil mineral N concentration and texture could be useful for constructing N mineralization prediction models to improve N fertilizer management in agricultural soils.

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1. Introduction

Particulate organic matter (POM) is widely recognized as a labile fraction of soil organic matter (SOM) that is actively involved in N cycling in agricultural soils (Haynes, 2005; Gosling et al., 2013). The POM fraction is composed of partially decomposed plant residues and may account for as much as 60% (average of 14%) of total soil N (Gregorich et al., 2006). The POM is a site of intense microbial and enzymatic activity because it serves as a readily decomposable substrate for soil microorganisms (Magid and Kjærgaard, 2001). Some studies indicate that the contribution of POM to total soil N mineralization is proportional to the POM content of SOM (Yakovchenko et al., 1998; Whalen et al., 2000). Other studies indicate that POM may cause N immobilization because it is physically stabilized within aggregates

(Cambardella and Elliott, 1994), or because it has a wider C/N ratio than soil (Gregorich et al., 2006). Parfitt and Salt (2001) reported that net N mineralization from POM differed with land management, with greater N mineralization under corn (*Zea mays* L.) than pasture that was attributed to the greater C/N ratio of POM under pasture than corn. Research on POM chemistry is needed to understand its relative contribution to N mineralization, which may enhance our knowledge of soil N cycling.

Cropping practices influence both the quality and the quantity of unharvested residues that are returned to agricultural soils. Thus they directly impact POM characteristics, such as its biodegradability and the proportion of total soil N present in the POM fraction (Cambardella and Elliott, 1992; Haynes, 2005). For example, Spargo et al. (2011) explained that the greater N concentration in the POM and the lower POM C/N ratio in soil under crop rotations with a greater frequency of legumes [alfalfa (*Medicago sativa* L.)] than grains (corn) was due in part to the greater quantities of N-rich residues returned to the soil from legumes. Crop residues with high N concentrations, low C/N ratios and low lignin concentrations such as those derived from legumes tend to decompose faster (Chivenge et al., 2011; Yanni et al., 2011), such that legume residues enter the POM pool and are then

Abbreviations: C–S–C–F–F, corn–soybean–corn–forage–forage rotation; C–S–F–F–F, corn–soybean–forage–forage–forage rotation; MIR, mid infrared reflectance spectroscopy; NIR, near infrared reflectance spectroscopy; POM, particulate organic matter; SOM, soil organic matter.

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transformed to soluble substrates, including mineral N, more quickly than non-legume residues, regardless of soil texture. In soils incubated with ^{15}N labelled faba bean (*Vicia faba* L.) and wheat (*Triticum aestivum* L.) residues, St. Luce et al. (2014a) found a greater ^{15}N concentration in POM in faba bean-amended soils than wheat-amended soils.

The breakdown of crop residues, leading to the formation of POM and its subsequent transformation into soluble organic matter, is mediated by soil microorganisms (Cotrufo et al., 2013). Hence, the extent to which POM contributes to N mineralization may depend on soil properties such as texture, mineral N concentration, pH and the quantity and quality of the POM due to their influence on microbial accessibility, microbial community structure and decomposition rates (Marschner et al., 1999, 2001; Murphy et al., 2011; Shen et al., 2013). Soils with high clay contents protect crop residues and POM from decomposition (Six et al., 2002; Cotrufo et al., 2013). Nitrogen transformation rates of added organic N sources are generally faster in coarse- than fine-textured soils (St. Luce et al., 2014a), because of the lower degree of SOM physical stabilization in coarse- than fine-textured soils (Six et al., 2002; Cotrufo et al., 2013), rather than the fact that POM accounts for a larger proportion of total soil N in coarse- than fine-textured soils (Gregorich et al., 2006).

There is scant information on how POM derived from agricultural soils with different cropping history and texture affects N mineralization. Previous studies focused on either one site with uniform soil texture and agricultural management (Yakovchenko et al., 1998), on the impact of disturbance in agricultural and forest soils (Whalen et al., 2000), or on forest soils only (Boone, 1994). This study sought to examine the contribution of POM to N mineralization, as a function of POM chemical characteristics, using POM that came from four agricultural fields with different cropping systems and soil textures. To our knowledge, this is the first study in which native and non-native POM were added to soils to examine the effect of POM on net N mineralization. Our hypotheses were that (i) net N mineralization from added POM would be greater for POMs with higher N and lower lignin concentrations, regardless of soil texture and (ii) the contribution of POM to net N mineralization would be more strongly related to POM chemistry, such as N and lignin concentration, than soil properties.

2. Materials and methods

2.1. Soils

Composite soil samples, hereafter referred to as soil, were collected from the upper layers (0–15 cm) from four fields in spring 2011. Two fields were located at Agriculture and Agri-Food Canada's Harlaka Research Farm (46° 47'N, 71°08'W) and the other two fields were located at a farm in St-Nicolas (46° 41'N, 71°28'W), both near Quebec City, Canada. At the Harlaka site, a Kamouraska clay (fine, mixed, frigid, Typic Humaquept) soil was collected from a field that was under corn since 2008, while a St-André loam (loamy, mixed, frigid, Dystrochrept) was collected from a field under alfalfa since 2009. At the St-Nicolas site,

a St-Antoine sandy-loam (loamy, mixed, frigid, Dystrochrept) was collected from a field where the preceding crops were corn in 2006 and 2008, soybean (*Glycine max* L.) in 2007 and pasture [45% alfalfa/55% timothy (*Phleum pratense* L.)] in 2009 and 2010. The other soil from St-Nicolas, a Tilly silty-clay-loam (fine, mixed, frigid, Typic Dystrochrept), was collected from a field where the preceding crops were corn in 2006, soybean in 2007 and pasture (45% alfalfa/55% timothy) in 2008, 2009 and 2010. Field moist soil samples were frozen ($-20\text{ }^{\circ}\text{C}$) for about 1 year. At the beginning of the experiment, the soil samples were thawed and large plant materials were removed manually before passing through a 6-mm sieve. The soils were air-dried and a subsample was ground to pass through a 2-mm sieve. Soil chemical and physical properties at each site are given in Table 1.

2.2. POM fractionation

The POM was separated by size fractionation following the procedure of Gregorich and Beare (2008). Briefly, 100 g of coarsely sieved ($>6\text{ mm}$) air-dried soil was dispersed by shaking in 400 mL of deionized water with 40 glass beads (6 mm) for 16 h. The dispersed soil was passed through a 53 μm sieve. The retained sand and macroorganic matter were dried at 50 $^{\circ}\text{C}$ and weighed. This procedure was repeated with additional soil until sufficient POM was obtained. The POM and a sub-sample of the air-dried soil were ground using a mortar and pestle to pass through a 250 μm sieve.

2.3. POM and soil characteristics

To characterize the POM and soil, all analyses were done in triplicate. Total N and organic C concentrations of the POM and soil samples were determined by dry combustion using an Elementar CN Analyzer (Elementar Analysensysteme GmbH, Hanua, Germany). Total C was considered to represent organic C since no carbonates were detected upon treatment with 6% (w/v) H_2SO_3 solution. The N concentration of the POM was expressed as $\text{mg N g}^{-1}\text{ POM}$. The POM C/N ratio was also used as a quality indicator. The acid unhydrolyzable fraction, a proxy for lignin concentration of the POM ($\text{mg g}^{-1}\text{ POM}$), was determined using the acid detergent fiber method (Goering and Van Soest, 1970). Hereafter, lignin and not acid unhydrolyzable fraction is used.

Near infrared reflectance spectroscopy (NIR) was also used to indirectly assess the chemical composition of the POM samples. The NIR spectral region is typically weak and is characterized by overtones and/or combinations of fundamental vibrations which occur in the mid infrared (MIR) region. Nevertheless, the NIR region contains useful information on organic constituents in soils (Stenberg et al., 2010). Certain wavelengths in the NIR region were shown to correlate with some biochemical components of SOM, including carbohydrates and protein, mostly due to their corresponding assignments on the MIR wavebands (Stenberg et al., 2010; Cécillon et al., 2012; Forouzangohar et al., 2013). In addition, NIR was also used to identify and discriminate between soils and SOM (Ben-Dor et al., 1997; Ertlen et al., 2010; Hedde

Table 1
Soil characteristics at the four agricultural fields used in the experiment.

Soil texture	Crop	pH ^a	Sand ^b	Silt ^b	Clay ^b	Mineral N ^c	Total N ^d	Organic C ^d	C/N
			g kg ⁻¹ soil			mg kg ⁻¹ soil		g kg ⁻¹ soil	
Clay	Corn	5.52	302	292	406	11.6	3.2	35	11
Loam	Alfalfa	5.41	435	363	202	24.0	3.5	37	11
Sandy-loam	C-S-C-F-F ^e	6.23	683	164	152	20.6	2.3	25	11
Silty-clay-loam	C-S-F-F-F ^f	5.77	187	428	385	20.5	2.9	28	10

^a pH in water (1:2 soil:water slurry) (Hendershot et al., 2008).

^b particle size by hydrometer method (Kroetsch and Wang, 2008).

^c Initial soil mineral N concentration ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) in 2 M KCl (Maynard et al., 2008).

^d Total N and organic C determined by dry combustion.

^e C-S-C-P-P, corn-soybean-corn-forage-forage rotation.

^f C-S-F-F-F, corn-soybean-forage-forage-forage rotation.

et al., 2013; Huerta et al., 2013; St. Luce et al., 2014b). Absorbance [$\log(1/R)$, where R is the reflectance] of the POM samples from the four fields [2–3 g and finely ground (<0.25 mm)], was recorded between 1100 and 2500 nm at 2-nm intervals using the spinning (ring) cup with an adapter on a FOSS NIRSD2500 Instrument (Foss NIRSystem, Silver Spring, MD). Three sub-samples of each POM were scanned. Thirty-two scans were recorded per sub-sample. The acquired spectra were processed with WinISI IV software (ver. 4.6.8, Infrasoft International, LLC, State College, PA, USA). The 2nd derivative of the NIR spectra, with a four point gap and four point smoothing, was used to accentuate the signals (Shenk et al., 2007; Stenberg et al., 2010). Standard normal variate and detrending was also applied to reduce the scatter, and to also remove the linear or curvilinear trend of each spectrum and particle size effect, and to enhance spectral features (Barnes et al., 1989).

2.4. Incubation

Net N mineralization was determined using 50 g air-dried (oven-dry basis; <2 mm sieved) soil and 50 g air-dried soil thoroughly mixed with 5 g POM, packed to a bulk density of 1.1 g cm^{-3} in a 250-mL glass jar and moistened to 60% water-filled pore space (WFPS) with deionized water. The WFPS was calculated based on soil gravimetric water content, soil bulk density and particle density (Franzluebbers, 1999) and 60% WFPS was chosen as it is regarded as the optimum soil moisture content for microbial processes (Linn and Doran, 1984). Four replicates of each treatment were prepared. The jars were covered with parafilm punched with pin holes to maintain aerobic conditions and incubated in the dark at 25 °C for 28 days. Moisture content was adjusted every 2–3 days by weighing and adding deionized water as needed. After 28 days, the jars were removed from the experiment and thoroughly mixed before sampling.

The amount of POM added was chosen to provide sufficient N so that N mineralized from the POM could be detected. In addition to mixing the POM with the soil from which it was extracted (native POM, soil + POM), POM extracted from the loam (soil + POM_A, alfalfa) and from the sandy-loam soil [soil + POM_B, corn-soybean-corn-forage-forage (C-S-C-F-F)], respectively, were also added to the other soils. This resulted in four treatments for the clay and silty-clay-loam, respectively, and three treatments for the loam and sandy-loam, respectively. The POM from the loam and sandy-loam were selected for two reasons: (1) N content of the POM from the loam soil was four times greater than that from the sandy-loam soil and (2) more POM was extracted from these soils than the other two soils.

2.5. Analysis of incubated and non-incubated soils

After 28 days, gravimetric soil moisture contents of the soil and the soil + POM mixtures were determined by oven drying a 5 g sub-sample at 105 °C for 24 h. Mineral N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) was immediately extracted with 2 M KCl using 5 g of moist soil (1:10 soil:solution ratio) followed by filtration through Whatman #42 filter paper (Maynard et al., 2008). Mineral N forms were determined on an automated colorimeter (QuickChem 8000 Lachat autoanalyzer, Lachat Instruments, Loveland, CO); $\text{NO}_3\text{-N}$ was determined by cadmium reduction and $\text{NH}_4\text{-N}$ was determined using salicylate-nitroprusside reaction. Net N mineralization or immobilization (mg N kg^{-1} soil) was determined as the difference in mineral N before and after the 28 days incubation.

2.6. Statistical analyses

All statistical analyses were performed using SAS statistical software (SAS Institute, 2010). The net N mineralization data was checked for normality with the Shapiro-Wilk test and log transformed when necessary. Analysis of variance (ANOVA) was performed using the MIXED procedure to test the effect of POM source on net N mineralization,

separately for each soil texture (clay, loam, sandy-loam, silty-clay-loam). When the effect of POM source was significant ($P < 0.05$), means were compared with a post-hoc least square means test at 95% confidence interval. ANOVA was also used to assess the differences in net N mineralization among soils, incubated in the absence of POM. The functional relationships between soil properties, POM chemical characteristics and net N mineralization were determined using Pearson correlation analysis with all data ($n = 56$). Simple linear regression was used to relate net N mineralized, as a result of POM addition, to the total amount of N added from the POM (based on initial N concentration of the POM). The relative importance of soil properties and POM chemical characteristics in influencing net N mineralized from POM was evaluated using stepwise multiple regression analysis. Net N mineralized from added POM was the difference between mean net N mineralized in soil and soil + POM mixtures ($n = 10$). The significance level to enter the model was 0.50, and the significance level to stay in the model was 0.05. Collinearity between independent parameters was evaluated using the condition index (COLLIN) (SAS Institute, 2010). Statistical analysis including calibration was not performed on the NIR spectra since the purpose for using the NIR was to have a semi-quantitative assessment of the chemical composition of the POM samples.

3. Results

3.1. POM characteristics

The N concentration of the POM used in the study ranged from 0.60 to 2.6 mg N g^{-1} POM (Table 2). The POM from the loam soil under alfalfa tended to have greater N concentration than the POM from the sandy-loam soil with a corn-soybean-corn-forage-forage rotation (C-S-C-F-F) and the POM from the clay soil under corn. The POM fraction contained as much as 28% of total soil N in the loam soil under alfalfa but only 9 and 11% for the clay soil under corn and the silty-clay-loam with the corn-soybean-forage-forage-forage rotation (C-S-F-F-F), respectively. The POM C/N ratios varied from 12.4 to 14.9. Lignin concentrations ranged from 562 to 755 mg g^{-1} POM and tended to be greater for the POM from the sandy-loam soil with a C-S-C-F-F rotation followed by the clay soil under corn, and lowest for the loam soil under alfalfa.

The original NIR spectra for the four POMs revealed differences between the POM from the clay soil under corn and the silty-clay-loam soil with the C-S-F-F-F rotation (Fig. 1a). Although it is not possible to assign specific wavelengths to particular chemical compounds or functional groups using original NIR spectra, the 2nd derivative of the NIR spectra (Fig. 1b) can be compared to infrared wavebands reported in the literature. Unlike MIR wavebands, the NIR wavebands are not specific to any compound or chemical structure but may be derived from corresponding MIR wavebands. The intense peaks at around 1400 and 1900 nm (O-H 1st overtone-water) are mostly related to free water in the POMs. The small peak at 1364 nm [stretching and bending of C-H bonds (cellulose)] was slightly higher for the POM from the sandy-loam soil with the C-S-C-F-F rotation, followed by

Table 2
Particulate organic matter (POM) characteristics at the four agricultural fields.

Soil texture	Crop	Total N	Lignin	C/N	Proportion of soil total N ^c %
		mg g^{-1} POM			
Clay	Corn	1.1	642	14.9	9
Loam	Alfalfa	2.6	562	13.7	28
Sandy-loam	C-S-C-F-F ^a	0.6	755	12.4	17
Silty-clay-loam	C-S-F-F-F ^b	1.9	607	14.5	11

^a C-S-C-F-F, corn-soybean-corn-forage-forage rotation.

^b C-S-F-F-F, corn-soybean-forage-forage-forage rotation.

^c Calculated on a mass basis.

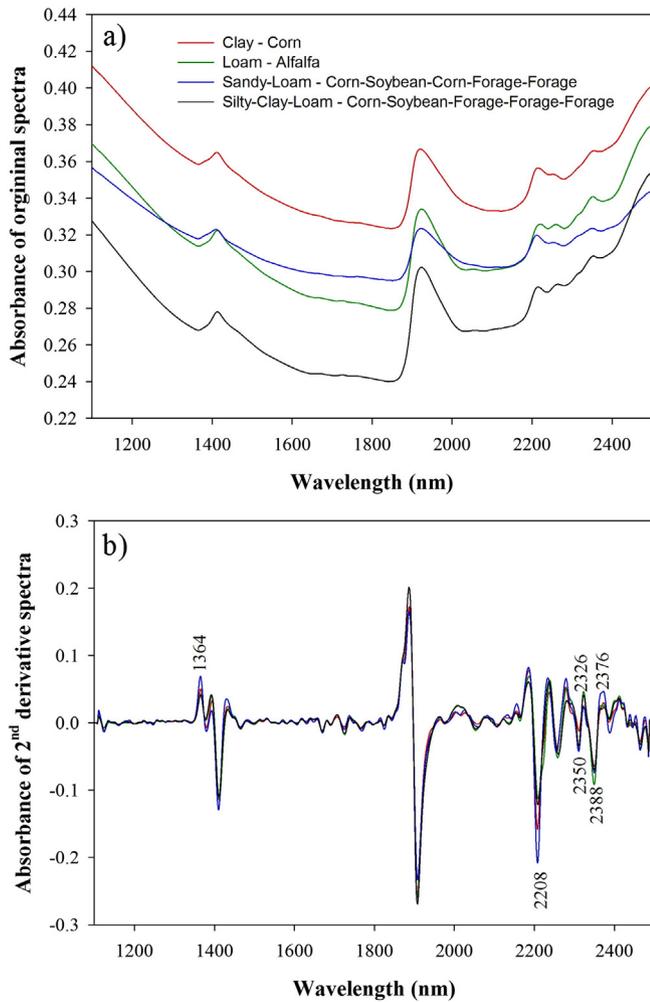


Fig. 1. Mean original near infrared reflectance spectroscopy (NIR) spectra of particulate organic matter (POM) extracted from four fields (a) and their 2nd derivatives (b). The 2nd derivative was calculated after scatter correction and detrending with a gap of four data points and smoothing of four.

the clay soil under corn. The strong peak around 2208 nm (C–H stretch/C=O combination in cellulose) and a weaker peaks at 2376 and 2388 nm (C–H stretch/C–C) were also more intense for the POM from the sandy-loam soil with the C–S–C–F–F rotation, followed by the clay soil under corn. The peak at 2326 nm may be related to starch (C–H stretch/CH₂ deform) and was more intense for the POMs derived from the loam soil under alfalfa and the silty-clay-loam soil with the C–S–F–F–F rotation. The peak at 2350 nm (CH₂ bend 2nd overtone in cellulose and protein) was slightly greater in the POM from the loam soil under alfalfa compared to the other POMs. The small peaks from 2450 to 2480 nm (combination bands including C–H stretch/C–C bond in cellulose) were somewhat more intense for the POM from the sandy-loam soil with the C–S–C–F–F rotation and the clay soil under corn. In summary, the NIR data suggest greater concentration of carbohydrates (cellulose) in the POMs from the sandy-loam soil with the C–S–C–F–F rotation and the clay soil under corn than the loam soil under alfalfa and the silty-clay-loam soil with the C–S–F–F–F rotation.

3.2. Net N mineralization

Net N mineralized after 28 days in soil varied ($P < 0.0001$) among the soils and followed the order of loam soil under alfalfa > silty-clay-loam soil with the C–S–F–F–F rotation > sandy-loam soil with the C–S–C–F–F rotation > clay soil under corn (Fig. 2). Net N mineralization in each soil was further influenced by the source of POM added

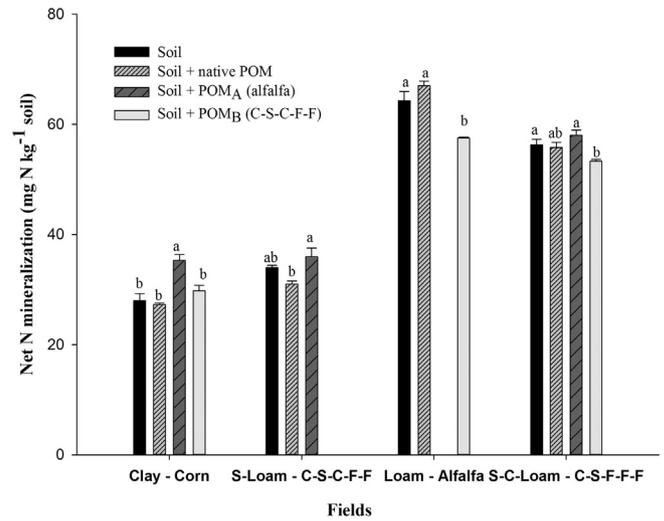


Fig. 2. Net N mineralization in soil and soil + particulate organic matter (POM) mixtures after 28 days. Bars with a different lower case letter for each field are significantly different ($P < 0.05$). Error bars represent standard error ($n = 4$). S–L–C–S–C–F–F, sandy-loam-corn-soybean-corn-forage-rotation; S–C–L, silty-clay-loam-corn-soybean-forage-rotation. The forage was 45% alfalfa and 55% timothy.

($P < 0.001$ for the clay; $P < 0.001$ for the loam; $P = 0.037$ for the sandy-loam; $P = 0.014$ for the silty-clay-loam). Although not significant ($P > 0.05$), net N mineralized in soil + native POM mixtures was about 4% and 9% lower than in the soil of the clay under corn and the sand-loam with the C–S–C–F–F rotation, respectively. For the loam soil under alfalfa and the silty-clay-loam soil with the C–S–F–F–F rotation, net N mineralized in soil + native POM mixtures was either numerically equal to or about 5% greater ($P > 0.05$) than their corresponding soil (Fig. 2).

Addition of non-native POM derived from the loam soil under alfalfa (POM_A) resulted in 25% ($P < 0.001$) greater net N mineralization than in the clay under corn soil. Although not significant ($P > 0.05$), addition of POM_A also resulted in 6% and 4% greater net N mineralization than the sandy-loam and silty-clay-loam soils, respectively. Conversely, addition of non-native POM derived from the sandy-loam soil with the C–S–C–F–F rotation (POM_B) reduced net N mineralization with 9% ($P = 0.001$) and 5% ($P < 0.05$) than in the loam and silty-clay-loam soils, respectively. Net N mineralized in the clay soil + POM_B mixture did not differ from the clay only soil (Fig. 2). In cases where both POM_A and POM_B were added to soils, net N mineralization was always greater ($P < 0.001$) for the POM_A mixture than the POM_B mixture.

Table 3

Correlation coefficients (r) between soil and particulate organic matter (POM) characteristics and net N mineralized in soil and soil + POM mixtures ($n = 56$).

Parameter	Net N mineralization
N concentration of POM (mg N g ⁻¹ POM)	0.45***
POM lignin concentration (mg g ⁻¹ POM)	-0.34*
POM C/N ratio	0.01 ns
Initial soil mineral N concentration (mg N kg ⁻¹ soil)	0.77***
Soil total N (g kg ⁻¹ soil)	0.41**
Soil organic C (g kg ⁻¹ soil)	0.16 ns
Soil C/N ratio	-0.65***
Soil pH	-0.33*
Sand content (g kg ⁻¹ soil)	-0.30*
Silt content (g kg ⁻¹ soil)	0.73***
Clay content (g kg ⁻¹ soil)	-0.14 ns ^a

* Significant at $P < 0.05$.

** Significant at $P < 0.01$.

*** Significant at $P < 0.001$.

^a ns, not significant ($P > 0.05$).

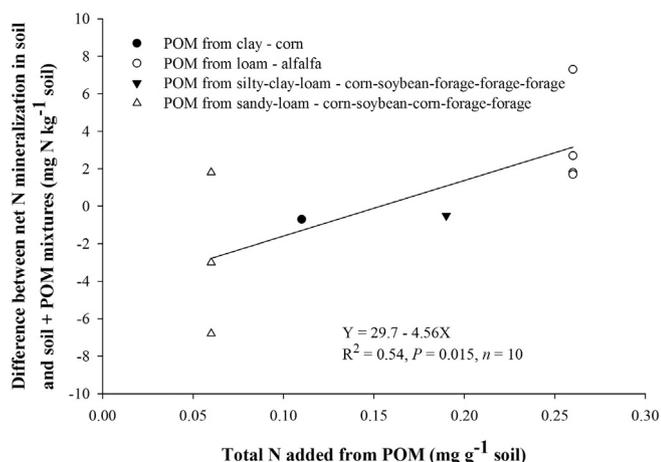


Fig. 3. Relationship between the mean difference in net N mineralized between soil and soil + particulate organic matter (POM) mixtures and total N added from POM.

Net N mineralization in soil and soil + POM mixtures was most strongly correlated to the initial soil mineral N concentration ($r = 0.77$, $P < 0.001$), the soil silt content ($r = 0.73$, $P < 0.001$), the N concentration in POM ($r = 0.45$, $P < 0.001$) and total soil N ($r = 0.41$, $P < 0.01$) (Table 3). Net N mineralization was negatively correlated with soil C/N ratio ($r = -0.65$, $P < 0.001$), POM lignin content ($r = -0.34$, $P < 0.01$), soil pH ($r = -0.33$, $P < 0.05$) and sand content ($r = -0.30$, $P < 0.05$) (Table 3). Total N added from the POM, which is a reflection of the N concentration of the POM, explained 54% ($P = 0.015$) of the difference between net N mineralized in soil and soil + POM mixtures (Fig. 3). To determine if the contribution of POM to net N mineralization (considered to be the difference between net N mineralization in soil + POM and soil alone) was better related to POM characteristics or to soil properties, stepwise multiple regression was performed with all the parameters in Table 3. As also noted in Fig. 3, the N concentration in the POM explained 54% of the variation in the model, with initial soil mineral N concentration increasing the variance explained to 87% (Table 4). The only other significant parameter was the POM lignin concentration, which improved the explained variation to 94% (data not shown), but it was excluded from the final model due to collinearity between POM lignin concentration and N concentration of POM.

4. Discussion

4.1. POM characteristics among fields

Our study used POM with a range of chemical characteristics, specifically N and lignin concentrations. Since POM is a by-product of plant residue decomposition, the chemical characteristics of the POMs were probably influenced most by the chemistry of the plant residue input to each field over time (cropping history), although other factors such as soil type, decomposer communities and land management practices cannot be ruled out. Using solid state ^{13}C nuclear magnetic resonance spectroscopy, Clemente et al. (2013) showed that changes in SOM

Table 4

Stepwise multiple regression equations relating particulate organic matter (POM) and soil characteristics to net N mineralized from added POM, calculated as the mean difference between net N mineralized in soil and soil + POM mixtures.

Parameter	Parameter estimate	Partial R^2	Model adjusted R^2
Intercept	3.35		0.87***
N concentration of POM	3.18	0.54***	
Initial soil mineral N concentration	-0.44	0.33**	

** Significant at $P < 0.01$.

*** Significant at $P < 0.001$.

composition were related to the chemical composition of the plant tissue from which it was derived. The greater N and lower lignin concentrations in the POMs extracted from the loam soil under alfalfa and the silty-clay-loam soil with the C-S-F-F rotations could be related to the continuous and/or greater frequency of legumes in crop rotations (Marriott and Wander, 2006b; Hernandez-Ramirez et al., 2009; Spargo et al., 2011). The NIR peaks in the POM around 2200 and 2380 nm, and the NIR spectra from 2400 to 2500 nm are indicative of organic carbon, particularly carbohydrates (Ono et al., 2007; Shenk et al., 2007; Forouzangohar et al., 2013), and were slightly more intense for the POMs from the sandy-loam and clay soils. Absorbance at 2350 nm was previously shown to be associated with N compounds, such as protein and amino sugar (Ono et al., 2007; Shenk et al., 2007), and was slightly greater in the N-rich POM from the loam soil under alfalfa (2.6 mg N g^{-1} POM) compared to other POMs (0.6 to 1.9 mg N g^{-1} POM). We also infer that the POM from the loam soil under alfalfa was less depleted than the other POMs because it represented a larger proportion (28%) of the total soil N and thus contained a greater reservoir of organic N that could be susceptible to decomposition and N mineralization. It is likely that the continuous alfalfa production in the loam soil under alfalfa increased soil aggregation, thus providing some level of protection to this POM from depletion (Marriott and Wander, 2006a). Together, these findings suggest that the chemical composition of our POMs was most likely related to cropping history.

4.2. POM effect on net N mineralization

Our first hypothesis was that net N mineralization from added POM would be greater for POMs with higher N and lower lignin concentrations, regardless of soil texture. Our results were consistent with this hypothesis in that net N mineralization was positively related to the N concentration in POM and negatively related to POM lignin concentration. Greater net N mineralization from the N-rich POMs derived from the loam soil under alfalfa and the silty-clay loam soil with the C-S-F-F rotation can be attributed to the higher N and lower lignin concentrations in these POMs compared to the POMs from soils under corn and the C-S-C-F-F rotation. These findings are consistent with other reports that greater N concentration in SOM or added residues increases net N mineralization (Prescott, 2010; Chivenge et al., 2011; Yanni et al., 2011; St. Luce et al., 2014a) and that net N mineralization is negatively correlated to lignin concentration of organic substrates (Johnson et al., 2007; Yanni et al., 2011; Cotrufo et al., 2013). However, our findings are the first to support this hypothesis using native and non-native POMs as substrates or added residues, which were extracted from agricultural soils with different cropping histories.

Higher POM lignin concentration in POMs from the sandy-loam soil with the C-S-C-F-F rotation and the clay soil under corn may be a reflection of the high ligno-cellulosic concentrations of the crop residues returned to these soils. Lignin degrades slowly in soils due to its biochemical recalcitrance (Johnson et al., 2007; Clemente et al., 2013) and also shields interior N-rich materials (e.g., proteins, enzymes) from microbial access, thereby slowing down decomposition and N mineralization. In these POMs, the lignin will dominate after the small quantities of easily decomposable compounds are mineralized. Hence, the ability of soil microorganisms to adequately utilize N in added POM with elevated lignin concentrations is greatly reduced, and results in lower net N mineralization or N immobilization, as observed for the POM derived from the sandy-loam soil with the C-S-C-F-F rotation. Peaks on the NIR spectra that may be related to cellulose (C-H stretch/C=O and C-H stretch/C-C combinations bonds) were slightly more intense for the POMs from the sandy-loam soil with the C-S-C-F-F rotation and the clay soil under corn compared to the POMs from the other two soils. In contrast, peaks on the NIR spectra that may be related to starch (C-H stretch/CH₂ deform) were slightly more intense for the POMs from the loam soil under alfalfa and the silty-clay-loam soil with the C-S-F-F rotation. Since starch is more easily degraded

than structural carbohydrates like cellulose (Warren, 1996), this implies that POMs with greater starch content are susceptible to decomposition and N mineralization, which is consistent with our findings.

The strong correlation between net N mineralization in soil and soil + POM mixtures and soil silt content (Table 3) may be due to the fact that the soils with the greatest silt contents also had the greatest N concentration in POM. These soils were either cropped to legumes or had a longer frequency of legumes in rotation. In agreement with our findings, other studies also reported strong positive relationships between net N mineralization and initial soil mineral N concentration (Recous et al., 1995; St. Luce et al., 2014a), as well as negative relationships between net N mineralization and soil C/N ratio (Springob and Kirchmann, 2003). Increasing soil acidity was also shown to retard N mineralization in soils due to lower microbial activity (Kemmitt et al., 2006).

4.3. POM contribution to net N mineralization

The major assumption we made is that enhanced net N mineralization in soil + POM mixtures was due to N released from the added POM, and this permitted us to assess the contribution of POM to net N mineralization. The N mineralized from POM ranged from –11 to 3%, lower than the –0.1 to 6% observed in other studies (Yakovchenko et al., 1998; Whalen et al., 2000). In addition to the longer duration of the study by Yakovchenko et al. (1998), variations in POM chemical characteristics as influenced by vegetation cover or cropping history, and to a lesser extent soil types, may account for this difference. We cannot neglect to mention that net N mineralized in soil + POM mixtures may have been due to positive or negative priming of native SOM decomposition following the addition of POM (Kuzayakov et al., 2000; Blagodatskaya and Kuzayakov, 2008). If this were the case, addition of N-rich POM derived from the loam soil under alfalfa to all soils had a positive priming effect leading to net N mineralization, while addition of N-poor POM derived from the sandy-loam soil with the C–S–C–F rotation to all soils generally had a negative priming effect (N immobilization). Future studies with ¹⁵N-labelled POM are required to distinguish the source of mineral N, whether produced from the mineralization of organic N contained in SOM or POM.

Our second hypothesis was that the contribution of POM to net N mineralization would be more strongly related to POM chemistry than soil properties. Stepwise multiple regression showed that the contribution of POM to net N mineralization in our study was more strongly related to the N concentration of POM than any soil property. Our results are in agreement with other studies that emphasized the greater importance of SOM quality versus soil properties in controlling decomposition and N mineralization (Gregorich et al., 2006; Zhang et al., 2008; Prescott, 2010; St. Luce et al., 2014a). In tree plantation (*Eucalyptus globulus*) and pasture soils, Mendham et al. (2004) measured greater net N mineralization from pasture-derived POM than plantation-derived POM due to greater decomposition of the pasture-derived POM that had less lignin and tannin materials, despite the greater total soil N in the plantation. We found soil properties were less important in predicting N mineralization from POM, as initial soil mineral N concentration was the only other parameter included in the final regression model. The negative correlation between net N mineralization from POM and initial soil mineral N concentration meant that a slower rate of POM mineralization is expected when the low soil mineral N concentration limits microbial activity (Recous et al., 1995). Other soil properties (e.g. silt content, soil C/N ratio, soil total N, soil pH and sand content) that were significantly correlated with net N mineralization in soil and soil + POM mixtures in the simple correlation analysis were eliminated in the multiple regression analysis because they were not significant. It is important to note that stepwise regression was done on net N mineralized due to POM addition, that is, the difference between net N mineralized in soil and soil + POM mixtures, and not on net N mineralized in soil and soil + POM mixtures.

The fact that POM contributes to net N mineralization, which can be predicted from two variables (namely the N concentration in POM and initial soil mineral N concentration), implies that it could be relatively simple to incorporate POM-N turnover into models of soil N mineralization to improve N fertilizer management in agricultural soils. Potential N availability in agricultural soils is generally estimated based on total SOM (Stanford and Smith, 1972; St. Luce et al., 2011). However, N mineralized in the short term is predominantly derived from the labile organic N pool in agricultural soils, of which POM may be the most important fraction (St. Luce et al., 2014a). Hence, assessment of potential quantity of N that may be mineralized from POM may be more accurate and therefore may help to improve the efficiency of N fertilizer recommendations. To be clear, the POM pool in our study represents the unprotected SOM pool, which has a more rapid turnover time than occluded or protected SOM (Six et al., 2002). Still, this work needs to be repeated across a wider diversity of soil types and cropping systems, and those studies should consider the method of removal or addition of POM to soils (Gregorich et al., 2006), which can affect the experimental results. The extent to which POM contributes to N mineralization may also depend on the time of year the soil was sampled for POM extraction (Boone, 1994; Yakovchenko et al., 1998) since there is a seasonality to plant residue inputs that undergo decomposition to yield POM. Further investigation of POM chemistry as related to decomposition and N mineralization is also recommended, together with isotopic tracer studies to quantify the contribution of POM to N mineralization and to gain a more comprehensive understanding of N transformation from POM.

It is likely that some of the N was lost during the incubation through gaseous N emissions. However, quantification of gaseous N losses was not the focus of our study and was therefore not addressed. The soils used in our study were stored at –20 °C for about 1 year before the start of the incubation. Freezing and thawing soils before incubation was shown to stimulate microbial activity and cause a flush in N mineralization, similar to what occurs after drying-wetting cycles (DeLuca et al., 1992; Stenberg et al., 1998; Urakawa et al., 2014). This temporal increase in N mineralization is due in part to re-mineralization of lysed microorganisms upon thawing and may last for about 1 week (DeLuca et al., 1992). Hence, it is possible that there was a flush of mineralized N in the first few days after the incubation was initiated, probably more so for soils with greater soil microbial populations and SOM. Since all soils were handled and stored in the same way, and the field sampling was completed in the same period of the year (spring 2011), any artifacts induced by this procedure were consistent across soils and do not affect the comparisons that can be made. It is also unlikely that our storage process affected the microbial community in our soils because they were obtained from a region where multiple freezing-thawing occurs in the winter and spring periods. Stenberg et al. (1998) indicated that soil microorganisms that are subjected annually to severe freeze-thaw cycles are more resistant to freezing than microorganisms in soils where freeze-thaw cycles occur infrequently. Since the effects of soil storage on microbial biomass and activity were more pronounced in refrigerated than frozen soils in their study, Stenberg et al. (1998) recommended that soils should be stored preferably at –20 °C than at 2 °C.

5. Conclusions

Addition of native and non-native POM to agricultural soils indicate that the contribution of POM to net N mineralization is influenced more by POM N and lignin concentrations than soil properties. Initial soil mineral N concentration is the most important soil property that may affect POM turnover in agricultural soils. Therefore, we suggest that information on POM chemistry, specifically its N concentration, in conjunction with selected soil properties (at least the initial soil mineral N concentration) could be useful for constructing N mineralization prediction models to improve N fertilizer management in agricultural soils. Future

studies should make use of more powerful tools such as ^{15}N stable isotope tracers, nuclear magnetic resonance spectroscopy and mid infrared reflectance spectroscopy to better understand POM chemistry and its turnover as mineral N in soil.

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