Pelletized paper mill waste promotes nutrient input and N mineralization in a degraded Alfisol

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ABSTRACT

Pulp and paper mill waste, such as biomass fly ash and sewage sludge, is commonly disposed of in landfills. This waste can be valuable as nutrients and C sources for degraded soils. Ash and sludge samples were chemically characterized before ash/sludge pellets were experimentally manufactured for use as soil amendment. An incubation experiment was carried out with controlled moisture and temperature; nutrient input and N mineralization were evaluated at 0, 15, 30, 45, and 60 d intervals using three pellet types with different proportions of ash, sludge, and gypsum (as a binder) and applied at four doses equivalent to 0, 10, 20, and 40 Mg ha^{-1}. Results indicated that the Alfisol that was amended with pelletized residues increased P Olsen and exchangeable K and Ca contents, as well as soil pH ($p < 0.05$) in direct response to the applied doses. Organic matter decreased during incubation at all the doses and pellet types ($p < 0.05$); however, N mineralization did not show a clear pattern during incubation. Nitrogen mineralization potential (N_0) was different depending on pellet types and application rates; Pellet 2 (10% sludge) exhibited the highest N_0 values, while Pellet 3 (20% sludge) had lower N_0 than the control. Pulp and paper mill waste can be used to amend degraded soils by creating sustainable use through pelletizing because it facilitates transport and can evenly distribute sludge and ash on soils in a single application.

Key words: Nitrogen modeling, pulp and paper mill waste, pelletized waste, pelletized ash/sludge, soil incubation.

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INTRODUCTION

In 2013, worldwide pulp production reached 179 million Mg and the United States was the largest global producer with 30%, followed by China, Canada, Brazil, and Sweden, while Chile ranked tenth with 3.1%. The ten largest world cellulose producers account for 90% of total production (ODEPA, 2014). In Chile, pulp and paper mills generated 10.4 million Mg of waste in 2009. An alternative valuation of waste from paper mills is their use to amend or improve degraded soils, a problem that affects a large portion of the agricultural and forestry soils in pulp and paper producing countries. The option of using these residues in agricultural soils has been impeded by social factors, such as concerns about environmental pollution (Arellano and Ginocchio, 2013; Gallardo et al., 2016). It is therefore necessary to analyze residues to discard any that might contain hazardous compounds and ensure that heavy metal contents are at sufficiently low levels so as not to limit their application to soil (Rios et al., 2012). Industries have implemented actions to achieve sustainable development, including reducing the amount of generated waste and avoiding their disposal in landfills due to high disposal costs.

Paper mills generate two major types of waste: biomass combustion ash and sludge from effluent treatment systems. They produce between 2% to 6% ash for each mega gram (Mg) of bark burned; one third is bottom ash while the rest is fly ash. Sludge from effluent treatment reaches 240 Mg per 10 000 Mg of produced paper. Although partly reused as fuel for boilers, it is mostly deposited in landfills.

Wood ash is a source of minerals, such as P, K, Mg, and Ca, but C and N are volatilized during combustion; it has an alkaline pH of 9.5, suggesting that it could be used as a liming agent or fertilizer (Odlare and Pell, 2009; Pan and Eberhardt, 2011). Globally, most pulp and paper industries operate using the kraft process, which uses a recycling mill as a supplementary unit where a large fraction of the hemicellulose is released into the black liquor. It eventually burns in the recovery boiler to generate steam and electricity, thus reducing final waste production (Thompson et al., 2001).

Regarding the use of ash to amend soil, Ochecova et al. (2014) reported that soils treated with wood ash showed increases in nutrients and pH and caused a decrease in the mobility of potentially toxic elements for plants. Ash also has a liming effect by increasing base saturation, cation exchange capacity, and pH of forest soils (Ingerslev et al., 2014). However, neither major increases in heavy metals nor negative effects to the

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microbiological processes in soil have been attributable to soils amended with wood ash (Makela et al., 2012; Nayak et al., 2015).

There is evidence that adding paper mill sludge to the soil increases organic matter (OM) content, P, SO_4-S, Zn, and would also improve the pH of an Alfisol (Rios et al., 2012). An increase in microbial respiration and greater stability of aggregates have also been reported, helping to prevent soil physical degradation. Likewise, an increase in soil OM and P content has been found to generate increased biomass of *Lolium perenne* L. grown in Andisols. Kumar and Chopra (2014) reported increases in stems, root length, and yield of *Phaseolus vulgaris* L. fertilized with effluent from paper mills; the accumulation of metals in plants increased with increasing sludge doses. Repeated applications of pulp mill sludge increased nitrate and ammonium concentrations in the leachates of an amended Andisol with sludge derived from paper production (Gallardo et al., 2016). Sludge and ash have also been pelletized to reduce the water content of sludge and ash volume, which facilitates transport, packaging, and soil application (Steenari et al., 1999; Watanabe and Tanaka, 1999). Immobilization of heavy metals is enhanced whenever soil pH increases. However, this has not been observed at lower doses of granulated ash, at least not in the short term when a great deal of Ca may still be in an insoluble form. Furthermore, ash nutrient retention in the recipient soil greatly varies among elements as well as among sites; especially K may be lost through leaching (Huotari et al., 2015).

Nitrogen mineralization of soil OM indicates the amount of organic N transformed into inorganic N under optimal moisture, incubation time, and soil temperature conditions to develop microorganisms involved in this process. Two factors are important in the transformation of nitrogenous organic compounds in the soil. The first is potentially mineralizable N (N_0), which is the maximum amount of inorganic N that can be formed and depends on the mineralization and immobilization processes determined by the C/N substrate ratio. The second factor is the N mineralization rate (k), which depends on soil type, environmental conditions, and more or less labile OM (Gil et al., 2011). The concept of N_0 was proposed by Stanford and Smith (Stanford and Smith, 1972), and it refers to the amount of organic N that can be turned into soluble inorganic forms, mainly NH_4^+ and NO_3^- through microbial biomass activity. This model allows quantifying N soil or substrate contribution that are potentially available for crops and generating sustainable recommendations for N fertilizer doses (Campbell et al., 1995). However, these are direct impacts, while other indirect benefits from ash are through changes in soil processes induced by altered soil chemistry (Huotari et al., 2015). The hypothesis of our research was that the application of pelletized amendments composed of paper mill ash and sludge improves N mineralization and provides mineral nutrients to the soil. The objective was to evaluate pelletized pulp and paper mill waste on N mineralization potential and nutrient supply in a degraded Alfisol.

MATERIALS AND METHODS

The waste used in pellet manufacturing was obtained from the Papeles Biobío Company, Concepción, Chile. The Technological Development Unit (Unidad de Desarrollo Tecnológico, UDT) of the Universidad de Concepción experimentally manufactured pellets. The waste was multicyclone and precipitator fly ash from a thermoelectric generation boiler using plant biomass combustion mainly consisting of wood and pine bark mixed at a 50:50 w/w ratio. Sewage sludge was also used, which was dehydrated to obtain adequate moisture content for the pellets. Pellets were mostly composed of ash (56% to 70%), sewage sludge (0% to 20%), and mineral gypsum, which was incorporated as a binder and cement (24% to 30%). Three pellet types (Pellets 1, 2, and 3) with different sludge and ash ratios were manufactured (Table 1). For the incubation test, pellets were crushed to obtain a uniform mixture and higher contact area with the soil. Pellets were manufactured by compression until they reached adequate sizes and firmness to be handled and applied to agricultural soils (Figure 1).

Characterization of paper mill waste in pellet manufacturing

The waste used in pellet manufacturing was characterized by chemical analysis. Three types of ash were sampled from plant biomass combustion, which corresponded to grill, multicyclone, and precipitator ashes; sewage sludge and pellet samples were also analyzed. The pH was determined by chemical analyses, total P by colorimetry with a spectrophotometer (Perkin-Elmer model Lambda 3B,

Table 1. Proportion of ash, sludge, and gypsum for each pellet type.

	Boiler ash	Sewage sludge	Mineral gypsum
		%	
Pellet 1	70	0	30
Pellet 2	63	10	27
Pellet 3	56	20	24

Figure 1. Cylindrical aspect of pellets manufactured by compressing ash and sludge from a paper mill.

Phoenix, Arizona, USA) (Sadzawka et al., 2006; Cieslik et al., 2015), and various metal elements as total or pseudo total by acidic and alkaline digestions to quantify Cr, Zn, Ni, Cu, Pb, Cd, Ba, Mo, Sb, Se, As, Hg, Mg, Al, Fe, Ca, Na, and K according to USEPA Method 3051A (HNO_3/HCl) (Lapa et al., 2007; Barbosa et al., 2013). Metals were quantified by atomic absorption spectroscopy. Alkaline digestion was performed following USEPA Method 3060A using a NaOH + Na_2CO_3 mixture. Chromium VI was quantified as per USEPA Method 7196A. The content of C, N, and S was measured with a Leco automatic analyzer (LECO Corporation, Saint Joseph, Michigan, USA) (Barbosa et al., 2013; Cieslik et al., 2015). Pellet 2 was also analyzed by the same methodologies to obtain a reference composition with respect to raw materials such as sewage sludge, fly ash, and mineral gypsum.

Soil characterization and incubation experiment with pellets

The soil was an Ultic Palexeralfs (Stolpe et al., 2008) obtained from an arable layer at 0-20 cm depth with low-yield grassland cover in Ranquil (36°37'19" S, 72°19'42" W) in the Biobío Region, Chile. Soil samples were dried at room temperature and sieved (2 mm); soil chemical characteristics, such as OM, N, P, K, exchange cations, and micronutrients, were determined according to methodologies mentioned by Sadzawka et al. (2006) (Table 2).

An incubation experiment was conducted to evaluate the mineralization potential of the incubated soil together with the crushed pellets. The three pellet types were used at four rates equivalent to 0, 10, 20, and 40 Mg ha^{-1} in 200 g soil. The selected experimental application rates have a high limit so as not to damage seed germination. The pellet/soil mixtures were placed in plastic containers, 20 cm diameter and 10 cm height, under controlled conditions at 25 °C and constant moisture at field capacity, which is equivalent to the optimum with an adequate relationship between water and air at 1/3 atm. Bulk density was considered to calculate water and applied doses (Table 2). Treatments were carried out in triplicate, including a control with only soil. The experimental design was completely randomized with factorial arrangement, which resulted in 50 treatments that accounted for three factors: dose, pellet type, and incubation time.

Table 2. Chemical characterization of Alfisol used in incubation experiments with pellets.

Property	Value
Bulk density, g cm^{-3}	1.20
pH_{H_2O}	6.16
Organic matter, %	2.02
Inorganic N (NH_4+NO_3), mg kg^{-1}	4.30
P Olsen, mg kg^{-1}	2.20
Exchangeable K, $cmol_{(+)}$ kg^{-1}	0.33
Exchangeable Ca, $cmol_{(+)}$ kg^{-1}	5.08
Exchangeable Mg, $cmol_{(+)}$ kg^{-1}	1.42
Exchangeable Na, $cmol_{(+)}$ kg^{-1}	0.05
Exchangeable Al, $cmol_{(+)}$ kg^{-1}	0.01
Available SO_4-S, mg kg^{-1}	2.60
B, mg kg^{-1}	0.10
Fe, mg kg^{-1}	18.40
Mn, mg kg^{-1}	26.20
Zn, mg kg^{-1}	0.80
Cu, mg kg^{-1}	1.10

The evolution of mineral N and changes in chemical properties were evaluated at 15, 30, 45, and 60 d. Samples were air-dried and analyzed for mineral N (NH_4^+ + NO_3^-) by extraction with 2 M KCl (ratio 1:5) and analyzed calorimetrically by reducing nitrate to nitrite with Cd/Cu and flux injection segmented with an autoanalyzer (Skalar SA 4000, Skalar Analytical B.V., Breda, The Netherlands). Organic matter was obtained by determining organic C content using the dichromate oxidation method and colorimetric determination of reduced chromate (Cr^{+3}). The pH was measured in a 1:2.5 (w/v) soil/water mixture, while available P (P Olsen) was extracted with sodium bicarbonate (0.5 M, pH 8.5) and determined colorimetrically by the molybdate-ascorbic acid method. Available macro- and microelements were determined by atomic absorption spectrophotometry (Shimadzu GBC Sens AA). Calcium, Mg, K, and Na were quantified after extraction with 1 M ammonium acetate, pH 7.0, and expressed in $cmol_{(+)}$ kg^{-1}. On the other hand, Fe, Mn, Cu and Zn were quantified after extraction with a solution composed of diethylenetriaminepentacetic acid (DTPA), calcium chloride, and triethanolamine (TEA) buffered at pH 7.3. Aluminum was quantified after extraction with 1 M KCl (1:10 soil:solution ratio) and determined by atomic absorption spectrophotometry. Available SO_4-S was extracted with 0.01 M Ca $(H_2PO_4)_2$ and determined by turbidimetry. Available B was determined by extraction with 0.01 M $CaCl_2$ and colorimetry with azomethine (Sadzawka et al., 2006).

Nitrogen mineralization potential

The N mineralization potential was obtained from mineral N results by calculating net mineralized N for each sampling time minus the quantity determined at zero time according to the methodology applied by Hirzel et al. (2010). A regression analysis was used to determine the N mineralization potential where N mineralization was a first order equation (Tyson and Cabrera, 1993; Hirzel et al., 2010) indicated by Equation [1]:

$$Nm_t = No\left[1 - e^{(-kt)}\right] \quad [1]$$

where Nm_t is mineral N accumulated at a specific time (mg kg^{-1}), N_0 is potentially mineralizable N (mg kg^{-1}), k is the mineralization rate constant, and t is incubation time (wk).

Statistical analysis

The statistical analysis of data from soil incubations and N mineralization was performed by ANOVA, while the effect of means was analyzed by the LSD test with a 95% confidence level ($\alpha = 0.05$). Potentially mineralizable N (N_0) and the mineralization rate constant (k) were determined by the Gauss-Newton method for nonlinear least squares. Data were analyzed with SAS software (SAS Institute, Cary, North Carolina, USA).

RESULTS AND DISCUSSION

Chemical characterization of ash, sludge, and pellets

Waste used in pellet manufacturing contributes chemical elements that function as plant nutrients and are beneficial to the soil; C is prominent in ash, sludge, and analyzed pellets (23.5%) (Table 3). Only Pellet 2 was analyzed because it was representative of the other pellets, which were manufactured with different ratios of the analyzed ash and sludge. Only C from sewage sludge was organic, whereas C from ashes was biochar generated by incomplete combustion of plant biomass, which is recalcitrant C that is very seldom mineralizable in soil and not a source of energy for microorganisms (Shrestha et al., 2010); however, it enhances physical properties and cation exchange (Liang et al., 2006). The N and P contents in Pellet 2 were low in the original materials, as well as in the pellets, with values between 0.31% and 0.33%, respectively (Table 3). In ash, N was especially low because N compounds are volatilized during the wood combustion process; therefore, ash contributes very little to pellet N. However, K and Mg contribution was mainly from ash with 2.37% and 0.89% Mg, respectively. These values were similar to values obtained by Brannvall et al. (2015), who pelletized fly ash with municipal biosolids and applied them to forest soils, as well as those found by other authors who studied fly ash as amendments (Mladenov and Pelovski, 2012; Ochecova et al., 2014). Ash composition results were similar to those reported in the literature (Lapa et al., 2007; Brannvall et al., 2015) with high contents of elements such as Ca, Al, and Si (Table 4). In our study, the high Ca content (reaching values of 9.07%) in pellets was attributable to using gypsum as a binder (Table 1); ash and sludge only contributed 3.00% and 0.25%, respectively. Likewise, S in pellets (3.92%) was due to the contribution of gypsum as compared to ash (0.33%) and sludge (0.52%). The S content in ash was similar to the value found in other studies in which fly ash contents were between 0.16% and 0.41% (Barbosa et al., 2013), while bottom ash had a lower S content (0.12%) (Tan and Lagerkvist, 2011).

Table 3. Chemical characterization of ash and sludge used in pellet manufacturing and in a specific pellet type.

Property	Ash[1]	Sludge	Pellet 2
Humidity, %	0.99 ± 0.95	11.10	12.60
Bulk density, g cm^{-3}	0.48		
EC, µS cm^{-1}	3.16		
pH	5.18	8.16	
N, %	0.57 ± 0.09	1.68	0.31
C, %	36.25 ± 2.19	26.00	23.50
P, %	1.25 ± 0.07	0.29	0.33
Ca, %	3.00 ± 1.57	0.25	9.07
Mg, %	1.13 ± 0.28	0.14	0.89
K, %	2.51 ± 2.28	0.09	2.37
Na, %	0.37 ± 0.13		1.17
S, %	0.33 ± 0.53	0.52	3.92
Cl, %	0.14 ± 0.18	0.01	
Fe, %	2.13 ± 0.39	0.16	1.54
Mn, %	1.29 ± 0.35		0.09
B, mg kg^{-1}	< 1†	< 5†	7.30
Cu, mg kg^{-1}	81.00 ± 8.20	69	56
Zn, mg kg^{-1}	60.50 ± 7.68	156	265

[1]Ash values are the mean of three samples ± standard deviation.
†Value under the detection limit of the method; EC: electrical conductivity.

Table 4. Heavy metal content in ash and sewage sludge used in pellet manufacturing and in a specific pellet type.

Element	Ash[1]	Sludge	Pellet 2
Aluminum, %	1.04 ± 0.20		
Strontium, %	0.14 ± 0.04		
Silicon, %	6.71 ± 1.75		
Titanium, %	1.50 ± 0.84		
Arsenic, mg kg^{-1}	32.33 ± 15.50	< 10†	< 10†
Barium, mg kg^{-1}	23.00 ± 5.29		
Beryllium, mg kg^{-1}	< 5†		
Bismuth, mg kg^{-1}	< 5†		
Cadmium, mg kg^{-1}	< 2†	< 2†	< 2†
Cobalt, mg kg^{-1}	8.00 ± 1.73		
Chromium, mg kg^{-1}	67.33 ± 22.72	8	151
Mercury, mg kg^{-1}	< 1†	< 1†	< 1†
Lanthanum, mg kg^{-1}	< 5†		
Molybdenum, mg kg^{-1}	< 5†		
Nickel, mg kg^{-1}	22.00 ± 2.65	< 5†	13
Silver, mg kg^{-1}	< 5†		
Lead, mg kg^{-1}	14.50 ± 13.44	< 5†	9
Selenium, mg kg^{-1}	< 10†	< 10†	< 10†
Scandium, mg kg^{-1}	< 10†		
Antimony, mg kg^{-1}	< 5†		
Vanadium, mg kg^{-1}	78.50 ± 2.12		

[1]Ash values are the mean of three samples ± standard deviation.
†Value under the detection limit of the method.

The chemical parameters of pulp and paper mill waste indicated they contained elements that could contribute to increased fertility in degraded soils; moreover, pellet pH (8.16) could help to reduce soil acidity and levels of nutrients, such as Ca, Mg, and K, as revealed in studies of ash applications to soil (Mladenov and Pelovski, 2012; Nurmesniemi et al., 2012).

Sludge exhibited 1.68% N and low contents of bases, such as Ca, Mg, and K (less than 0.25%) (Table 3), and P content of 0.29%, which was similar to results reported by Walter et al. (2006). The sludge had acidic pH (5.18), making it suitable to be mixed with pelletized fly ash to neutralize its acidifying potential, thus complementing the contribution of elements, particularly in degraded soils (Park et al., 2012; Brannvall et al., 2015). Furthermore, sludge contributed 26.0% organic C that compensated for the biochar or black C contributed by ash, and it was not an energy source for soil microorganisms.

As for the metals analyzed in bottom and fly ashes, high concentrations of Al, Si, and Ti (Table 4) were observed as being the elements with the greatest contribution in all the ash produced in plant biomass combustion with values of 1.04 %, 6.71%, and 1.50%, respectively, and which was followed by Sr with 0.14%. The concentrations of other metals, that is, V, Cr, As, Ba, Ni, Pb, and Co, were much lower and the lowest was between 78.5 and 8.0 mg kg^{-1} (Table 4) (Norris and Titshall, 2011; Ingerslev et al., 2014; Olsson et al., 2017). Other metals, such as Cd and Hg, with values lower than 2 and 1 mg kg^{-1}, respectively, were not detected in the ashes because their concentrations were below the sensitivity of the analytical method. In general, the heavy metal content in ash was lower than values reported by Lapa et al. (2007) for Cr, Cu, Fe, and Al because ash mainly came from the combustion of wood and pine bark. Lapa et al. (2007) also reported Al contents from 2% to 4% in fly ash. Norris and Titshall (2011) found high Al, Fe, and Mn contents, but these were lower than those found in our study; this could have been attributable to the type of waste and biomass used in the combustion that generated the ash. For sludge and pellets, only some of the most toxic metals, such as As, Cd, Hg, and Se, were analyzed due to the detection limits of the analytical equipment. Sewage sludge results showed only 8 mg Cr kg^{-1} (Table 4), but also detected Cu and Zn contents of 69 and 156 mg kg^{-1}, respectively (Table 3); these are considered as beneficial nutrients in normally deficient degraded soils (Norris and Titshall, 2011; Ingerslev et al., 2014). The analyzed pellet displayed Ni and Pb values of 13 and 9 mg kg^{-1}, respectively, originating from ash. In contrast, 151 mg Cr kg^{-1} could be increased by gypsum and ash contributions (Table 4).

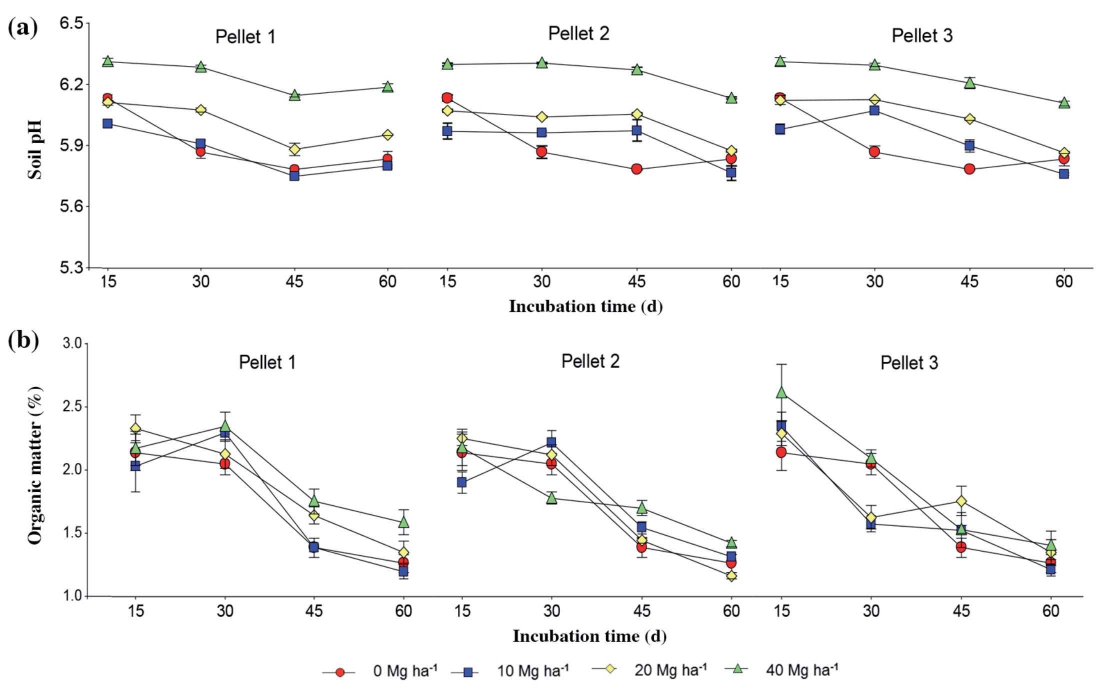
Nutrient input from three pellet types incubated in a degraded Alfisol

The incubation of a low-fertility degraded Alfisol (Table 2) showed changes in some selected properties, such as pH and OM content, after 60 d incubation at 25 °C and moisture at field capacity. The pH decreased with incubation in the control treatment from 6.16 in the original soil (Table 2) to 5.82 at 45 d incubation. This occurred naturally due to the increase in microorganism activity and optimal moisture and temperature conditions of the incubated soil (Tambone and Adani, 2017). In addition, soil with the three pellet types exhibited similar behavior (Figure 2a) and pH values decreased slightly between 15 and 60 d; however, the decrease in pH was less marked than in the control, demonstrating the power of pelletized amendments to correct soil pH. The three pellet types showed significant differences ($p < 0.05$) between 10, 20, and 40 Mg ha^{-1}, especially Pellet 1, which contained a higher proportion of fly ash. The highest pH values occurred at the highest dose of 40 Mg ha^{-1} in amended soil (Gagnon et al., 2012; Brannvall et al., 2015). This indicated that pellets containing fly ash can correct the acidity of degraded soil; on average, 0.1 pH unit per 5.5 Mg pellets was the result in the studied Alfisol that showed low buffer capacity.

The OM content of soil incubated with the three pellet types decreased significantly during the incubation period (Figure 2b). This was consistent with initial soil levels and amounts of added C (de Andrade et al., 2013), especially Pellet 3 with 20% sludge (Table 1), which more noticeably reduced OM. This was due to higher microorganism activity in the soil, which favors higher organic C content contributed by sludge (Odlare et al., 2014). Pellet 3 had the highest initial OM content at 15 d incubation ($p < 0.05$) and 40 Mg ha^{-1} because of greater sewage sludge contribution; however, the content was lower than in Pellet 1 at 60 d incubation. Pellet 3 had higher organic C content, resulting in more energy for soil microorganisms. Pellet 1 contained only inorganic C or black C, which is not mineralizable (Figure 2b).

The control treatment (no pellet amendment) also showed a considerable decrease in OM content during incubation and the low organic C present in the soil was

Figure 2. Soil pH (a) and organic matter (b) during 60 d incubation of an Alfisol amended with different doses and pellet types. Vertical bars correspond to the standard error of the three samples.



used by microorganisms as an energy source due to optimal development conditions and ideal moisture and temperature conditions provided in the incubation experiment (Tambone and Adani, 2017; Yanardag et al., 2017). Additionally, the Alfisol under study had no forms of C protection because it was not degraded with clay or amorphous elements to protect C, for example, the Al content was very low (Table 2).

The evolution of N mineral contents in soil incubated with the three pellet types did not display a clear pattern with doses and pellet type (Figure 3a), indicating that mineral N changed very little during incubation time. The exception was Pellet 1 at 10 Mg ha^{-1}, which increased markedly at 30 d incubation, but then decreased; this was possibly due to a lack of organic C that slows down the activity of N-mineralizing microorganisms. Pellet 2 was the only type with higher contents for the three doses at 60 d incubation ($p < 0.05$) and positive slopes in the curves (Figure 3a). Given these results, N mineralization must be evaluated according to more complex models that allow determining mineralization potential and its projection over time (Stanford and Smith, 1972; Cabrera, 1993; Tyson and Cabrera, 1993).

The evolution of P Olsen in soil incubated with pellets indicated a slight increasing trend during incubation for the three pellet types, as well as the control treatment (Figure 3b). Pellets did not activate an extra release of P Olsen; however, a dose effect was observed through higher contents at 40 Mg ha^{-1} for the three pellet types ($p < 0.05$) due to fly ash contributions (Nurmesniemi et al., 2012; Ingerslev et al., 2014; Brannvall et al., 2015).

Unlike other analyzed elements, interchangeable K and Ca contents in the degraded Alfisol were present at sufficient levels for crop nutrition. In addition, the soil did not naturally increase its contents with incubation time (Figures 4a and b) as seen for 15 and 60 d incubation ($p > 0.05$). This was similar to outcomes indicated by several authors (Park et al., 2012; Brannvall et al., 2015), who described that both exchange bases increased with applied doses, but that there was no contribution from the soil related to incubation time. Fly ash partly contributed to Ca exchange (3.00%) and gypsum, used as a binder, contributed in a higher proportion (9.07%). This was reflected in the final pellet content (Table 2) and was therefore expressed in higher contents at the 40 Mg ha^{-1} dose for the three pellet types throughout the incubation period ($p < 0.05$) (Figure 4b).

Potentially mineralizable N

Net N mineralization exhibited differences according to treatments applied to the soil and incubation times (Table 5). The control treatment had relatively stable net N mineralization rates between 30 and 60 d incubation (between 4.32 and 6.65 mg kg^{-1}, Table 5) and the lowest was at 15 d. Net mineralized N displayed contrasting behaviors in the incubation of Alfisol amended with pellets, depending on pellet type and dose, because of the low contribution of C from sludge and ash for soil microorganism development (Table 2). This contrasted with findings by San Martin et al. (2016), who supplemented pellets with seaweed. Organic N sources applied to soils with less C, as an energy source for microorganisms, reduced N losses because of a lower mineralization rate and prevented N_2O generation. Furthermore, moisture content can affect microorganism growth, while drying and rewetting of added residues as amendments affect the dynamics of C and N (Shi

Figure 3. Availability of mineral N (a) and P Olsen (b) during 60 d incubation in an Alfisol amended with different doses and pellet types. Vertical bars correspond to the standard error of the three samples.

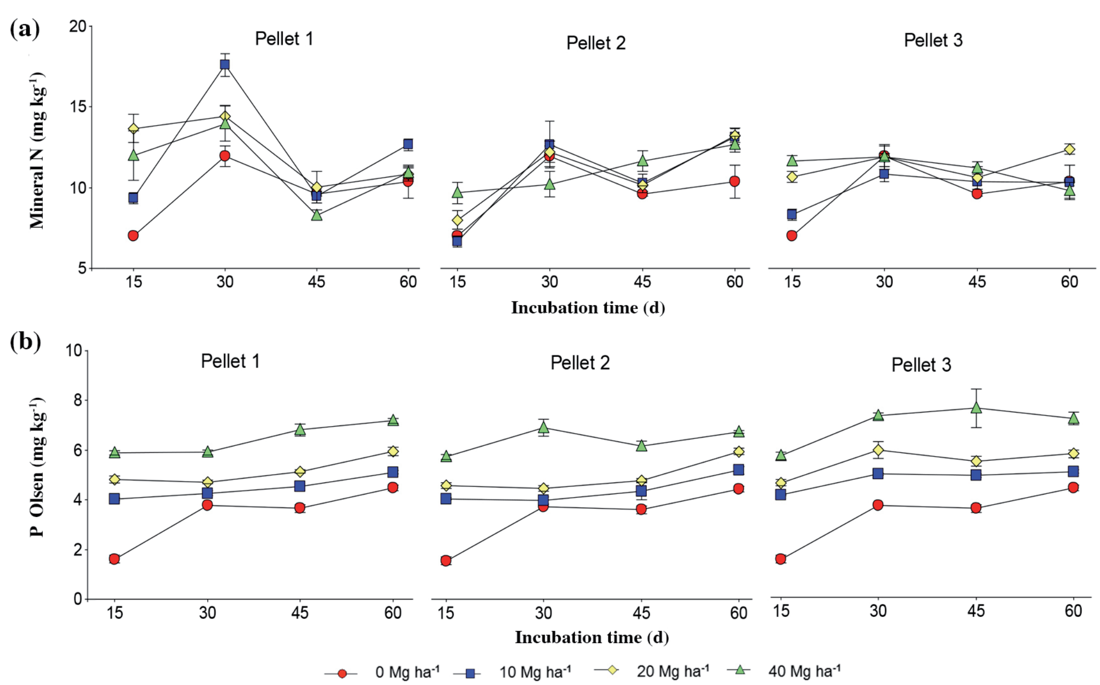


Figure 4. Availability of exchangeable K (a) and Ca (b) during 60 d incubation in an Alfisol amended with different doses and pellet types. Vertical bars correspond to the standard error of the three samples.

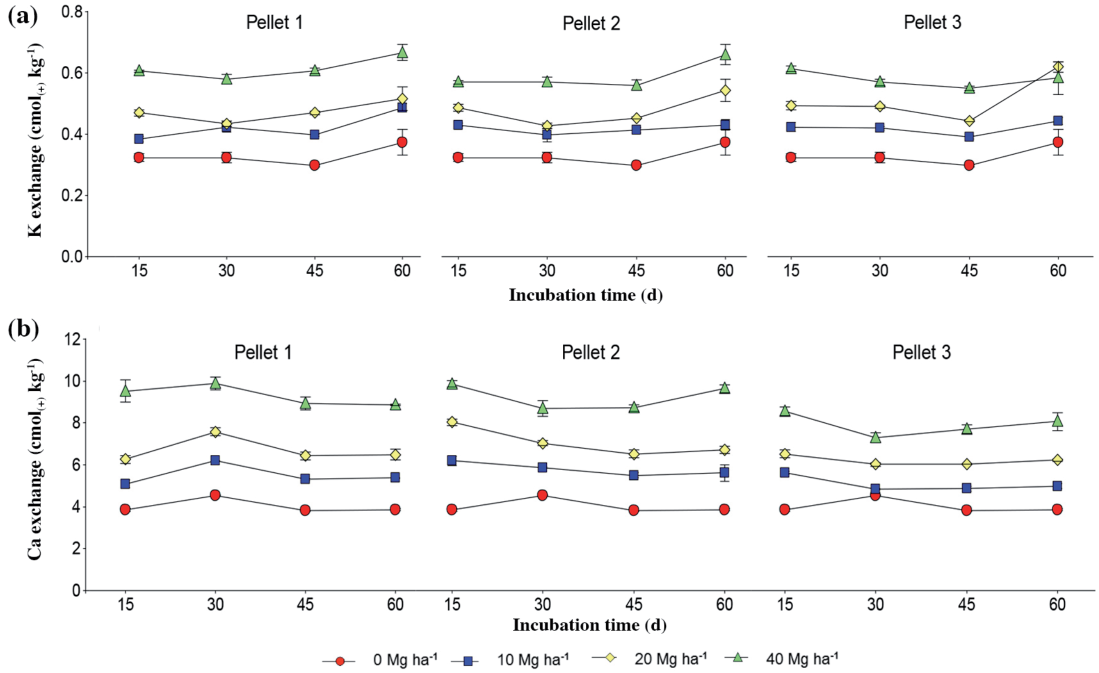
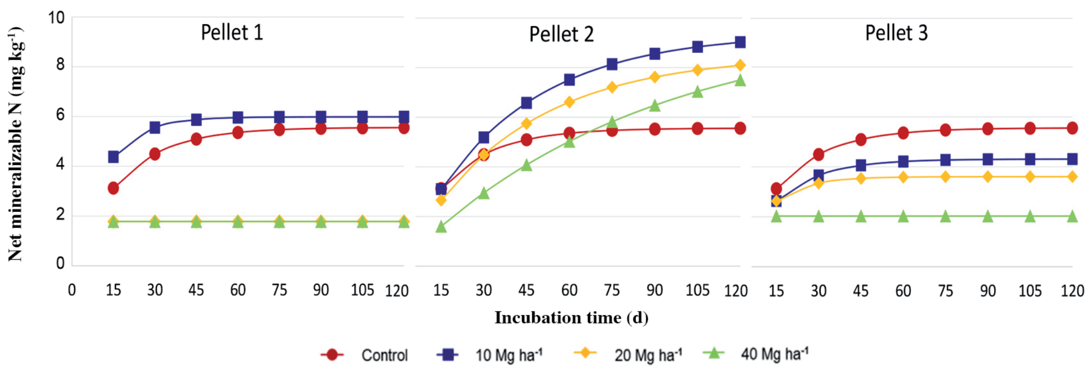


Figure 5. Nitrogen mineralization potential curves projected at 120 d by a first order nonlinear regression in an Alfisol amended with different doses and pellet types.



and Marschner, 2014), especially in pellets with high non-organic C contents contributed by ash with low N content (Table 3). The control treatment showed lower N mineralization rates at 15 d, which was similar to results obtained by Rios et al. (2012) despite soil moisture control (Jeke et al., 2015).

Soil mineralized N content did not change for any of the tested amendments. However, the method to evaluate potentially mineralizable N showed differences with nonlinear regression equations, and this was better to indicate the behavior of different pellet types and applied doses. Higher values of potentially mineralizable N (N_0) were found in Pellet 2 (Table 5), which contained 10% sludge (Table 1), with N_0 values of 9.405, 8.525, and 9.911 mg kg^{-1} at doses of 10, 20, and 40 Mg ha^{-1}, respectively. Slopes for Pellet 2 curves projected at 120 d were above the control treatment (Figure 5). The estimation of N mineralization potential through nonlinear regression equations allows comparing different pellets because it is simpler than isotopic techniques.

Pellet 3 (20% sewage sludge) showed inhibition in N mineralization potential because the curves of net mineralized N projected at 120 d were below the control treatment with lower slopes (Figure 5). The mineralization rate constant (k) obtained for Pellet 2 was lower than findings by Hirzel et al. (2010) for an Andisol where a broiler bed was added. Pellet 1 (only biomass ashes and gypsum as a binder, Table 5) behaved in a similar way at doses of 20 and 40 Mg ha^{-1}, and N_0 values were lower than those in the control treatment.

Results show promising advantages when applying pelletized pulp and paper mill waste to improve degraded soils because it allows sustainable use of industrial waste and recycling of nutrients in forest soils. These residues would

Table 5. Net nitrogen mineralization (Nm_t) of soil/pellet mixture during 60 d incubation period in an Alfisol amended with different doses and pellet types.

Treatments	Net N mineralization (mg kg^{-1})				Mineralization equation
	15 d	30 d	45 d	60 d	
Control	1.77c	6.65abc	4.32a	5.07ab	$Nm_t = 5.561 [1- e^{(-0.0549t)}]$
P1T10	2.28bc	10.77a	2.64ab	5.81ab	$Nm_t = 5.985 [1- e^{(-0.0875t)}]$
P1T20	3.31a	3.92bc	-0.45b	0.33e	$Nm_t = 1.776 [1- e^{(-31595.5t)}]$
P1T40	2.53abc	4.44bc	-1.24b	1.39cde	$Nm_t = 1.782 [1- e^{(-61468.9t)}]$
P2T10	1.75c	7.41ab	5.00a	7.90a	$Nm_t = 9.405 [1- e^{(-0.0267t)}]$
P2T20	1.91bc	6.18bc	4.12a	7.19ab	$Nm_t = 8.525 [1- e^{(-0.0249t)}]$
P2T40	2.01bc	2.65c	4.07a	5.12ab	$Nm_t = 9.911 [1- e^{(-0.0818t)}]$
P3T10	2.13bc	4.43bc	3.96a	3.94bcd	$Nm_t = 4.312 [1- e^{(-0.0628t)}]$
P3T20	2.57ab	3.78bc	2.49ab	4.25bc	$Nm_t = 3.606 [1- e^{(-0.0870t)}]$
P3T40	2.41bc	2.82c	2.15ab	0.73de	$Nm_t = 2.030 [1- e^{(-3757.2t)}]$
CV	12.10	28.32	50.81	28.65	
LSD	0.79	4.34	3.98	3.46	

Control: Soil without amendment; P1T10: soil with 10 Mg ha^{-1} Pellet 1; P1T20: soil with 20 Mg ha^{-1} Pellet 1; P1T40: soil with 40 Mg ha^{-1} Pellet 1; P2T10: soil with 10 Mg ha^{-1} Pellet 2; P2T20: soil with 20 Mg ha^{-1} Pellet 2; P2T40: soil with 40 Mg ha^{-1} Pellet 2; P3T10: soil with 10 Mg ha^{-1} Pellet 3; P3T20: soil with 20 Mg ha^{-1} Pellet 3; P3T40: soil with 40 Mg ha^{-1} Pellet 3; CV: coefficient of variation; LSD: last significant difference.
Different letters in the columns indicate differences according to the LSD test ($p < 0.05$).

otherwise be discarded in sanitary landfills, thus giving them a further use as degraded soil fertility enhancers for their input of nutrients, such as K, Ca, P, to improve acidic soils (Park et al., 2012) and activate N mineralization attributable to organic C from sludge (San Martin et al., 2016). Pelletizing is also important because it allows handling two different waste mixtures under controlled proportions, facilitates transport, and is applied to the soil with conventional agricultural machinery, which provides an adequate dose and uniform application. Another positive aspect of pelletizing is that mixing ash and sludge produces a synergistic effect on soils, especially on N mineralization potential.

Although the use of biomass ash as soil amendment has been investigated, very few practical approaches have been researched, such as pelletizing. It reduces ash volume by 75% by compressing pellets, improving transport efficiency (Watanabe and Tanaka, 1999), and avoiding wind drift losses.

Pelletizing technology allows the sustainable use of waste that can be reused and recycled (Brannvall et al., 2015; San Martin et al., 2016). Therefore, future research is necessary to continue evaluating binders that are more suitable than gypsum, testing sludge/ash proportions, or incorporating another type of waste from the pulp and paper industry. This can contribute useful elements to spatially degraded or eroded soils where forest production is carried out for pulp and paper raw materials, thus achieving sustainable production systems through waste recycling.

CONCLUSIONS

A degraded Alfisol amended with pelletized pulp and paper mill waste exhibited different behaviors depending on the nutrient under study, dose, and proportion of ash and sludge in the pellets. Pellets contained elements that increased the fertility of degraded soils and reduced soil acidity. The higher proportion of ash determined a higher K content and gypsum provided exchangeable Ca. Soil P increased due to pellet contribution and incubation time.

The method of evaluating potentially mineralizable N showed differences in soil N mineralization activation according to pellet type and doses. The highest dose at 40 Mg ha^{-1} presented potentially mineralizable N curves below the control treatment for all pellet types.

Some heavy metals appeared at low concentrations or below detection limits. Chromium, Ni, and Pb were present in the analyzed pellet with 151, 13, and 9 mg kg^{-1}, respectively, but they did not generate an increase in soil concentration due to the dilution effect based on the doses used.

According to our results, pulp and paper mill waste can be used to amend degraded soils and create their sustainable use. In addition, pelletizing facilitates transport and requires a single application to evenly distribute sludge and ashes on the soils that needs to be amended. This process allows for the sustainable use of these residues, makes them useful for forestry and agricultural production, and prevents further pollution.

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