Universidad de Concepción
Dirección de Postgrado
Facultad de Agronomía - Programa de Doctorado en Ciencias de la Agronomía

Evaluación en condiciones controladas de una enmienda para suelos proveniente del reciclaje de residuos peletizados de la industria del papel

Tesis para optar al grado de Doctor en Ciencias de la Agronomía

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CHILLAN - CHILE
2017

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AGRADECIMIENTOS

Mis más sincero agradecimiento a todas las personas que durante todo este tiempo me han apoyado en el desarrollo del presente trabajo: En primer lugar a mi profesor guía y director de tesis, Dr. Marco Sandoval Estrada, por su dedicación, sus buenas ideas y su paciencia para orientarme y soportar el lento avance. A la Sra. Carla Pérez de la Unidad de Desarrollo Tecnológico UDT de la U. de Concepción por el financiamiento de los experimentos y el desarrollo de los pellets, y también por su paciencia.

A mis Profesores Asesores Dr. Juan Hirzel Campos del Instituto de Investigaciones Agropecuarias, INIA-Quilamapu, y al Dr. José Celis Hidalgo de la Facultad de Medicina Veterinaria de la U. de Concepción, por sus aportes en la revisión del proyecto de tesis y en la corrección del documento final. A todos los profesores que he tenido en las distintas asignaturas del doctorado por su gran nivel docente y por inducirme a tener espíritu investigador.

También a Patty y Diego, mi mujer y mi hijo por su apoyo y comprensión durante los años dedicados al desarrollo de la investigación; sin ellos no hubiera logrado concretar los años de estudio y la finalización del doctorado.

TABLA DE CONTENIDOS

INDICE DE TABLAS

INDICE DE FIGURAS

RESUMEN

El uso de residuos de madera para la producción de energía y vapor en las industrias de celulosa y papel genera desechos en forma de cenizas, que junto a los lodos de depuración son normalmente desechados en vertederos. La ceniza de madera contiene nutrientes que las plantas necesitan en proporciones adecuadas, y el pellet de lodos y cenizas es un fertilizante potencial. Sin embargo, estos residuos concentran elementos nocivos, como metales pesados, que generan preocupación. Estos residuos pueden ser valorizados como fuentes de nutrientes y carbono para suelos degradados. El objetivo del estudio fue evaluar residuos peletizados de la industria de pulpa y papel en cuanto a los posibles efectos tóxicos de los residuos peletizados de la industria de pulpa y papel mediante bioindicadores y su potencial de mineralización de N y aporte de nutrientes en un Alfisol degradado. Se realizó un muestreo de cenizas y lodos para su caracterización química y luego se fabricaron en forma experimental pellets de ceniza/lodo para ser utilizados como enmienda de suelos. Se realizó un experimento de incubación con humedad y temperatura controladas, donde se evaluó el aporte de nutrientes y mineralización de N a 0, 15, 30, 45 y 60 d utilizando tres tipos de pellets con distintas proporciones de cenizas, lodos y yeso como aglomerante, aplicados en cuatro dosis equivalentes a 0, 10, 20, y 40 Mg ha^{-1}. También se realizaron dos experimentos controlados con semillas de rabanitos (*Raphanus sativus* L.) y ballica perenne (*Lollium perenne* L.), en el primero se determinó el índice de germinación (GI) y crecimiento de radículas en extractos de suelo incubados con residuos peletizados. El segundo consistió en un experimento de macetas donde se sembraron semillas de ballica en un Alfisol enmendado con residuos peletizados, donde se determinó la producción de biomasa aérea y de raíces. En ambos experimentos se probaron tres tipos de pellets de residuos compuestos de lodos y cenizas en tres dosis, incluyendo un tratamiento control. Los resultados indican que el Alfisol enmendado con residuos peletizados aumentan los contenidos de P Olsen, K y Ca de intercambio, y el pH del suelo ($p < 0,05$) con una respuesta directa a las dosis aplicadas. La materia orgánica disminuyó durante la incubación con todas las dosis y tipos de pellets ($p < 0,05$), sin embargo el N no presenta un patrón claro durante la incubación, no así el N potencialmente mineralizable (N_0) que indican mejor los comportamientos de los tipos de pellets y dosis aplicadas, donde el pellet 2 presenta los mayores valores de N_0 que contiene 10% de lodos. El pellet 3 con 20% de lodos presenta N_0 por debajo del control. El Alfisol enmendado con residuos peletizados no presenta efectos tóxicos agudos o sub agudos en la germinación de rabanitos, incluso con dosis de 40 Mg ha^{-1} no evidencian deterioro en la germinación o elongación de la radícula para ninguno de los pellets evaluados. El mayor crecimiento de la radícula se obtuvo con el pellet 2 en dosis de 40 Mg ha^{-1} con 14,03 mm, siendo mayor que el tratamiento control con 11,71 mm ($p < 0,05$). La germinación de semillas estuvo entre 93,9% y 100%. La mayor biomasa aérea de ballica se obtuvo con los pellets 1 y 2, 2,91 y 3,14 g, respectivamente, y el pellet 3 produjo la menor biomasa con 2,46 g ($p < 0,05$). La biomasa de raíces alcanzó a 2,11 g con la dosis de 40 Mg ha^{-1} diferenciándose del tratamiento control que alcanzó 1,44 g ($p < 0,05$). Los residuos peletizados de la industria del papel no presentan efectos de toxicidad leve ni aguda, tanto en la germinación de semilla de rabanito como en la producción de biomasa aérea y de raíces de ballica sembradas en un suelo degradado, donde más bien se detectan efectos positivos. Los residuos de pulpa y papel pueden ser utilizados como enmiendas para suelos degradados, creando un uso sostenible a través de la peletización, ya que facilita el transporte y puede distribuir uniformemente los lodos y cenizas en los suelos en una sola aplicación.

Palabras clave: Residuos de la industria de pulpa y papel; ceniza/lodos peletizados; residuos peletizados; incubación de suelos, modelo de N, rabanitos; bioensayos de toxicidad; ballica.

SUMMARY

The use of wood residues to produce energy and steam in the pulp and paper industry generates ash waste that is usually disposed of in garbage dumps along with sewage sludge. Wood ash contains nutrients plants need in appropriate proportions, and the sludge and ash pellet is a potential fertilizer. However, these residues concentrate harmful elements, such as heavy metals, that create concern. Pulp and paper mill wastes can be valuable as nutrient and carbon sources for degraded soils. The objective of this study was to evaluate pelletized waste from the pulp and paper industry as to the possible toxic effects using bioindicators and their potential of N mineralization and nutrient contribution in a degraded Alfisol. Samples of ash and sludge were chemically characterized before ash/sludge pellets were experimentally manufactured to be used as a soil amendment. An incubation experiment was carried out with controlled humidity and temperature where the input of nutrients and N mineralization were evaluated at 0, 15, 30, 45, and 60 d at intervals using three pellets types with different proportions of ash, sludge and gypsum (as a binder), and applied in four doses equivalent to 0, 10, 20, and 40 Mg ha^{-1}. Also two controlled experiments were conducted with radish seeds (*Raphanus sativus* L.) and perennial ryegrass (*Lollium perenne* L.) seeds. The first experiment determined the germination index (GI) and root growth in soil extracts incubated with pelletized waste. The second was a pot experiment in which ryegrass seeds were sown in an amended Alfisol with pelletized waste; aerial and root biomass production was determined. Both experiments tested three types of waste pellets consisting of sludge and ash at three doses, including a control treatment. The results indicated that the Alfisol amended with pelletized residues increased contents of P Olsen, exchangeable K and Ca, and soil pH ($p < 0.05$) in direct response to the applied doses. The organic matter decreased during incubation with all doses and pellet types ($p < 0.05$); however, N mineralization did not show a clear pattern during incubation. Nitrogen mineralization potentials (N_0) were different depending on pellet types and application rates, where Pellet 2 (containing 10% sludge) presented the highest N_0 values. Pellet 3 (with 20%

sludge) had lower N_0 than the control. The Alfisol amended with pelletized waste did not exhibit any acute or sub-acute toxic effects in radish germination; none of the evaluated pellets showed evidence of deterioration in root elongation, including at the 40 Mg ha^{-1} dose. The highest root growth was obtained with pellet 2 at the 40 Mg ha^{-1} dose with 14.03 mm, which was higher than the control treatment with 11.71 mm ($p < 0.05$). Seed germination was between 93.9% and 100%. The highest ryegrass aerial biomass occurred with pellets 1 and 2 with 2.91 and 3.14 g, respectively, and pellet 3 produced the lowest biomass with a value of 2.46 g ($p < 0.05$). Root biomass reached 2.11 g at the 40 Mg ha^{-1} dose, which differed from the control treatment with 1.44 g ($p < 0.05$). Pelletized waste from the paper industry exhibited neither mild nor acute toxicity effects in both radish seed germination and aerial and root biomass production of ryegrass sown in degraded soil where rather positive effects were detected. Pulp and paper waste can be used as amendments for degraded soils, creating a sustainable use through pelletizing as it facilitates transport, and can evenly distribute sludge and ash in the soils in a single application.

Key words: Pulp and paper mill waste; pelletized ash/sludge; pelletized waste; soil incubations; N modeling; radish; toxicity bioassay; ryegrass.

I. INTRODUCCIÓN GENERAL

La producción mundial de celulosa en 2013 alcanzó 179 millones de toneladas métricas, donde Estados Unidos es el mayor productor global, con 30% del total, seguido por China, Canadá, Brasil y Suecia, mientras que Chile se encuentra en la décima posición, con un 3,1%. Los diez mayores productores mundiales de celulosa representan el 90% de la producción (ODEPA, 2014).

En Chile los tres principales productos silvoagropecuarios exportados en el año 2014 fueron celulosa, uvas y vino con denominación de origen, donde la celulosa representó el mayor porcentaje de exportación con el 16% del total. La capacidad productiva de celulosa se sustenta en 16,6 millones de hectáreas con cobertura de bosques, de las cuales 2,7 millones corresponden a plantaciones forestales de pino radiata (*Pinus radiata* D. Don), y eucaliptus (*Eucalyptus globulus* Labill.). Con esto, Chile tiene condiciones de producir casi 6 millones de toneladas de celulosa al año, donde la Región del Biobío concentra dos tercios de la capacidad total, con dos empresas, la Compañía Manufacturera de Papeles y Cartones (CMPC), seguida por Celulosa Arauco y Constitución (CELCO) (ODEPA, 2014). La industria del papel está creciendo continuamente, por tanto existe la necesidad de encontrar una solución ecológica para el manejo de residuos generados, sobre todo cuando la tendencia indica que la demanda mundial de este producto va en aumento (Rios et al., 2012).

En Chile, durante el año 2009 se generaron 17 millones de toneladas de residuos domiciliarios e industriales, excluyendo la minería, de las cuales 10,4 millones de ton correspondían a residuos industriales, y un 18% de esto es generado por la industria manufacturera, incluida la fabricación del papel (CONAMA, 2010). El manejo de residuos orgánicos se ha limitado principalmente a la recolección y disposición final en vertederos y rellenos sanitarios, con poca atención en alternativas de valorización (MMA, 2011). Del total de biosólidos generados por los tratamientos de aguas servidas en el año 2012, el 40% se disponen en rellenos sanitarios y solo un 10% es utilizado como enmiendas al suelo, del resto no se dispone de información, mientras que de los residuos orgánicos de agroindustrias, el 30% se utilizan para compostaje y un 20% se disponen en vertederos, y el resto se mantienen en las plantas industriales que los generan, o se les da otro uso no especificado (Arellano and Ginocchio, 2013). La falta de valoración de residuos se atribuye principalmente a barreras legales y de procedimiento, las que desincentivan la puesta en marcha de proyectos que intentan reutilizar o valorizar los residuos orgánicos (Arellano and Ginocchio, 2013).

Una alternativa de valorización de los residuos de la industria del papel, es el uso como mejoradores de suelos degradados o erosionados, que es un problema que afecta a gran parte de los suelos agrícolas y forestales del país donde un 64%, presentan algún tipo de erosión, y de estos, el 49% presenta niveles de erosión moderada a muy severa. Las regiones que tienen mayor superficie en riesgo de erosión, son Coquimbo, Valparaíso y del Libertador Bernardo O'Higgins. Sin embargo la Región del Biobío presenta un 32% de su superficie con algún grado de erosión, donde las comunas más afectadas son San Fabián, Quirihue, Pinto y Ninhue (CIREN, 2010). Los suelos con erosión podrían ser utilizados como reservorios para el reciclaje de residuos orgánicos. Dentro de estos suelos, destaca el orden Alfisol que son representativos del secano interior y cordillera de la costa del centro sur de Chile, donde se concentran gran parte de las plantaciones forestales, que se utilizan principalmente en producción de pulpa y papel. En general estos suelos presentan diferentes grados de erosión y de degradación, y por esto son interesantes para evaluar la aplicación de enmiendas de residuos peletizados de la industria de celulosa.

La valorización de los residuos orgánicos como enmiendas de suelos agrícolas degradados se ha visto frenada en el país por diversos motivos, siendo el más relevante el factor social, particularmente en el caso de los biosólidos, por preocupaciones de las comunidades relacionadas con contaminación ambiental (Arellano and Ginocchio, 2013). Por lo tanto se debe investigar y probar que los residuos no contienen compuestos peligrosos, como ácidos de resina o concentraciones de metales pesados que sobrepasen las normas establecidas que puedan limitar la aplicación al suelo (Rios et al., 2012)

1.1. Residuos de la industria papelera.

En la Región del Biobío, la industria del papel genera 4961 ton al año de residuos industriales no peligrosos, a una tasa de 15 a 30 kg por cada tonelada de papel producida, incluyendo lodos, cenizas y aguas residuales (CORMA, 2012). Las empresas de la industria del papel, han implementado medidas para alcanzar un desarrollo sustentable con el medio ambiente. Específicamente tratando de disminuir los residuos generados por sus actividades o evitar disponerlos en rellenos sanitarios, ya que los costos de eliminación son muy altos, además de la contaminación que se produce al disponerlos.

Las empresas de la industria del papel generan dos tipos de residuos: las cenizas producidas por la combustión de biomasa y los lodos generados en los sistemas de tratamiento de efluentes. Desde las calderas de combustión de biomasa se genera entre un 2-6% de cenizas por cada tonelada de corteza quemada, que se fraccionan en 1/3 de cenizas de fondo de parrilla y 2/3 de cenizas volantes provenientes del multiciclón y del precipitador de la caldera de biomasa. El otro residuo que generan las actividades de una industria papelera son los lodos provenientes de las plantas de tratamiento de efluentes, donde se estima en 240 t de lodos por 10.000 t de papel producido. En algunos casos, parte de este lodo se reutiliza como combustible para las calderas, pero la mayor parte es dispuesta en rellenos sanitarios.

Existe evidencia que muestra que la adición de lodos derivados de la fabricación del papel al suelo aumentan el contenido de materia orgánica (MO), P, S-SO_4, Zn y también mejorarían el pH de un Alfisol (Rios et al., 2012). Por su parte, Mendez et al. (2012) reportaron un aumento de la respiración microbiana y mayor estabilidad de los agregados, lo que ayuda a prevenir la degradación física del suelo. Igualmente se ha determinado un aumento de la MO y del contenido de P del suelo, generando un aumento de la biomasa en *Lolium perenne* L. cultivada en Andisoles (Gallardo et al., 2012). Mientras que Kumar and Chopra (2014) reportaron aumentos de los tallos, longitud de la raíz y en el rendimiento de *Phaseolus vulgaris* L. al ser fertilizado con efluentes de la industria papelera, donde la acumulación de metales en la planta se incrementó con el aumento de la dosis de lodos. Sin embargo se debe cuidar las cantidades adicionadas, ya que se ha evidenciado un aumento en las concentraciones de nitrato y amonio en los lixiviados de un Andisol enmendado con lodos derivados de la fabricación del papel (Gallardo et al., 2016).

La ceniza de madera es una fuente de minerales como P, K, Mg y Ca, a excepción de C y N que mayoritariamente se volatilizan durante la combustión, igualmente posee un pH alcalino que alcanza a 9,5, sugiriendo que podría ser utilizado como un agente encalador y/o un fertilizante (Odlare and Pell, 2009, Pan and Eberhardt, 2011).

A nivel mundial la mayor parte de la industria de pulpa y papel opera con el proceso Kraft, que utiliza un molino de reciclaje como una unidad suplementaria, donde una gran fracción de la hemicelulosa se libera en el licor negro, que eventualmente se quema en la caldera de recuperación para la generación de vapor y electricidad, por tanto la generación de residuos finales es reducida (Thompson et al., 2001).

Con respecto a la utilización de las cenizas como enmienda de suelos, Ochecova et al. (2014) reportaron que los tratamientos con ceniza de madera mostraron aumentos de nutrientes y de pH en los suelos, causando una disminución de la movilidad de los elementos potencialmente tóxicos para las plantas. También se les ha atribuido un efecto encalador aumentando los niveles de saturación de bases, la capacidad de intercambio catiónico y el pH de un suelo forestal (Ingerslev et al., 2014). Los lodos y cenizas se pueden peletizar para disminuir el contenido de agua del lodo y el volumen de la ceniza, lo que facilitaría su transporte, envasado y aplicación al suelo (Steenari et al., 1999, Watanabe and Tanaka, 1999).

1.2. Bioensayos de toxicidad con germinación de semillas

La realización de bioensayos de toxicidad, ayudan a determinar el éxito o aptitud de una plántula para establecerse en un ambiente determinado, lo que es relevante para garantizar la supervivencia de la especie (Sobrero and Ronco, 2004). La fitotoxicidad es el resultado de una combinación de varios factores que interfieren en la germinación y crecimiento de plantas, tales como la exposición a metales pesados, amoníaco y sales, entre otros (Hoekstra et al., 2002). Los metales pesados son considerados contaminantes y tóxicos para los cultivos como el Cd, Cr, Cu, Ni, Pb y Zn, los que pueden inhibir la germinación de las semillas y la elongación de la raíz cuando su concentración supera lo tolerado por las plantas (Chapman et al., 2010). Los bioensayos de toxicidad se pueden realizar con plantas o con un crustáceo de agua dulce. Dos especies de plantas son comúnmente utilizadas en bioensayos de fitotoxicidad, el trigo (*Triticum aestivum* L), y la lechuga (*Lactuca sativa* L), y el crustáceo conocido como pulga de agua (*Daphnia magna*) los que incluso están estandarizados como métodos analíticos (ISO11269-2, 2012, ISO17126, 2005).

Con respecto a la adición de residuos al suelo y la evaluación de fitotoxicidad con semillas, se ha reportado que al aplicar extractos de un suelo Alfisol en mezcla con lodos de salmonicultura y lodos municipales, no se generaron efectos negativos sobre la capacidad de germinación y desarrollo de semillas de lechuga, cuando la dosis aplicada no superó el equivalente a 100 Mg ha^{-1} de lodo seco (Celis et al., 2007). Igualmente al evaluar la toxicidad en semillas de lechuga en extractos de un suelo Entisol en mezcla con biosólidos de salmonicultura, piscicultura y lodos urbanos, se encontró que el lodo de salmonicultura fue el que presentó mejor índice de germinación (IG) en la lechuga, seguido del biosólido de piscicultura. Por el contrario, el lodo urbano fue el que presentó menor IG, crecimiento de la radícula y desarrollo del hipocotilo de la lechuga, cuando las dosis de lodo aplicado al suelo alcanzaron los 150 Mg ha^{-1} (Celis et al., 2006). Se ha encontrado una inhibición en la germinación de berro (*Lepidium sativum* L.), cebada (*Hordeum vulgare* L.) y avena (*Avena sterilis* L.), al ser evaluadas en extractos de lodos del tratamiento de aguas residuales. Los lodos podrían utilizarse como enmienda al suelo, por sus altos niveles de nutrientes y su contenido de metales pesados más bajos que los niveles máximos permitidos por la legislación española (Walter et al., 2006).

1.3. Modelos de mineralización de nitrógeno

La evaluación de la mineralización del N de la MO del suelo, es un indicador de la cantidad de N orgánico transformado a inorgánico en condiciones de humedad, tiempo de incubación y temperatura del suelo óptimos para el buen desarrollo de los microorganismos, que intervienen en este proceso (Gilmour and Mauromoustakos, 2011). Dos factores principales se han definido importantes en la trasformación de compuestos orgánicos nitrogenados en el suelo. El primero es el N potencialmente mineralizable (N_0) que se refiere a la máxima cantidad de N inorgánico que se puede formar dependiente de los procesos de mineralización y de inmovilización que están determinados por la relación de C/N del sustrato. El segundo factor es la tasa de mineralización de N (k), que depende del tipo de suelo, condiciones ambientales y la forma más o menos lábil de la MO (Gil et al., 2011). El concepto de *No* fue propuesto por Stanford and Smith (1972), y se refiere a la cantidad del N orgánico que puede ser trasformado a formas inorgánicas solubles, principalmente NH_4^+ y NO_3^- por la actividad de la biomasa microbiana. Esto permite cuantificar el aporte de N del suelo o de algún sustrato y que está potencialmente disponible para los cultivos, y permite generar recomendaciones sustentables de aplicación de fertilizantes nitrogenados (Campbell et al., 1995).

Es importante cuantificar los factores de N_0 y k, incorporándolos en modelos matemáticos relacionados con el ciclo de N en el suelo. El uso de estos modelos tiene como objetivo evaluar o predecir los fenómenos observados de datos experimentales con el propósito principal de obtener datos cuantitativos de los aportes potenciales, para recomendar la adición de N al suelo (Camargo et al., 2002). Se han utilizado diferentes modelos para determinar la cinética de mineralización de N en el suelo encontrándose modelos exponenciales simples, dobles y especiales, igualmente modelos parabólicos e hiperbólicos, donde según Gil et al. (2011), el modelo que mejor se ajustaría después de un año de evaluaciones de mineralización por incubación de suelos es el modelo exponencial simple descrito por Stanford and Smith (1972), mientras que a los 2 años de incubación sería más adecuado utilizar el modelo exponencial especial, determinado por Bonde and

Rosswall (1987). Con respecto a la adición de residuos en el suelo y mineralización de N, algunos autores como N'Dayegamiye (2009) encontró aumentos en la mineralización de N, la tasa de respiración microbiana y el contenido de C, después de que un suelo franco arenoso fue enmendados con una mezcla de lodos derivados de la fabricación del papel. Mientras que de Andrade et al. (2013) reportaron que aplicaciones sucesivas de los lodos de depuradora incrementaron el C y N potencialmente mineralizable en el suelo estudiado.

1.4. Hipótesis

La aplicación de enmiendas peletizadas compuestas por cenizas y lodos de la industria del papel mejoran la fertilidad de un Alfisol degradado.

1.5. Objetivos

1.5.1. Objetivo General

Evaluar el potencial de residuos peletizadas de la industria de la pulpa y papel como enmienda en un Alfisol degradado.

1.5.2. Objetivos específicos

- Evaluar la toxicidad por aplicación de dosis creciente de pellet de ceniza y lodos con plantas indicadoras.
- Evaluar el potencial de disolución de macro y micronutrientes de pellet aplicados en diferentes dosis en un Alfisol.
- Determinar la evolución de la mineralización de N proveniente de los pellet de cenizas y lodos.

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II. CAPITULO 1: PELLETIZED PAPER MILL WASTE PROMOTES NUTRIENT INPUT AND N MINERALIZATION IN A DEGRADED ALFISOL

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Artículo aceptado para publicación en Chilean Journal of Agricultural Research, Volumen 77, Número 4, Diciembre 2017.

2.1. ABSTRACT

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

Key words: soil incubations; N modeling; paper and pulp mill waste; pelletized wastes; pelletized ash/sludge.

2.2. INTRODUCTION

In 2013, worldwide pulp production reached 179 million Mg, with the United States the largest global producer at 30%, followed by China, Canada, Brazil and Sweden, with Chile in tenth position at 3.1%. The ten largest world producers of cellulose account for 90% of production (ODEPA, 2014). In Chile, the paper and pulp mills generated waste that reached 10.4 million Mg in 2009. An alternative valuation of waste from paper mills is their use as amendments or improvers of degraded soils, a problem that affects a large portion of the agricultural and forestry soils in pulp and paper producing countries. This option of using these residues in agricultural soils has been slowed down by social factors such as concerns over environmental pollution (Arellano and Ginocchio, 2013, Gallardo et al., 2016). Therefore, it is necessary to analyze the residues to discard any that may contain hazardous compounds, and that the heavy metal contents are at sufficiently low levels to not limit their application to soil (Rios et al., 2012). Industries have implemented actions to achieve sustainable development, including reducing the amount of waste generated 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 generate between 2–6% of ash for each mega gram (Mg) of bark burned, with a third being bottom ash and the rest fly ash. Sludge from effluent treatment reaches 240 Mg per 10000 Mg of produced paper, which is partly reused as fuel for boilers, but is mostly deposited in landfill.

Wood ash is a source of minerals such as P, K, Mg and Ca, with the exception of C and N that 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, which eventually burns in the recovery boiler for steam and electricity generation, therefore reducing the final waste production (Thompson et al., 2001).

Regarding the use of ash as a soil amendment, Ochecova et al. (2014) reported that soils treated with wood ash showed increases in nutrients and pH, causing a decrease in mobility of potentially toxic elements to plants. Ash also has a liming effect by increasing base saturation, cation exchange capacity, and the pH of forest soils (Ingerslev et al., 2014). However, no major heavy metal increases have been attributed to soils amended with wood ash, or negative effects to the microbiological processes in soil (Makela et al., 2012, Nayak et al., 2015).

There is evidence that the addition of sludge from paper mills to soil increases the organic matter (OM) content, P, SO_4-S, Zn and would also improve the pH of an Alfisol (Rios et al., 2012). It has also been reported an increase in microbial respiration and greater stability of aggregates, which helps prevent soil physical degradation. Likewise, an increase in OM and P content in soil have been found to generate an increase in the biomass of *Lolium perenne* L. grown in Andisols. While Kumar and Chopra (2014) reported increases of stems, and root length and yield of *Phaseolus vulgaris* L. fertilized with effluent from paper mills, where the accumulation of metals in the plants increased with increasing sludge dosage. However, 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 has 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. This has not, however, been observed with smaller doses of granulated ash, at least not in the short term when much of the Ca may still be in an insoluble form. Furthermore, the retention of nutrients contained in the ash in the recipient soil varies greatly among elements as well as among sites; K, especially, may be readily lost through leaching (Huotari et al., 2015).

The N mineralization of soil OM is an indicator of the amount of organic N transformed to inorganic N under optimal conditions of humidity, incubation time, and soil temperature for the development of microorganisms involved in this process. Two factors are important in the transformation of nitrogenous organic compounds in the soil, the first is the potentially mineralizable N (N_0) that refers to the maximum amount of inorganic N that can be formed dependent on the mineralization and immobilization processes determined by the C/N ratio of the substrate. The second factor is the mineralization rate of N (k), which is dependent on soil type, environmental conditions, and more or less labile OM form (Gil et al., 2011). The concept of *No* was proposed by Stanford and Smith (Stanford and Smith, 1972), and refers to the amount of organic N that can be turned into soluble inorganic forms, mainly NH_4^+ and NO_3^- by the microbial biomass activity. With this model, it is possible to quantify N contribution of soil or substrates potentially available for crops, and allows the generation of sustainable recommendations for the dosage of N fertilizers (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 soil. The objective was to evaluate pelletized pulp and paper mill waste on the potential N mineralization and nutrient supply in a degraded Alfisol.

2.3. MATERIALS AND METHODS

The waste used in manufacturing the pellets were obtained from the Papeles Biobío, Concepción, Chile. The Unidad de Desarrollo Tecnológico (UDT) of the Universidad de Concepción manufactured pellets experimentally. The waste corresponded to multicyclone and precipitator fly ash of a thermoelectric generation boiler from vegetal biomass combustion consisting mainly of wood and pine bark mixed at a ratio of 50:50 w/w. Sewage sludge was also used, which was dehydrated to obtain adequate moisture content for the pellets. Pellets were composed mostly of ash (56–70%), sewage sludge between 0– 20%, and mineral gypsum was used as a binder and cement, which was incorporated between 24–30%. Three types of pellets (Pellets 1, 2, and 3) with different sludge and ash ratio were manufactured (Table 2.1). For the incubation test, pellets were minced to obtain a uniform mixture and higher contact area with the soil. The pellets were manufactured by compression until they reached adequate sizes and firmness to be handled and applied to agricultural soils (Figure 2.1).

Table 2.1. Proportion ash, sludge and gypsum (%), for each type of pellet.

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

Figure 2.1. Cylindrical aspect of manufactured pellets for compress with ash and sludge from a paper mill.

2.3.1. Characterization of Paper Mill Waste for Pellet Manufacturing

The waste used for pellet manufacturing was characterized through chemical analysis. Three types of ash were sampled from the vegetal biomass combustion, corresponding to grill, multicyclone and precipitator ashes; sewage sludge samples and pellet were also analyzed. Chemical analyses determined pH, total P by colorimetry with a spectrophotometer (Perkin-Elmer model Lambda 3B, Phoenix, Arizona, USA) (Sadzawka et al., 2006, Cieslik et al., 2015), and various metal elements were determined as total or pseudototal by acidic and alkaline digestions for quantification of Cr, Zn, Ni, Cu, Pb, Cd, Ba, Mo, Sb, Se, As, Hg, Mg, Al, Fe, Ca, Na and K according to the USEPA Method 3051A (HNO_3/HCl) (Lapa et al., 2007, Barbosa et al., 2013). The quantification of metals was achieved through atomic absorption spectroscopy. The alkaline digestion was performed following USEPA Method 3060A using a mixture of NaOH + Na_2CO_3. The quantification of Cr VI was conducted as per USEPA Method 7196A. The content of C, N, and S was measured using an automatic analyzer Leco (LECO Corporation, Saint Joseph, Michigan, USA) (Barbosa et al., 2013, Cieslik et al., 2015). Pellet 2 was also analyzed, with the same methodologies to obtain a reference composition with respect to what raw materials such as sewage sludge, fly ash and mineral gypsum were used in the manufacture of pellets.

2.3.2. Soil Characterization and Incubation Experiment with Pellets

The soil was an Ultic Palexeralfs (Stolpe et al., 2008) obtained from an arable layer 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 to 2 mm, and soil chemical characteristics such as OM, N, P, K, exchange cations, and micronutrients were determined using the methodologies of Sadzawka et al. (2006) (Table 2.2).

An incubation experiment was carried out to evaluate the mineralization potential of the incubated soil together with the disintegrated pellets. The three pellet types were used in four rates equivalent to 0, 10, 20, and 40 Mg ha^{-1} in 200 g soil (the application rates are ha). The selected application rates are experimental and high, in limit so as not to cause damage in seed germination. The pellet/soil mixtures were placed in plastic containers of 20 cm diameter and 10 cm height, under controlled conditions at 25 °C and constant moisture at field capacity, equivalent to the optimum with an adequate relationship between water and air to 1/3 atm. For the calculation of water and applied doses, bulk density was considered (Table 2.2). Treatments were carried out in triplicate, including a control with soil alone. The experimental design was completely randomized with factorial arrangement, which resulted in a total of 50 treatments that considered three factors: dose, pellet type, and incubation time.

Table 2.2. Chemical characterization of Alfisol used in incubation experiments with pellets.

Property[1]	Value
Bulk density, g cm^{-3}	1.20
pH_{H2O}	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}	26.2
Zn, mg kg^{-1}	0.80
Cu, mg kg^{-1}	1.10

[1] All these elements are plant available.

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

2.2.3. Potential of N Mineralization

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

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

where Nm_t is the mineral N accumulated at a specific time (mg kg^{-1}); No is the potentially mineralizable N (mg kg^{-1}); k is the mineralization rate constant; and t is the time of incubation in weeks.

2.3.4. Statistical Analysis

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

2.4. RESULTS AND DISCUSSION

2.4.1. Chemical Characterization of Ash, Sludge, and Pellets

Waste used in the manufacture of pellets present important contributions of chemical elements that function as nutrients for plants, and are beneficial to soil, where C stands out in ash, sludge, and in analyzed pellets (23.5%) (Table 2.3). Only Pellet 2 was analyzed as it was representative of the other pellets which were manufactured with different ratios of the analyzed ash and sludge. Only the C from sewage sludge was organic; the one from the ashes was biochar generated by incomplete combustion of vegetal biomass, which is recalcitrant C that is very seldom mineralizable in soil, and not a source of energy for microorganisms (Shrestha et al., 2010), but enhances physical properties and cation exchange (Liang et al., 2006). N and P contents in Pellet 2 were low in the original materials as well as the pellets, with values between 0.31% and 0.33%, respectively (Table 2.3). In ash, N is especially low because during the wood combustion process, N compounds are volatilized, and therefore the ash contributes very little to pellet N. However, K contribution was mainly from ash with 2.37% and 0.89% Mg, similar to values obtained by Brannvall et al. (2015) who pelleted fly ash with municipal biosolids and applied them to forest soils, and to those found by other authors who studied fly ash as amendments (Mladenov and Pelovski, 2012, Ochecova et al., 2014). Ash composition was 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 2.4). In our study, the high content of Ca (reaching values of 9.07%) in pellets was due to use of gypsum as a binder (Table 2.1), whereas ash and sludge only contributed 3.00% and 0.25%, respectively. Likewise, S in the pellets was 3.92% due to the contribution of gypsum, in contrast to the contribution by ash (0.33%) and sludge (0.52%). The sulfur content in ash was similar to those found in other investigations with fly ash content between 0.16% and 0.41% (Barbosa et al., 2013), while bottom ash had a lower S content (0.12%) (Tan and Lagerkvist, 2011).

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

Sludge presented 1.68% N and low contents of bases such as Ca, Mg and K (less than 0.25%) (Table 2.3), and a content of 0.29% P, similar to that reported by Walter et al. (2006). The sludge had acidic pH (5.18), making it suitable for use as a mixture with pelletized fly ash to neutralize its acidifying potential and thus complementing the contribution of elements, especially in degraded soils (Park et al., 2012, Brannvall et al., 2015). Furthermore, the sludge contributed 26.0% organic C that compensated for the biochar or black C contributed by the ash and was not an energy source for soil microorganisms.

Of the metals analyzed in the bottom and fly ashes, high concentrations of Al, Si, and Ti (Table 2.4) were observed being the elements with the greatest contribution in all ash produced in the combustion of vegetal biomass, with values of 1.04 %, 6.71%, and 1.50% respectively, followed by Sr with 0.14%. The others metals were in much lower concentrations, being V, Cr, As, Ba, Ni, Pb, and Co, the lowest between 78.5–8.0 mg kg^{-1} (Table 2.4) (Norris and Titshall, 2011, Ingerslev et al., 2014, Olsson et al., 2017).

Table 2.3. Chemical characterization of ash and sludge used in the manufacture of pellets and a manufactured pellet.

Property	Ash[1]	Sludge	Pellet 2
Humidity, %	0.99 ± 0.95	11.1	12.6
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	26.0	23.5
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	0.003	
Fe, %	2.13 ± 0.39	0.16	1.54
Mn, %	1.29 ± 0.35		0.09
B, mg kg^{-1}	$<1^{(\dagger)}$	$<5^{(\dagger)}$	7.3
Cu, mg kg^{-1}	81.00 ± 8.20	69	56
Zn, mg kg^{-1}	60.50 ± 7.68	156	265

[1] Ash values are mean of three samples; ± standard deviation; $^{(\dagger)}$value under the detection limit of method; EC: electrical conductivity.

Other metals were not detected in the ashes as their concentrations were below the sensitivity of the analytical method, such as Cd and Hg with values lower than 2 and 1 mg kg^{-1}, respectively. In general, the heavy metal content in ash was lower than those reported by Lapa et al. (2007) for Cr, Cu Fe and Al as the ash came from the combustion of mainly wood and pine bark.

Table 2.4. Content of heavy metals in ash and sewage sludge used in the manufacture of pellets and a manufactured pellet.

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		
Chromo, 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(†)		
Nyquil, 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 method.

Lapa et al. (2007) also reported Al contents of 2–4% in fly ash. Norris and Titshall (2011) found high Al, Fe, and Mn contents, though lower than those found in our study, which may have been due to the type of waste used and the biomass used in combustion that generated the ash. In the sludge and pellets, only some of most toxic metals such as As, Cd, Hg and Se were analyzed due to the detection limits of the analytical equipment. Results of the sewage sludge showed only 8 mg Cr kg^{-1} (Table 2.4), but also detected contents of Cu and Zn of 69 and 156 mg kg^{-1}, respectively (Table 2.3), which are considered as beneficial nutrients in normally deficient degraded soils (Norris and Titshall, 2011, Ingerslev et al., 2014). The analyzed pellet presented values of Ni and Pb of 13 and 9 mg kg^{-1}, respectively, coming from the ash. In contrast, 151 mg Cr kg^{-1} could be increased by contributions of gypsum and ash (Table 2.4).

2.4.2. Nutrients Input from Three Types of Pellets Incubated in a Degraded Alfisol

The incubation of low fertility degraded Alfisol (Table 2.2) showed changes in some selected properties, such as pH and OM content, after 60 d incubation at 25 °C and humidity at FC. The pH decreased with incubation in the control treatment from 6.16 of the original soil (Table 2.2) to 5.82 at 45 d of incubation. This occurred naturally due to the increase in microorganism activity because of the optimal conditions in humidity and temperature of the incubated soil (Tambone and Adani, 2017). In addition, the soil with three types of pellets presented similar behavior (Figure 2.2a), pH values decreased slightly between 15 and 60 d; however, the pH decrease was less marked than in the control, demonstrating the power of palletized amendments to correct soil pH. Three pellet types showed significant differences ($p < 0.05$) between 10, 20, and 40 Mg ha^{-1}, especially for Pellet 1, which contained a higher proportion of fly ash. The highest pH values were presented with the highest dose of 40 Mg ha^{-1} in amended soil (Gagnon et al., 2012, Brannvall et al., 2015), which demonstrated that pellets containing fly ash could correct the acidity of degraded soil; on average 0.1 pH unit per 5.5 Mg of pellets according our results in the studied Alfisol that presented a low buffer capacity.

The OM content of soil incubated with three pellet types decreased significantly during the incubation period (Figure 2.2b). This was consistent with the initial soil levels and amounts of C added (de Andrade et al., 2013), especially with Pellet 3 containing 20% sludge (Table 2.1), which made the reduction of OM more pronounced. This was due to higher activity by the microorganisms present in the soil that favor the higher organic C content contributed by the sludge (Odlare et al., 2014). Furthermore, Pellet 3 had the highest initial OM content at 15 d of incubation ($p < 0.05$) at 40 Mg ha^{-1} due to the greater contribution of sewage sludge, but at 60 d of incubation, the content was lower than that of Pellet 1 as Pellet 3 had a higher content of organic C, and therefore more energy for soil microorganisms. Pellet 1 contained only inorganic C or black carbon, which is not mineralizable (Figure 2.2b).

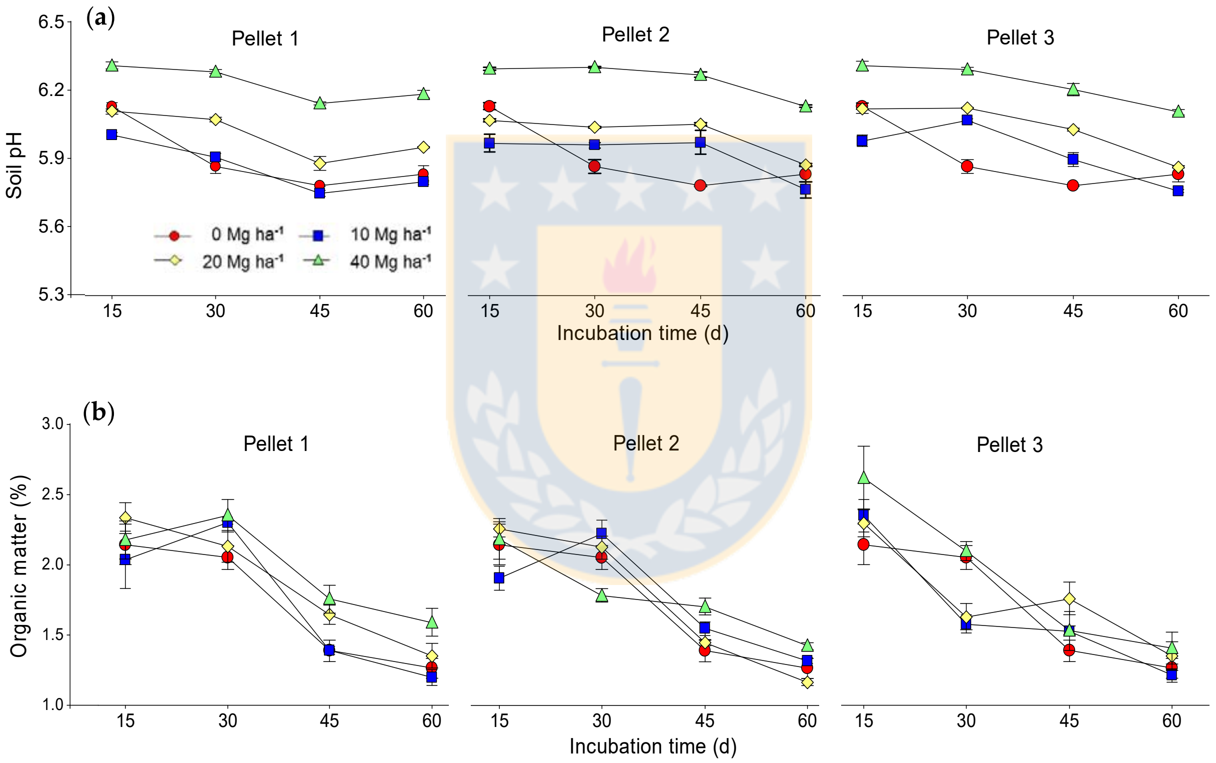

Figure 2.2. (a) Soil pH, and (b) organic matter during 60 d incubation of an Alfisol amended with different doses and pellet types. Vertical bars correspond to standard error of the three samples.

The control treatment (that did not receive pellets as an amendment), also showed a considerable decrease in OM content during incubation time as the low organic C present in soil was utilized by microorganisms as an energy source due to the optimal conditions for development, with the ideal humidity and temperature conditions provided in the incubation experiment (Tambone and Adani, 2017, Yanardag et al., 2017). Additionally, the Alfisol utilized did not have forms of C protection as it as degraded with no clays or amorphous elements to protect the C, for example, Al content was very low (Table 2.2).

The evolution of N mineral contents in soil incubated with the three pellet types did not present a clear pattern with doses and type of pellet (Figure 2.3a), indicating that mineral N changed very little during the incubation time, with the exception of Pellet 1 at 10 Mg ha^{-1}, which increased markedly at 30 d incubation, but then decreased, possibly due to a lack of organic C which slows down the activity of N mineralizing microorganisms. Pellet 2 was the only one with higher contents for the three doses at 60 d incubation ($p < 0.05$) and with positive slopes in the curves (Figure 2.3a). Due to these results, the mineralization of N must be evaluated according to more complex models that allow the determination potential of mineralization 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 tendency to increase during incubation for the three pellet types, as well as the control treatment (Figure 2.3b). Pellets did not activate an extra release of P Olsen; but dose effect was observed, finding higher contents with 40 Mg ha^{-1} for the three pellet types ($p < 0.05$) due to contributions of fly ash (Nurmesniemi et al., 2012, Ingerslev et al., 2014, Brannvall et al., 2015).

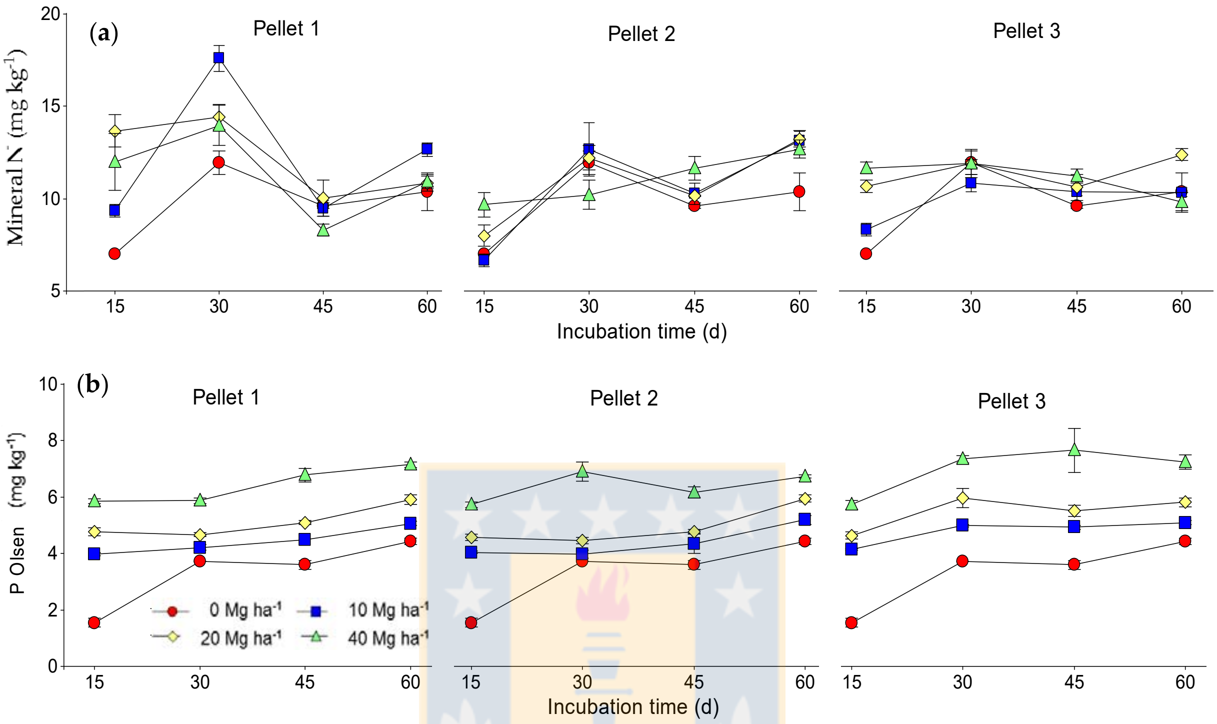

Figure 2.3. Availability of (a) N mineral, and (b) P Olsen during 60 d incubation in an Alfisol amended with different doses and pellet types. Vertical bars correspond to standard error of the three samples.

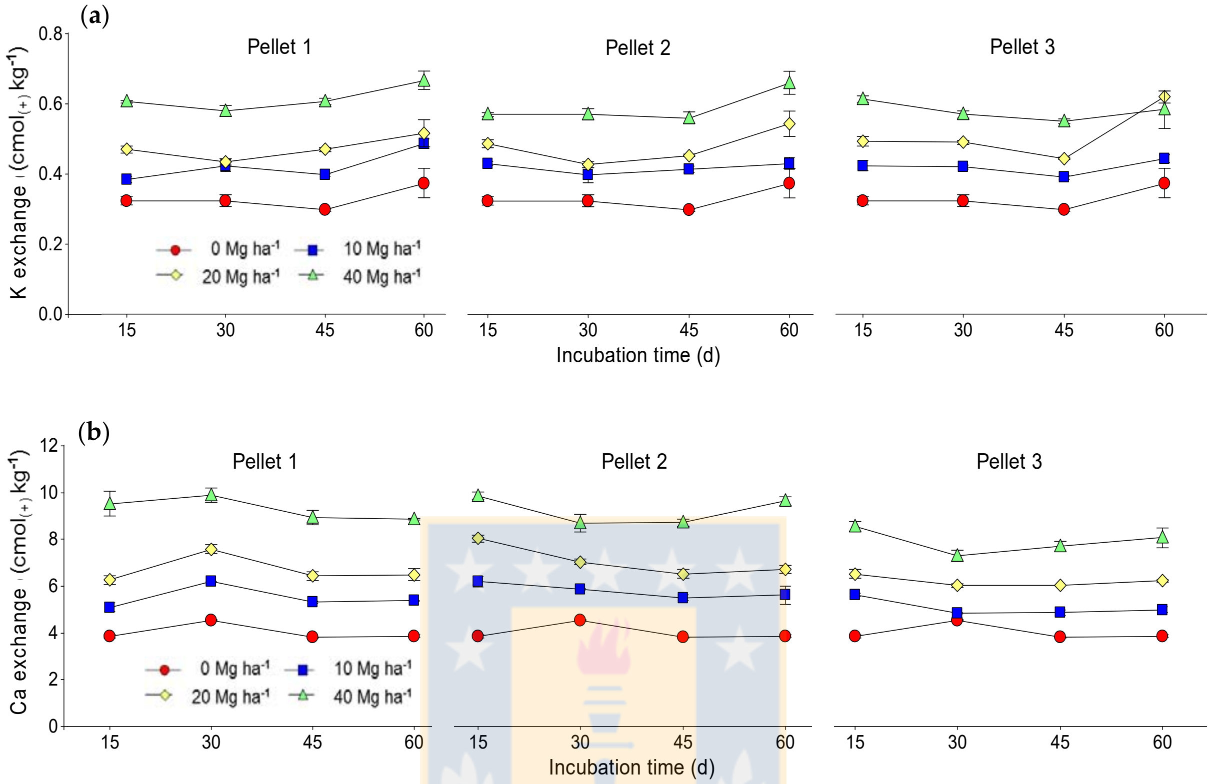

Figure 2.4. Availability of (a) exchange K, and (b) Ca during 60 d incubation in an Alfisol amended with different doses and pellet types. Vertical bars correspond to standard error of the three samples.

Contents of interchangeable K and Ca in degraded Alfisol, unlike other elements analyzed, were present in soil at sufficient levels for crop nutrition, and soil did not naturally increase its contents with incubation time (Figures 2.4a and 2.4b), as seen at 15 and 60 d of incubation ($p > 0.05$). This was similar to that indicated by several authors in References (Park et al., 2012, Brannvall et al., 2015), who described that both exchange bases increased with applied doses, but there was no contribution from soil for incubation time. Ca exchange was contributed in part by fly ash (3.00%), and to a greater proportion by the gypsum used as a binder (9.07%), which was reflected in the final content of the pellets (Table 2.2), and therefore expressed in higher contents for the 40 Mg ha^{-1} dose for the three pellet types throughout the incubation period ($p < 0.05$) (Figure 2.4b).

2.4.3. Potential Mineralizable N

The net mineralization of N presented differences according to treatments applied to the soil and incubation times (Table 2.5). 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 2.5), with the lowest at 15 d. Net mineralized N presented contrasting behaviors in the incubation of Alfisol amended with pellets depending on the pellet type and dose due to little contribution of C from sludge and ash for soil microorganism development (Table 2.2), which was in contrast to that found by San Martin et al. (2016), who supplemented pellets with seaweed. The application of organic N sources to soils with less C as an energy source for microorganisms reduced N losses due to a lower rate of mineralization and prevented the generation of N_2O. Furthermore, moisture content is capable of affecting microorganism growth, and the drying and rewetting of added residues as amendments affect the dynamics of C and N (Shi and Marschner, 2014), especially in pellets with high contents of non-organic C contributed by ash, with low N content (Table 2.3). The control treatment showed lower N mineralization rates at 15 d, which was similar to that obtained by Rios et al. (2012) despite the control of soil moisture (Jeke et al., 2015).

Table 2.5. Net mineralization of N (*Nmt*) of soil/pellet mixture during 60 d incubation period, in an Alfisol amended with different doses and pellet types.

Treatments	Net mineralization of N (mg kg^{-1})				Mineralization equation
	15 d	30 d	45 d	60 d	
Control	1.77 c	6.65 abc	4.32 a	5.07 ab	$Nm_t = 5.561\,[1 - e^{(-0.0549\,t)}]$
P1T10	2.28 bc	10.77 a	2.64 ab	5.81 ab	$Nm_t = 5.985\,[1 - e^{(-0.0875\,t)}]$
P1T20	3.31 a	3.92 bc	–0.45 b	0.33 e	$Nm_t = 1.776\,[1 - e^{(-31595.5\,t)}]$
P1T40	2.53 abc	4.44 bc	–1.24 b	1.39 cde	$Nm_t = 1.782\,[1 - e^{(-61468.9\,t)}]$
P2T10	1.75 c	7.41 ab	5.00 a	7.90 a	$Nm_t = 9.405\,[1 - e^{(-0.0267\,t)}]$
P2T20	1.91 bc	6.18 bc	4.12 a	7.19 ab	$Nm_t = 8.525\,[1 - e^{(-0.0249\,t)}]$
P2T40	2.01 bc	2.65 c	4.07 a	5.12 ab	$Nm_t = 9.911\,[1 - e^{(-0.0818\,t)}]$
P3T10	2.13 bc	4.43 bc	3.96 a	3.94 bcd	$Nm_t = 4.312\,[1 - e^{(-0.0628\,t)}]$
P3T20	2.57 ab	3.78 bc	2.49 ab	4.25 bc	$Nm_t = 3.606\,[1 - e^{(-0.0870\,t)}]$
P3T40	2.41 bc	2.82 c	2.15 ab	0.73 de	$Nm_t = 2.030\,[1 - e^{(-3757.2\,t)}]$
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 columns indicate difference according to LSD Test ($p < 0.05$).

The mineralized N content did not change in the soil for any of the amendments tested. However, the method of evaluating potential mineralizable N was able to show differences with nonlinear regression equations, which was better at indicating the behavior of different pellet types and applied doses. Higher values of potentially mineralizable N (N_0) were present in Pellet 2 (Table 2.5) containing 10% sludge (Table 2.1), with N_0 values of 9.405, 8.525, and 9.911 mg kg^{-1} for 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 2.5). The estimation of mineralization potentials of N through nonlinear regression equations as it allows for a comparison of the different pellets used given that it is a simpler tool than the isotopic techniques.

Pellet 3 (containing 20% of sewage sludge) showed inhibition in N mineralization potential, as the curves of the net mineralized N projected at 120 d were below the control treatment with lower slopes (Figure 2.5). The mineralization rate constant (*k*) obtained for Pellet 2 were lower than those obtained by Hirzel et al. (2010) for an Andisol with addition of broiler bed. Pellet 1 (containing only ashes of biomass and gypsum as a binder, Table 2.5), behaved similarly to doses of 20 and 40 Mg ha^{-1} where N_0 values were lower than the control treatment.

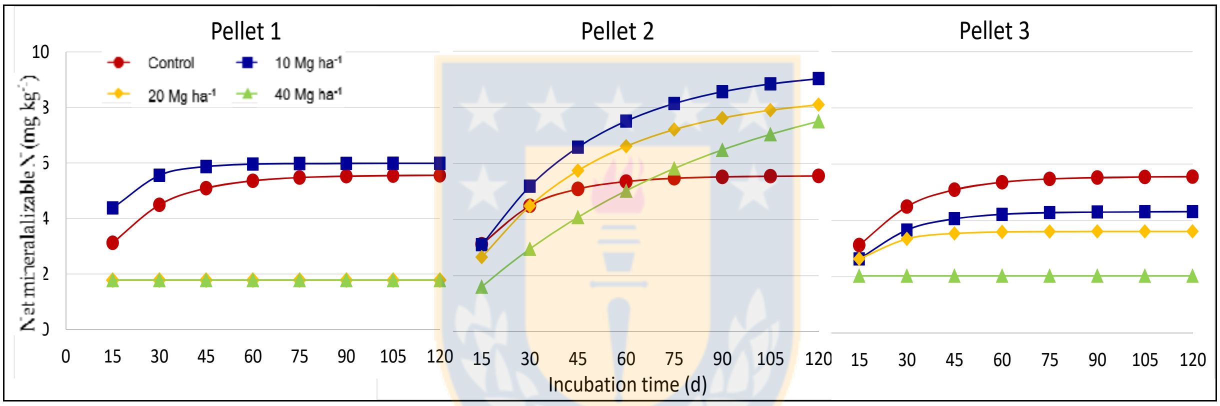

Figure 2.5. Potential N mineralization curves projected at 120 d by a first order nonlinear regression in an Alfisol amended with different doses and pellet types.

The results presented show promising advantages when applying the pelletized waste of pulp and paper mills as improvers for degraded soils, as it allows a sustainable use of industrial waste and a recycling of nutrients in forest soils. These residues would 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 due to organic C from sludge (San Martin et al., 2016). Pelletizing is also important as it allows the handling of two different wastes with mixtures in controlled proportions and facilitates transport and application to the soil with conventional agricultural machinery to achieve an adequate dosage and uniform application. Another positive aspect of pelletizing is that mixing the ash with the sludge produces a synergistic effect on the soils, especially in the mineralization potential of N.

Although the use of biomass ash as a soil amendment has been investigated, it has little been carried out with practical approaches such as pelletizing, which reduces ash volume by 75% by compressing pellets, improving efficiency in transport (Watanabe and Tanaka, 1999), and avoiding drift losses due to wind.

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 to evaluate more suitable binders than gypsum and the proportions of sludge, ash or the incorporation of other waste from the pulp and paper industry that can contribute useful elements to spatially degraded or eroded soils where forest production are carried out for pulp and paper raw materials, thus achieving sustainable production systems through the recycling of waste.

2.5. CONCLUSIONS

The amendment of a degraded Alfisol with pelletized waste from a paper and pulp mill presented different behaviors depending on the nutrient studied, dose, and proportion of ash and sludge present in the pellets. They contained elements that increased the fertility of degraded soils and to reduce soil acidity, and the higher proportion of ash determined a higher content of K and the gypsum used provided exchangeable Ca. Soil P increased due to the contribution of the pellets and time of incubation.

The method of evaluating of potential mineralizable N was able to show differences in activation of the N mineralization of the soil, according to pellet type and the doses used. Higher doses of 40 Mg ha^{-1} for all pellet types presented potentially mineralizable N curves below the control treatment.

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

Therefore, according to our results, pulp and paper waste can be used as amendments for degraded soils, creating a sustainable use of them. Pelletizing further facilitates transport and allows for a single application to evenly distribute sludge and ashes in the soils to be amended. This process allows for the sustainable use of these residues, giving them a utility for forestry and agricultural production thereby avoiding further pollution.

2.6. ACKNOWLEDGMENTS

This research was funded by the Unidad de Desarrollo Tecnológico (UDT), of Universidad de Concepcion, and Project INNOVA 13IDL-25554. UDT partially funded the research project of the Postgraduate Program in Agronomy Sciences of P. Undurraga.

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III. CAPITULO 2. TOXICITY OF PAPER MILL PELLETIZED WASTE USING GERMINATION AND BIOMASS PRODUCTION AS BIOINDICATORS

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Artículo en revisión en Ciencia e Investigación Agraria, 2017.

3.1. Abstract

P. Undurraga, J. Hirzel, J. Celis, C. Pérez and M.A. Sandoval. 2017. Toxicity of paper mill pelletized waste using germination and biomass production as bioindicators. Cien. Inv. Agr. The use of wood residues to produce energy and steam in the pulp and paper industry generates ash waste that is usually disposed of in garbage dumps along with sewage sludge. Wood ash contains nutrients plants need in appropriate proportions, and the sludge and ash pellet is a potential fertilizer. The objective was to evaluate the possible toxic effects of pelletized waste from the pulp and paper industry using bioindicators. Two controlled experiments were conducted with radish seeds (*Raphanus sativus* L.) and perennial ryegrass (*Lollium perenne* L.) seeds. The first experiment determined the germination index (GI) and root growth in soil extracts incubated with pelletized waste. The second was a pot experiment in which ryegrass seeds were sown in an amended Alfisol with pelletized waste; aerial and root biomass production was determined. Both experiments tested three types of waste pellets consisting of sludge and ash at three doses, including a control treatment. Results indicate that the Alfisol amended with pelletized waste did not exhibit any acute or sub-acute toxic effects in radish germination; none of the evaluated pellets showed

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evidence of deterioration in root elongation, including at the 40 Mg ha^{-1} dose. The highest root growth was obtained with pellet 2 at the 40 Mg ha^{-1} dose, which was higher than the control treatment ($p < 0.05$). Seed germination was between 93.9% and 100%. The highest ryegrass aerial biomass occurred with pellets 1 and 2 ($p < 0.05$). Pelletized waste from the paper industry exhibited neither mild nor acute toxicity effects in both radish seed germination and aerial and root biomass production of ryegrass sown in degraded soil where rather positive effects were detected.

Key words: Pulp and paper mill waste, pelletized ash/sludge, pelletized waste, radish, toxicity bioassay, ryegrass.

3.2. Introduction

Waste management in the pulp and paper industry has been mainly limited to collecting and disposing of waste in garbage dumps and landfills, and there has been little awareness of assessment alternatives (MMA, 2011). The lack of waste assessment is mainly attributable to legal and procedural barriers, which discourage the implementation of projects that attempt to reuse or valorize organic waste (Arellano and Ginocchio, 2013).

The three agricultural and forestry products mainly exported in Chile in 2014 were cellulose, grapes, and wine with protected designation of origin; cellulose represents the highest export percentage with 16% of the total. Cellulose production capacity is based on 16.6 million hectares of forest cover, of which 2.7 million are radiata pine (*Pinus radiata* D. Don) and eucalyptus (*Eucalyptus globulus* Labill.) plantations. This allows Chile to produce almost 6 million tons of cellulose annually, and two thirds of the total capacity is concentrated in the Biobío Region (ODEPA, 2014).

A waste assessment alternative of the pulp and paper industry is using it to improve degraded and eroded soils, which is a problem affecting most of the agricultural and forestry soils worldwide. In Chile, 64% of soils exhibit some type of erosion, and the Biobío Region has 32% of its area with some degree of erosion (CIREN, 2010). Eroded soils could be used as reservoirs to recycle waste; however, this has been curtailed by the social factor, especially in the case of biosolids, because of the concerns of communities about the possible effects of environmental pollution (Arellano and Ginocchio, 2013).

The paper industry annually generates approximately 4960 Mg of non-hazardous industrial waste in the Biobío Region at a rate of 15 to 30 kg for each ton of paper produced, including sludge, ash, and residual water (CORMA, 2012). This industrial waste is mainly ash from biomass combustion and sludge from the effluent treatment systems. Therefore, waste should be investigated and tested to ensure it does not contain any dangerous compounds, such as resin acids or heavy metal concentrations, that surpass the established norms and can limit its application to the soil (Rios *et al.*, 2012), as well as rule out toxic effects for grasslands, crops, and forest plantations.

Waste from the pulp and paper industry improves soil fertility and increases organic matter (OM) contents, nutrient content, such as N, P, and K, and can also increase the pH of acidified soils, which could be an alternative to using commercial lime (Faubert *et al.*, 2016). It can also improve physicochemical aspects, such as the structure and stability of aggregates, and enhance cation exchange capacity (Camberato *et al.*, 2006).

The first important evaluation stage is to determine the toxicity of waste that will be applied as soil amendments (Arellano and Ginocchio, 2013). Toxicity bioassays evaluate the success or aptitude of a plantlet to be established in a given environment (Sobrero and Ronco, 2004) because phytotoxicity results from combining factors that interfere with plant germination and growth, such as exposure to heavy metals, ammonia, and salts (Hoekstra *et al.*, 2002, Teaca and Bodirlau, 2008). The excess of heavy metals (e.g., Cd, Cr, Cu, Ni, Pb, and Zn) is contaminative and toxic for crops and can inhibit seed germination and root elongation when their concentration surpasses levels tolerated by plants (Chapman *et al.*, 2010). The toxicity bioassays can be conducted with plants; two species are commonly used, that is, wheat (*Triticum aestivum* L.) and lettuce (*Lactuca sativa* L.), as well as a crustacean known as the water flea (*Daphnia magna*), which are standardized as analytical methods (ISO11269-2, 2012, ISO17126, 2005).

Celis *et al.* (2007) evaluated toxicity by applying extracts of an Alfisol soil mixed with salmon farming sludge and municipal sludge; they used the germination and development capacity of lettuce seeds as indicators with doses equivalent to 100 Mg ha^{-1} dry sludge. Furthermore, salmon farming, fish farming, and urban sludge biosolids were applied to an Entisol (Celis *et al.*, 2006) to determine the germination index (GI), radicle growth, and hypocotyl development of lettuce with calculated doses of 150 Mg ha^{-1}. Other species, such as watercress (*Lepidium sativum* L.), barley (*Hordeum vulgare* L.), and oat (*Avena sterilis* L.) have also been used to evaluate sludge extracts from wastewater treatment (Rios *et al.*, 2012, Sobrero and Ronco, 2004). Assays have also been conducted with ryegrass in pots to evaluate the effects of residues in soil under controlled conditions (San Martin *et al.*, 2016, Sandoval *et al.*, 2013). The hypothesis is that the application of pelletized amendments composed of ash and sludge from the paper industry has a toxic effect on crops. The objective was to evaluate the phytotoxicity of waste from the paper industry and its potential as amendment in a degraded Alfisol soil by applying increasing doses of pellets composed of ash and sludge, and using radish and ryegrass as indicator plants.

3.3. Materials and Methods

3.3.1. Pellets and soil used in phytotoxicity experiments

The Papeles Biobío Company, Biobío Region, Chile generates waste used to manufacture pellets. Pellets were produced by compressing fly ash from the multicyclone and precipitator, biomass combustion residues from to generate energy in a 50:50 w/w ratio. Pellets mostly consist of ash (56% to 70%) to which 0% to 20% sewage sludge is added (Table 3.1) and 24% to 30% gypsum used for bonding and cementing. Three types of pellets were manufactured with different proportions of sludge and ash (Table 3.1). Pellets were experimentally produced by the Technological Development Unit (Unidad de Desarrollo Tecnológico, UDT) of the Universidad de Concepción. To conduct the experiments, the pellets were crushed to increase contact with the soil.

Table 3.1. Percentage composition of pellets experimentally manufactured by compression.

	Fly ash	Sludge	Gypsum
		——————————— % ———————————	
Pellet 1	70	0	30
Pellet 2	63	10	27
Pellet 3	56	20	24

The soil used for the toxicity experiments was a degraded Alfisol obtained at a 20 cm depth from the Huape sector (36º37’19” S, 72º19’42” W), Biobío Region, Chile. The soil belongs to the Cauquenes series and is classified as Ultic Palexeralfs (Stolpe *et al.*, 2008); it has an apparent density of 1.2 g cm^{-3} under cereal and naturalized grassland cultivation with degradation caused by water erosion. Natural vegetation is mainly hawthorn (*Vachellia caven* (Molina) Seigler & Ebinger) and litre (*Lithraea caustica* (Molina) Hook. & Arn.). Soil was dried at room temperature and sieved with a 2 mm sieve (Sandoval *et al.*, 2012). It exhibited the typical chemical characteristics of eroded soil with low fertility levels, 2.02% OM, pH 6.16 in water, mineral N and Olsen P values of 4.3 and 2.0 mg kg^{-1}, respectively, and medium to low exchange base values of 0.41, 5.08, and 1.42 $cmol_{(+)}$ kg^{-1} for K, Ca, and Mg respectively. Micronutrient levels of B, Zn, and Cu were 0.1, 0.8, and 1.1 mg kg^{-1}, respectively; these were determined by methods described by Sadzawka *et al.* (2006).

3.3.2. Phytotoxicity experiment with radish seeds

Three types of disaggregated pellets were added to 110 g sieved and air-dried Alfisol soil to generate homogeneous mixtures of three pellet:soil doses equivalent to 10, 20, and 40 Mg ha^{-1}. The mixtures were placed in polyethylene bags, incubated for 15 d in a growth chamber at a constant temperature of 20 °C, and moisture content was maintained at field capacity. A control treatment with soil only was included, and the experiment was triplicated. After incubation, the methodology described by Sobrero and Ronco (2004) was followed using radish seeds in a Petri capsule on Whatman N°3 filter paper saturated with 4 mL of extract obtained from each treatment. Twenty radish seeds were carefully placed using tongs and leaving enough space between them to allow radicle germination and elongation. Capsules were placed in a germination chamber where they were maintained for 120 h at 20 ± 2 °C. Capsules with distilled water were included as a negative control to ensure the radish seed germination potential; a positive control to ensure germination inhibition consisted of a 0.01 M Zn (II) salt concentration as a toxic reference.

The applied experimental design was a completely randomized factorial arrangement with three replicates. The factors were dose and pellet type.

Phytotoxicity was determined by GI suggested by Tiquia and Tam (1998), which allows evaluating the low or minor toxicity that affects root growth and high or major toxicity (Nafez *et al.*, 2015, Unuofin *et al.*, 2016), for the effect on radish seed germination expressed in equation 1:

$$GI = \frac{GxL}{G_c x L_c} x \quad 100 \qquad [1]$$

where *GI* is the germination index (%), *G* is the mean of germinated seeds in the sample, G_c is the mean of germinated seeds in the negative control, *L* is the mean of radicle length in the sample (mm), and L_C is the mean of radicle length in the negative control (mm). The value of GI can vary from 0 to more than 100%.

After 120 h, plantlets in the Petri capsules were counted and meticulously observed for any phytotoxicity indicator, such as necrotic root apices or poor development of absorbent hairs. The number of normally germinated seeds was recorded; the germination criterion was that the visible radicle was at least 5 mm in length. The radicle length of all the germinated seeds was also carefully measured.

3.3.3. Potted ryegrass biomass production

The experiment was conducted in pots under controlled conditions in the greenhouse of the Faculty of Agronomy of the Universidad de Concepción, Chillán. Each treatment used 1 kg of soil sieved with a 2 mm sieve and dried at room temperature (Sandoval *et* *al.*, 2013). The dose of disaggregated pellets was added to the soil of each pot, and the pellet and soil mixture was homogenized in a polyethylene bag. The treatment factors considered three types of pellets at four doses of 0, 10, 20, and 40 Mg ha^{-1}; ryegrass ‘Nui’ was sown at a dose of 1.5 g per pot with seeds previously disinfected with Thiram 0.5% fungicide. The experiment lasted three months and soil moisture was maintained at 80% field capacity (FC).

The experimental design was completely randomized with a factorial arrangement with four replicates. It included twelve treatments with four doses and three types of pellets, including a control treatment with only soil.

The aerial biomass evaluations were carried out with three cuttings when the ryegrass reached a height of 10 cm, leaving 2 cm of residue; this occurred 21 to 26 d between cuttings. Dry matter was measured at each cutting and the three cuttings were totaled. After the last cutting, plants were unpotted to quantify DM in the roots by carefully washing them with plenty of water. The DM of each ryegrass cutting and of the roots was determined by drying at 60 ºC in a forced-air oven until constant weight (Sandoval *et al.*, 2013).

3.3.4. Statistical analysis

The statistical analysis of data from the toxicity experiment with radish seeds and ryegrass biomass was performed with ANOVA, while the effect of means was analyzed by Tukey’s test with a confidence level of 95% ($\alpha = 0.05$). Data were analyzed with SAS software (SAS Institute, Cary, North Carolina, USA).

3.4. Results and Discussion

3.4.1. Phytotoxicity of evaluated pellets with radish seeds

In toxicity tests, inhibiting radicle or hypocotyl elongation has a sublethal effect, whereas inhibiting germination has a lethal effect. However, it must be corroborated that the seeds do not germinate because of embryo death; it must be ruled out that it was not simply a delay in the germination process and seed viability was maintained (Gvozdenac *et al.*, 2016, Rios *et al.*, 2012).

Table 3.2. ANOVA for the effects of dose and pellet type in a toxicity experiment with radish seeds.

Source of Variation	Germination index	Radicle length
Doses (D)	0.0287*	0.0211*
Pellet (P)	0.1965^{ns}	0.0944^{ns}
D × P Interaction	0.0015**	0.0048**

ns: nonsignificant; $*$ and $**$ significant at $p \leq 0.05$ or $p \leq 0.01$ by ANOVA, respectively.

Radish seed germination experiments in extracts of Alfisol incubated with different doses and pellets did not exhibit any toxic effects, including with the high doses up to 40 Mg ha^{-1}. These revealed no deterioration in radicle germination or elongation in any of the evaluated pellets. On the other hand, positive effects were detected on the evaluated parameters according to ANOVA (Table 3.2) with the Dose × Pellet type interaction. The highest radicle elongation in some treatments compared to the control (Table 3.3) is possibly attributable to positive stimulation (Teaca and Bodirlau, 2008). The highest radicle growth was obtained for pellet 2 at the 40 Mg ha^{-1} dose with a value of 14.03 mm, which was higher than the 11.71 mm value in the control treatment. Lower radicle growth values were exhibited in treatments with pellet 1 at 10 Mg ha^{-1}, pellet 2 at 20 Mg ha^{-1}, and pellet 3 at 40 Mg ha^{-1}, whose values were 11.52, 11.27, and 11.29 mm, respectively (Table 3.3); however, subacute toxicity cannot be considered because these values do not differ from the control ($p > 0.05$). Some plant species or populations are sensitive to abiotic stress or can be tolerant and show small inhibitions in germination or development in primary stages (Gvozdenac *et al.*, 2016, Mekki *et al.*, 2017). However, synergetic effects of doses and pellet types in our study generated positive effects in radicle elongation, GI, and radish seed germination (Table 3.3) similar to those found by other authors who studied pelletized residues (Rios *et al.*, 2012, San Martin *et al.*, 2016).

Table 3.3. Germination index (GI), germination (G), and radicle length of radish seeds germinated in soil extracts incubated with soil/pellet mixture in an Alfisol amended with different doses and pellet types.

Treatments		GI	G	Radicle length
Pellet	Dose	%		mm
Control	0	140.2abc	100.0a	11.71ab
Pellet 1	10	134.0abc	100.0a	11.52b
Pellet 1	20	140.4abc	100.0a	11.73ab
Pellet 1	40	145.8abc	96.7ab	12.58ab
Pellet 2	10	163.8a	100.0a	13.69ab
Pellet 2	20	125.9c	93.3ab	11.27b
Pellet 2	40	167.9a	100.0a	14.03a
Pellet 3	10	159.5ab	100.0a	13.32ab
Pellet 3	20	150.8abc	100.0a	12.59ab
Pellet 3	40	130.5bc	96.7ab	11.29b
SE		6.34	2.16	0.49
LSD		32.38	6.32	2.50

Control: Soil without amendment; SE: standard error; LSD = last significant difference. Different letters in columns indicate differences according to Tukey's test ($p < 0.05$).

Heavy metals or volatile substances can inhibit plant germination and growth and influence germination time (Nafez *et al.*, 2015, Opatokun *et al.*, 2017). Given the applied doses, the concentration of metals or other substances did not generate any toxicity level in pellets consisting of solid waste from the pulp and paper industry. The GI values were between 125.9% and 167.9% and germinated seeds between 93.9% and 100%

(Table 3.3). A GI greater than 80% indicates phytotoxicity-free material and a value less than 50% is considered as a high phytotoxicity level.

Seed GI is a direct indicator of residue or compost toxicity (Phoungthong *et al.*, 2016) because it directly establishes if the residues can inhibit plant growth when used as soil amendment or as a direct means of growth. A GI greater than 80%, observed for all the treatments in the present study, indicated that pellets mixed with a degraded Alfisol would have phytotoxin or heavy metal levels that do not affect plant growth (Unuofin *et al.*, 2016); instead, evaluated indices increased as indicated by the radish seed germination tests.

3.4.2. Aerial and root biomass of ryegrass amended with pellets

Fast-growing ryegrass plants were used as bioindicators of possible toxic effects of the amendment in a degraded Alfisol with ash and sludge pellets from the paper industry. The effects of doses and pellet types in the production and concentration of the aerial and root biomass of ryegrass sown in pots were evaluated (Table 3.4). The evaluated doses did not significantly affect biomass or DM concentration in the aerial part ($p > 0.05$), but differences were found in root biomass and DM production ($p < 0.05$; Table 3.4). On the other hand, pellet type showed differences in aerial biomass but not in root biomass (Table 3.4).

Table 3.4. ANOVA of the effects of dose and pellet type in ryegrass aerial and root biomass.

Source of Variation	Aerial biomass	Biomass % Aerial	Root biomass	Biomass % Root
Doses (D)	0.1972^{ns}	0.0745^{ns}	0.0002^{**}	$<0.0001^{**}$
Pellet (P)	0.0101^{*}	0.0003^{**}	0.2473^{ns}	0.5759^{ns}
D × P Interaction	0.0630^{ns}	0.0173^{*}	0.3522^{ns}	0.0221^{**}

ns: nonsignificant; ∗ and ∗∗ significant at $p \leq 0.05$ or $p \leq 0.01$ by ANOVA, respectively.

Aerial biomass is affected by pellet type; pellets 1 and 2 exhibited the highest productions with 2.91 and 3.14 g, respectively, and pellet 3 produced the lowest biomass with 2.46 g (Figure 3.1) after three cuttings in the three months that the experiment lasted. The low amounts of biomass were due to the low fertility of the degraded Alfisol, especially low levels of N, P, and micronutrients such as B. It must also be considered that the pellets contributed little N and P and instead contributed K, Ca, and S because of the ash, sludge, and gypsum proportions (Table 3.1). The ryegrass aerial biomass values were similar to those obtained by Celis *et al.* (2008), who used only sludge. This could explain the lower biomass production obtained with pellet 3, which contained the highest proportion of sewage sludge (20%; Table 3.1); this contrasts with pellet 1 without sludge and pellet 2 that included only 10%.

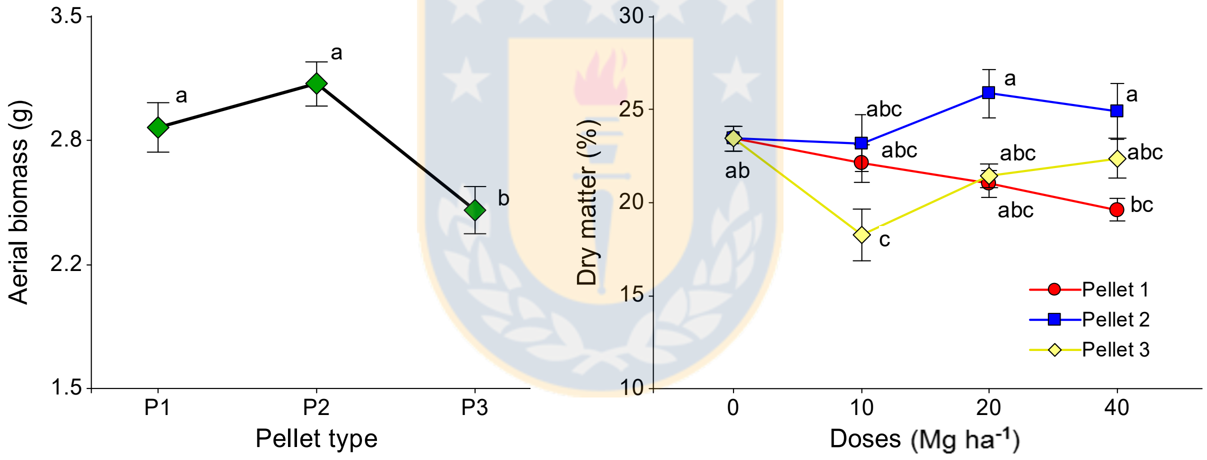

Figure 3.1. Ryegrass aerial biomass production with different pellet doses. (a) aerial biomass and (b) biomass dry matter concentration.

The dose and pellet type factors exhibited interaction on the aerial biomass DM concentration with the highest contents found for pellet 2 at the 20 and 40 Mg ha^{-1} doses with 25.9% and 24.9%, respectively (Figure 3.1b). These values are slightly higher than in the control treatment with soil only, which indicates that the pellet amendment does not generate any toxic or detrimental effects at the doses being used. However, DM content is not a good indicator of negative effects of using these pellet residues as amendments. In contrast, root DM contents were higher than in the aerial biomass, reaching 49.5% for pellet 1 at the 40 Mg ha^{-1} dose compared to the control (30%) (Figure 3.2b).

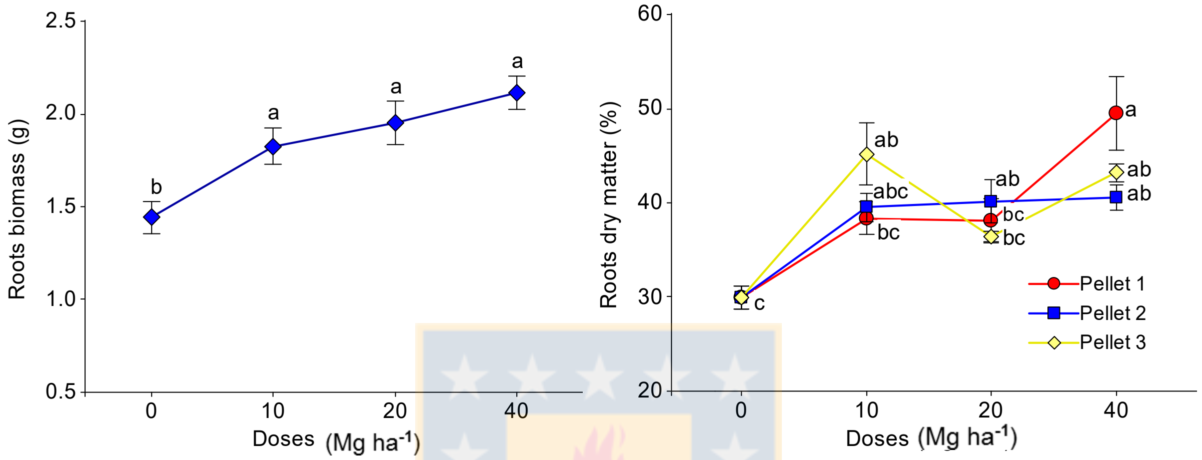

Figure 3.2. Ryegrass root biomass production at the end of the experiment. (a) root biomass and (b) root biomass dry matter concentration.

Root biomass production of ryegrass exhibited differences among treatments with dose being more important than pellet type. Root biomass responded to dose and reached 2.11 g at the 40 Mg ha^{-1} dose, which differed from the control treatment that did not apply pellets and obtained a value of 1.44 g ($p < 0.05$) (Figure 3.2b). In other words, applying pellets with ash and sewage sludge from the paper industry is beneficial for degraded soil and not detrimental or toxic (Adebayo *et al.*, 2015, Sharifi *et al.*, 2013); this indicates that the pellet components do not have toxic substances or heavy metals in concentrations that can affect germination or biomass production of indicator plants. This has been demonstrated by several authors using ash (Huotari *et al.*, 2015, Nayak *et al.*, 2015, Teaca and Bodirlau, 2008) as well as sewage sludge (Celis *et al.*, 2008, Faubert *et al.*, 2016, Nafez *et al.*, 2015). Although it is true that moderate doses do not exhibit toxic effects, they decrease germination or biomass production of indicator plants when they are only applied in doses greater than 60 Mg ha^{-1} (Celis *et al.*, 2008, Gerber *et al.*, 2017). For this reason, the use of pellet amendments consisting of waste from the pulp and paper industry is a good alternative. It complements the contribution of nutrients from sewage sludge and fly ash and decreases the detrimental or toxic effects that can be generated; pelletization also facilitates its application and uniform distribution in the field.

In conclusion pelletized waste from the paper industry exhibits neither mild nor acute toxic effects in radish seed germination evaluated by the germination index and radicle growth. On the contrary, beneficial effects were found that increased radicle development. This same behavior was demonstrated by applying the pellet with the highest proportion of ash and lower sludge content (up to 10%), which increased aerial and root biomass production of ryegrass sown in degraded soil amended with pelletized waste. The pellet with 20% sludge at the 40 Mg ha^{-1} dose decreased aerial biomass production, whereas pellet type had no effect on root biomass.

In accordance with these results, pelletizing ash and sludge waste from the pulp and paper industry becomes an alternative for use as amendment or fertilizer in degraded soils or as a complement to forestry or agricultural production because pellet technology facilitates the transport and application of waste. Furthermore, an alternative is generated to use environmentally sustainable waste and avoid disposal in garbage dumps.

3.5. Acknowledgements

This research was funded by the Unidad de Desarrollo Tecnológico (UDT) of the Universidad de Concepción and Project INNOVA 13IDL-25554. The UDT partially funded the research project of the Postgraduate Program in Agronomy Sciences of P. Undurraga.

3.6. Resumen

P. Undurraga, J. Hirzel, J. Celis, C. Pérez and M.A. Sandoval. 2017. Toxicity of paper mill pelletized waste using germination and biomass production as bioindicators. Cien. Inv. Agr. El uso de residuos de madera para producción de energía y vapor en industrias de celulosa y papel genera desechos en forma de cenizas, que junto a lodos de depuración son normalmente desechados en vertederos. La ceniza de madera contiene nutrientes que las plantas necesitan en proporciones adecuadas, y el pellet de lodos y cenizas es un fertilizante potencial. El objetivo fue evaluar posibles efectos tóxicos de residuos peletizados de la industria de pulpa y papel mediante bioindicadores. Se realizaron dos experimentos controlados con semillas de rabanitos (*Raphanus sativus* L.) y ballica perenne (*Lollium perenne* L.); en el primero se determinó el índice de germinación (GI) y crecimiento de radículas en extractos de suelo incubados con residuos peletizados. El segundo consistió en un experimento de macetas donde se sembraron semillas de ballica en un Alfisol enmendado con residuos peletizados, donde se determinó la producción de biomasa aérea y de raíces. En ambos experimentos se probaron tres tipos de pellets de residuos compuestos de lodos y cenizas en tres dosis, incluyendo un tratamiento control. Los resultados indican que el Alfisol enmendado con residuos peletizados no presenta efectos tóxicos agudos o sub agudos en la germinación de rabanitos, incluso con dosis de 40 Mg ha^{-1} no evidencian deterioro en la germinación o elongación de la radícula para ninguno de los pellets evaluados. El mayor crecimiento de la radícula se obtuvo con el pellet 2 en dosis de 40 Mg ha^{-1}, siendo mayor que el tratamiento control ($p < 0.05$). La germinación de semillas estuvo entre 93.9% y 100%. La mayor biomasa aérea de ballica se obtuvo con los pellets 1 y 2 ($p < 0.05$). Los residuos peletizados de la industria del papel no presentan efectos de toxicidad leve ni aguda, tanto en la germinación de semilla de rabanito como en la producción de biomasa aérea y de raíces de ballica sembradas en un suelo degradado, donde más bien se detectan efectos positivos.

Palabras clave: Residuos de industria de papel y celulosa, cenizas/lodos peletizados, residuos peletizados, rábano, bioensayo de toxicidad, ballica.

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IV. CONCLUSION GENERAL

La enmienda de un Alfisol degradado con residuos peletizados de la industria de papel y celulosa presentó comportamientos diferentes dependiendo del nutriente estudiado, la dosis y la proporción de cenizas y lodos presentes en los pellets. Estos contienen elementos que aumentan la fertilidad de suelos degradados y reducen la acidez del suelo, y la mayor proporción de cenizas determina un mayor contenido de K y el yeso utilizado como aglomerante proporciona Ca intercambiable. El P del suelo aumentó debido a la contribución de los Pellets y al tiempo de incubación.

El N potencial mineralizable fue capaz de mostrar diferencias en la activación de la mineralización de N del suelo, según el tipo de pellet y las dosis utilizadas. Dosis mayores de 40 Mg ha^{-1} para todos los tipos de pellets presentaron curvas N potencialmente mineralizable por debajo del tratamiento de control, sin embargo el pellet 2 que presenta proporciones intermedias de lodos y cenizas reportó los mejores valores de N potencialmente mineralizable.

Los metales pesados en las cenizas y lodos utilizados para la fabricación de los pellets, en general se presentaron en concentraciones bajas o por debajo de los límites de detección. Solamente los niveles de Cr, Ni y Pb presentaron niveles altos en el pellet 2 analizado, con 151, 13 y 9 mg kg^{-1}, respectivamente, pero no generaron un aumento en la concentración de suelos debido al efecto de dilución basado en las dosis utilizadas.

Los residuos como lodos de depuración y cenizas peletizadas de la industria papelera no presentan efectos tóxicos agudos o leves en la germinación de semillas de rábanito, evaluados por el índice de germinación y el crecimiento radicular. Por el contrario, se encontraron efectos beneficiosos en el aumento del desarrollo radicular. Este mismo comportamiento se demostró aplicando el pellet 1 y 2, con la mayor proporción de cenizas y menor contenido de lodo (hasta 10%), lo que aumentó la producción de biomasa aérea y de raíces de ballica sembrada en el suelo degradado enmendado con residuos peletizados. El pellet 3 con un 20% de lodo en dosis de 40 Mg

ha^{-1} disminuyó la producción de biomasa aérea, mientras que el tipo de pellet no tuvo efectos sobre la biomasa de las raíces.

De acuerdo con estos resultados, la peletización de los residuos de cenizas y lodos de la industria de pulpa y papel puede ser en una alternativa para su uso como enmienda o fertilizante en suelos degradados o como complemento a la silvicultura o producción agrícola debido a la tecnología de peletizado. Además, se genera una alternativa para la utilización de estos desechos que es ambientalmente sostenibles y evita su eliminación en vertederos.

Por lo tanto, de acuerdo con nuestros resultados, los residuos de papel y celulosa pueden ser utilizados como enmiendas para suelos degradados, ya que la peletización facilita el transporte y aplicación al suelo, además permite con una sola aplicación distribuir uniformemente los lodos y cenizas. Este proceso permite el uso sostenible de estos residuos, dándoles una utilidad para la producción forestal y agrícola, evitando así la contaminación adicional.