Antecedentes Norma Primaria de Suelos

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Hola, buenas tardes.

Estuve presente en el Webinar que se hizo hoy respecto a la norma de suelos que se está desarrollando y quiero aportar con antecedentes al respecto. En específico son antecedentes que hacen alusión a la aplicación de residuos industriales no peligrosos (RINP) de plantas de celulosa en suelos, como mejoradores.
Adjunto los papers que he leído al respecto, ya que estoy desarrollando un proyecto similar en mi empresa.

Saludos.

Sofía.

INFLUÊNCIA DA ADIÇÃO DE UM RESÍDUO ALCALINO DA....

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AFECCIÓN DE SUELOS AGRÍCOLAS POR METALES PESADOS EN ÁREAS LIMÍTROFES A EXPLOTACIONES MINERAS DEL SURESTE DE ESPAÑA

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RESUMEN

Se analiza la contaminación por metales en suelos agrícolas en el entorno de la Sierra minera de Cartagena-La Unión. El muestreo se realizó cogiendo 20 muestras de suelo en uso agrícola mediante una distribución aleatoria en un área de unos 100 km^2 en torno a la Sierra Minera.

Los resultados han detectado concentraciones importantes, que alcanzan y superan los niveles máximos permitidos por diversas normativas internacionales de hasta 11 de los elementos denominados «metales pesados». Aluminio y Hierro destaca sobre los demás con concentraciones medias porcentuales de 13% y 10% respectivamente. Pero hay que destacar la contaminación excesiva de plomo (Pb) y Zinc (Zn) que duplica e incluso triplica el máximo establecido por las leyes más permisivas, superando con mucho los niveles máximos a partir de los cuales se requiere una intervención obligatoria en todas las legislaciones consultadas.

Palabras clave: Minería, metales pesados, contaminación de suelos, sureste de España.

EFFECTS OF HEAVY METALS IN AGRICULTURAL SOILS ADJACENT TO MINING AREAS IN SOUTHEASTERN SPAIN

ABSTRACT

In this work we have analyzed metal pollution in agricultural soils near the mining district of Cartagena-La Union. Sampling was performed by taking 20 samples of agricultural soils through a random distribution in an area of 100 km^2 around the Sierra Minera.

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The results show significant concentrations that meet and exceed the maximum levels permitted by international regulations in eleven different heavy metals. Aluminum and Iron stand out above the others with mean concentrations of 13% and 10% respectively. It is also remarkable the excessive contamination of lead (Pb) and Zinc (Zn), doubling and even tripling the maximum established by the more permissive laws and exceeding by far the levels above which intervention is needed, after all consulted legislations.

Key words: Mining, heavy metals, soil contamination, southeastern Spain.

1. INTRODUCCIÓN

Como «metales pesados» son considerados todos aquellos elementos metálicos con peso atómico mayor que el del hierro (55,85 g/mol), en total 59 elementos. Pero si consideramos sólo estos elementos, quedarían fuera numerosos metales con pesos atómicos inferiores que con frecuencia pueden ser metales contaminantes como el Mn (54,44 g/mol) o el Cr (52,01 g/mol) y otros elementos contaminantes que no son metales como As, F y P. Por ello, siguiendo a Galan, Huertos y Romero Baena (2008), consideramos mejor hablar de «elementos traza» para todos aquellos elementos metálicos y no metálicos que pueden constituirse como contaminantes en un suelo, ya que, aunque hay que reconocer que la mayoría de los contaminantes inorgánicos son «metales pesados», a veces, la contaminación del suelo se puede producir por altas concentraciones de otros elementos mayoritarios como Na, Fe, o Al.

La presencia de los elementos traza o metales pesados en los suelos puede deberse a factores geológicos o antropológicos. Los primeros dependen, en gran medida, de la denominada geodisponibilidad, que hace referencia a la porción de un elemento o compuesto químico que puede liberarse a la superficie o cerca de ella, por procesos mecánicos, químicos o biológicos (Plumlee, 1994). Pero la geodisponibilidad de los elementos de las rocas y su aportación al suelo es insignificante en comparación con las derivadas de las acciones antropogénicas (Galan, Huertos y Romero Baena, 2008). Las principales concentraciones anómalas de metales pesados y elementos traza en suelos, procede mayoritariamente de la extracción de recursos minerales, sobre todo de menas metálicas (sulfuros, óxidos). Estas extracciones, han generado grandes beneficios que, en algunos casos, ha supuesto el desarrollo industrial y social de su entorno, pero las actividades mineras también son conocidas mundialmente por causar importantes efectos adversos al medioambiente, asociados, principalmente, con la deposición de grandes volúmenes de residuos, la mayoría con pirita y otros sulfuros, cuya oxidación libera grandes cantidades de metales pesados. Los residuos, se concentran generalmente en «escombreras», sobre todo en la minería a cielo abierto, pero también se depositan en «pantanos de lodos» procedentes del lavado del mineral.

La Sierra de Cartagena-La Unión ha sido uno de los distritos mineros más importantes de España y el más representativo de la Región de Murcia por sus yacimientos de hierro, plomo y zinc, de especial interés minero. Con más de 2.500 años de historia, la Sierra Minera, ha sido objeto de explotación desde la época de cartagineses y romanos hasta finales del siglo XX, con su máximo apogeo en los siglos XIX y XX.

A partir de 1992, el cese de las actividades mineras y el abandono de los pantanos de estériles, fácilmente erosionables tanto por erosión hídrica como eólica (Moreno Brotóns, *et al*., 2009), ha provocando la liberación y dispersión de metales pesados y elementos traza. Situación que, de no llevarse a cabo ninguna actuación de remediación, podría durar cientos de años (Gundersen *et al*., 2001; Tiwary, 2001). Sobre todo, teniendo en cuenta que se ha demostrado que estos estériles contienen importantes cantidades de metales pesados como plomo, zinc, cobre y cadmio, que exceden los niveles críticos europeos (Conesa *et al*., 2006), con una elevada movilidad potencial demostrada a través de pruebas de lavado y de extracciones secuenciales que podrían ser la causa de las elevadas concentraciones de metales pesados descritas en los suelos cercanos a la sierra minera (García *et al*., 2003), en los lechos de las principales ramblas de la zona (Simoneau, 1973), e incluso en los sedimentos del humedal de Lo Poyo adyacente a la laguna del Mar Menor y situado en la desembocadura de la rambla de El Beal que drena parte de la sierra minera (Álvarez Rogél *et al*., 2004).

En el entorno de esta histórica área minera, se desarrolla en la actualidad una importante agricultura de mercado en la que se sustenta una buena parte de la economía de la zona, que puede verse afectada por la contaminación procedente de la sierra minera. Tanto por deposición de polvo arrastrado por el viento, como por lodos canalizados a ramblas y depositados por las crecidas de estas en tormentas de alta intensidad.

El objetivo de este trabajo es evaluar la concentración de «metales pesados» y/o «elementos traza» en suelos agrícolas de una extensa zona (100 Km^2) adyacente a la sierra minera y valorar el nivel de contaminación por metales en los primeros 10 cm de capa arable, en comparación a los valores de referencia establecidos por diversas legislaciones.

2. ÁREA DE ESTUDIO

El distrito minero de Cartagena-La Unión (Figura 1) se ubica en el extremo oriental de la Comunidad Autónoma de la Región de Murcia (Sureste de España) y comprende los municipios de La Unión y las diputaciones (o pedanías) cartageneras de El Llano del Beal, El Beal, El Estrecho de San Ginés y Alumbres. Aunque la zona minera se encuentra, casi en su totalidad, en el municipio de La Unión y ocupa poco más de 50 Km^2.

3. METODOLOGÍA

3.1. Muestreo de suelos

Se tomaron 20 muestras de suelo en uso agrícola mediante una distribución aleatoria en un área de unos 100 km^2. Estas muestras eran parte de un muestreo más extenso con 52 muestras que incluían además 7 muestras en suelos de zonas naturales y 21 en suelos en el interior de la sierra minera, en escombreras, pantanos mineros y suelos alterados por la actividad minera. Además se tomaron otras 23 muestras en los cauces principales de 8 ramblas que drenan la Sierra Minera (Figura 2).

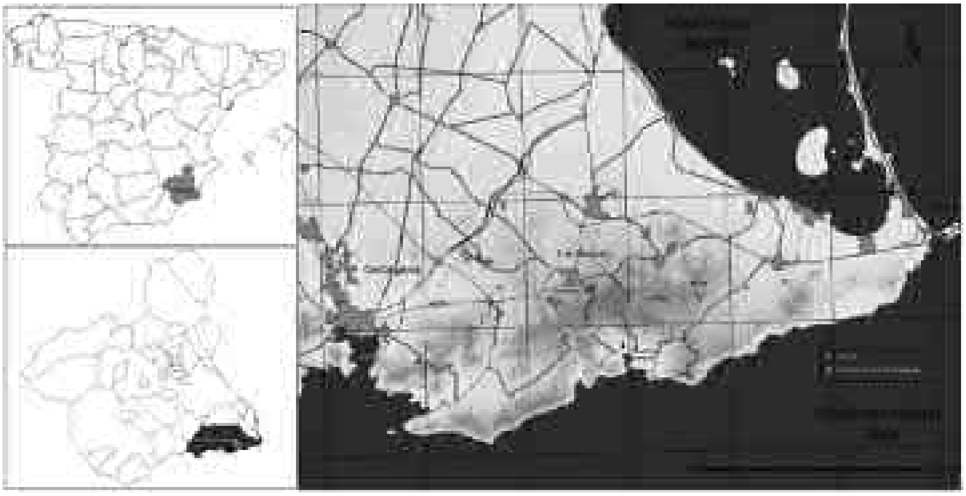

FIGURA 1
Localización del área de estudio.

3.2. Análisis de las muestras

Se realizaron 2 tipos de análisis: Fluorescencia de Rayos X, mediante un equipo Philips X'Pert, y ICP-MS y espectrometría, mediante un equipo Optical Emision Spectrometer OPTIMA 2000 DV.

Los valores obtenidos para metales pesados, fueron analizados en el ICP, tomando como referencia multipatrones realizados a tal efecto. Dichos patrones contenían concentraciones de metales que deleitaban un rango continuo, dentro del cual se previó que podrían entrar las muestras. Así se obtuvieron una serie de rectas de calibrado con un error casi despreciable ($r^2 = 0{,}99$), de manera que los datos derivados a partir de las mismas resultan fiables.

4. RESULTADOS Y DISCUSIÓN

4.1. Elementos detectados en las muestras

El análisis fluorométrico realizado a las 52 muestras de suelo ha detectado la presencia de 23 elementos metálicos y no metálicos que se muestran en la tabla 1. El Silicio es el elemento más abundante en todas las muestras con porcentajes del 55% en suelos de zonas naturales, 46% en suelos agrícolas y 40% en suelos mineros. Le siguen Aluminio (Al), calcio (Ca) y hierro (Fe), que en conjunto, con el silicio suponen el 80% en suelos mineros, 85% en suelos naturales y 82% en suelos agrícolas.

En cuanto a metales pesados o elementos traza presentes en las muestras, 10 son metales pesados en su significado más estricto, de los cuales seis, Ni, Cu, Zn, As, Sn y

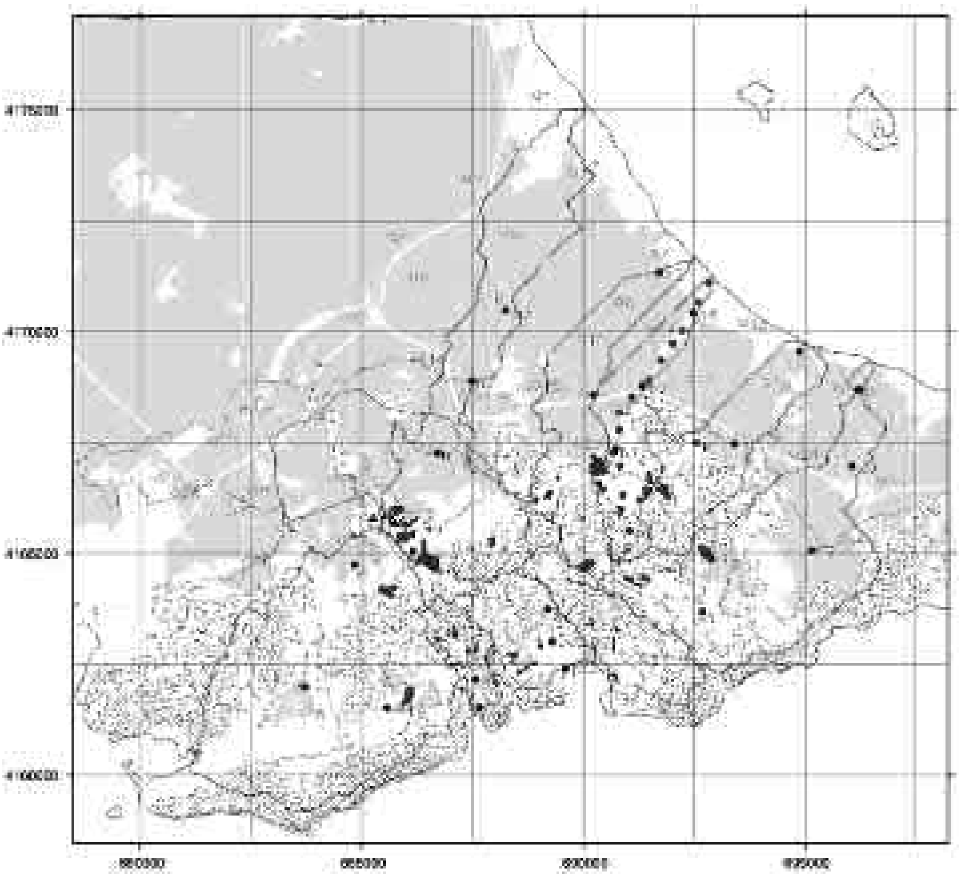

FIGURA 2
Localización de los puntos de muestreo y delimitación de la zona agrícola.

Pb, son considerados como muy tóxicos, junto con otro elemento traza, el Cromo (Cr). El resto, no son considerados como elementos especialmente tóxicos, al menos, no con la frecuencia de los mencionados.

4.2. Valores de referencia

Se habla de contaminación por metales pesados cuando el contenido en los mismos excede considerablemente de los valores «habituales» en el tipo de suelo que se está considerando. Bowie y Thornton, (1985) establecen una serie de valores para suelos considerados «normales» y para aquellos con valores excesivos, con independencia del tipo de suelo (Tabla 2).

TABLA 1

Concentración media en ppm de los elementos detectados en los suelos muestreados.

Elementos presentes en las muestras				
Peso atómico	**Elemento**	**Suelos mineros ppm**	**Suelos naturales ppm**	**Suelos agrícolas ppm**
Metales				
22,99	**Na *****	4.525	4.523	3.877
24,30	**Mg *****	30.587	19.257	21.291
26,98	**Al**	116.592	167.078	139.889
28,086	**Si**	397.015	547.809	460.998
39,098	**K *****	21.493	30.017	26.439
40,08	**Ca*****	157.561	62.108	152.590
47,90	**Ti ***	6.040	8.446	6.547
51,99	**Cr ****	125 (3 muestras)	92	189 (3 muestras)
54,94	**Mn ****	3.135	2.146	1.300
55,847	**Fe ****	129.769	70.009	66.123
«Metales pesados»				
58,71	**Ni ***	117 (3 muestras)	0	139 (7 muestras)
63,57	**Cu ****	320 (5 muestras)	0	148 (1 muestra)
65,37	**Zn ****	3.274	310	751
74,92	**As ****	556 (5 muestras)	0	0
85,47	**Rb**	4.824 (5 muestras)	0	101 (5 muestras)
87,62	**Sr**	157	0	254
91,22	**Zr**	184	236	253
118,69	**Sn ***	2.541 (2 muestras)	0	0
137,34	**Ba**	803	949	656
207,19	**Pb ***	5.208	486	1.210
Elementos no metálicos				
30,97	**P *****	2.173	1.582	2.316
32,074	**S *****	26.180	1.353	1.344
35,45	**Cl *****	928	472 (2 muestras)	887

- (3 muestras) = Entre paréntesis el número de muestras en las que aparece ese elemento a partir de las cuales se ha hecho el promedio. El cero indica que en ninguna muestra se ha detectado el elemento.

- Casillas con fondo más oscuro los «metales pesados» o «elementos traza», considerados como muy tóxicos y fácilmente disponibles en muchos suelos (Novotny, 1995) o dentro de la lista de contaminantes prioritarios de la US Environmental Protection Agency.

(***) = Macronutrientes (100 mg o más por día)
(**) = Micronutrientes esenciales (unos pocos mg por día)
(*) = Metales pesados no esenciales

TABLA 2
Concentraciones geoquímicas «normales y anómalas en algunos elementos traza y valores obtenidos en nuestro muestreo para suelos agrícolas.

Elemento	**Rango «normal» ppm**	**Concentraciones anómalas ppm**	**Suelos agrícolas ppm**
As	5-40	>2.500	0
Cu	60	>2.000	148
Ni	2-100	>8.000	139
Pb	10-150	≥10.000	1.210
Zn	25-200	≥10.000	751

Fuente: Bowie y Thornton (1985) y elaboración propia.

Con esto, una concentración en plomo de 1.000 ppm puede estar ocasionada por una contaminación externa o bien deberse a un nivel geoquímico muy alto del propio suelo. En nuestro muestreo, salvo el arsénico que no aparece en ninguna de las muestras, todos superan el rango considerado «normal» en suelos por Bowie y Thornton (1985). Sobre todo, Pb y Zn, muy por encima de la concentración «normal».

4.3. Máximos admisibles por diversas legislaciones

Los umbrales máximos admisibles por diversas legislaciones se encuentran recogidos en la tabla 3. En este caso, la concentración de metales pesados en los suelos agrícolas muestreados supera ligeramente las concentraciones máximas permitidas por muchas legislaciones para el caso del Cr, Ni y Cu, salvo las normas españolas y alemana, que parecen ser bastante más permisivas.

Pero las concentraciones medias de Zinc y, sobre todo Plomo en el área estudiada, superan ampliamente los límites máximos permitidos por todas las legislaciones consultadas, incluyendo las legislaciones españolas y alemana, bastante más permisivas. La concentración de plomo es 20 veces superior a nivel considerado como «contaminación» por la legislación Holandesa e incluso, dobla el nivel establecido como de necesidad de saneamiento urgente de esos suelos establecido por esa legislación. Cuadruplica el nivel máximo permitido por la Comunidad Europea, que lo establece en 300 ppm. Y es superior al nivel máximo permitido por legislaciones tan permisivas como la alemana.

El zinc dobla el nivel máximo establecido en la legislación española y supera también los niveles de la legislación alemana.

Por otra parte, los niveles de peligrosidad del plomo establecidos por la ley andaluza, la más próxima a la Región de Murcia, indican que es necesario un tratamiento de remediación, cuando la concentración es superior a 350 mg/Kg en suelos agrícolas; cuando supera los 1.000 mg/Kg en parques naturales y zonas forestales; y con niveles superiores a 2.000 mg/Kg en zonas industriales. En los suelos analizados por nosotros la concentración

TABLA 3
Valores máximos admisibles por la legislación de algunos países y comunidades autónomas españolas de contaminación por metales en suelos agrícolas (mg/kg).

País	Cr	Ni	Cu	Zn	Pb
UE (máximo)	-	75	140	300	300
Austria	100	100	100	300	100
Canadá	75	100	100	400	200
Polonia	100	100	100	300	100
Japón	-	100	125	250	400
G. Bretaña	50	50	100	300	100
Alemania	200	200	200	600	1.000
Holanda (*)	100	50	50	200	50
Holanda (**)	800	500	500	3.000	600
España (***)	100-1.000	30-300	50-1.000	150-2.500	50-750
Andalucía	250-400	80-200	150-300	300-600	250-350
P. Vasco	-	280	250	840	330
Nuestros suelos	**189**	**139**	**148**	**751**	**1.210**

(*) Niveles de contaminación.
(**) Niveles de necesidad urgente de intervención (Macías, 1993).
(***) En España se contempla la contaminación sólo en el caso de la adicción de lodos de depuradora como enmienda orgánica.

media de plomo en los suelos naturales alcanza las 485 mg/Kg, casi un 50% inferior al nivel de intervención. Pero, tanto los suelos agrícolas, con una concentración media de 1.210 mg/Kg, como los suelos industriales, con una concentración media de 5.208 mg/Kg, superan con mucho los niveles de intervención establecidos que son de 350 mg/Kg y 2.000 mg/Kg, respectivamente.

Con el zinc sucede lo mismo, los niveles tanto para suelos agrícolas como para suelos industriales duplican los niveles de referencia de la norma andaluza, que establece estos niveles en 600 mg/Kg y 1.000 mg/Kg, respectivamente.

5. CONCLUSIONES

En los suelos de la sierra minera y su entorno se han detectado concentraciones importantes, que alcanzan y superan los niveles máximos permitidos por diversas normativas internacionales de hasta 14 de los elementos denominados «metales pesados» o «elementos traza».

En suelos agrícolas, los metales pesados o elementos traza, que se han detectado, y que son considerados como muy tóxicos y fácilmente disponibles, son Cr, Ni, Cu, Zn, y Pb. Estos elementos presentan concentraciones superiores a los valores considerados «normales» en suelos, según Bowie y Thornton (1985).

Las concentraciones de metales pesados en los suelos agrícolas muestreados, supera ligeramente las concentraciones máximas permitidas por muchas legislaciones para el caso del Cr, Ni y Cu, salvo las normas españolas y alemana, que parecen ser bastante más permisivas. Pero las concentraciones medias de Zinc y, sobre todo Plomo, superan ampliamente los límites máximos permitidos por todas las legislaciones consultadas

La concentración de plomo es 20 veces superior al nivel considerado como «contaminación» por la legislación Holandesa e incluso, dobla el nivel establecido como de necesidad de saneamiento urgente de esos suelos, establecido por esa legislación. Cuadruplica el nivel máximo permitido por la Comunidad Europea, que lo establece en 300 ppm., y es superior al nivel máximo permitido por legislaciones tan permisivas como la alemana.

El zinc dobla el nivel máximo establecido en la legislación española y supera también los niveles de la legislación alemana.

Es importante resaltar que, aunque esto no ha sido objeto del presente trabajo, toda el área padece una fuerte sequía estival que reseca enormemente el suelo y facilita el proceso de erosión eólica, especialmente en suelos agrícolas y pantanos mineros, favoreciendo así la dispersión de los contaminantes que pasan incluso a las vías respiratorias y a los pulmones cuando las partículas movilizadas tienen un tamaño PM10.

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APLICACIÓN DE LODOS DE PLANTA DE TRATAMIENTO DE CELULOSA: EFECTO EN ALGUNAS PROPIEDADES FÍSICAS Y QUÍMICAS DE SUELOS VOLCÁNICOS

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Application of sludge from cellulose treatment plant: Effect in some physical and chemical properties of volcanic soils

Key words: degraded soils, cellulose sludge, chemical and physical soil properties.

ABSTRACT

The sludge from cellulose treatment plant is rich in organic matter (MO) and can be used to improve the chemical and physical properties of the soil. The aim of this study was to evaluate the effect of the application of sludge from cellulose wastewater treatment plant on the physical and chemical properties of volcanic soils (series Gorbea and Collipulli). There was added sludge (0, 10, 20, 30 and 50 Mg ha^{-1}) to the soils and were incubated for 75 days at 22 ± 2ºC. At 15 and 75 days the content of organic matter (MO), available nitrogen (N), pH, extractable Al, field capacity, bulk density and aggregate stability was determinated. The application of sludge improved significantly ($p \leq 0.05$) the levels of nitrogen and organic matter in both soils, as well as the pH, with the consistent decrease of Al level. On the other hand, the different doses of sludge did not improve significantly the physical properties of the soils, with the exception of the stability of the aggregates in the soil series Gorbea. The minor effect in the physical properties could happen due to the fact that the period of incubation (75 days) was not sufficient to provoke significant changes in the physical properties of the soils.

Palabras claves: Suelos degradados, celulosa, lodo, química de suelos, física de suelos

RESUMEN

Los lodos de planta de tratamiento de celulosa son ricos en materia orgánica (MO) y pueden ser utilizados para mejorar las propiedades químicas y físicas del suelo. El objetivo de este estudio fue evaluar el efecto de la aplicación de lodo de planta de tratamiento de aguas residuales de la industria de celulosa sobre las propiedades físicas y químicas de suelos volcánicos (Serie Gorbea y Collipulli). Se adicionó lodo (0, 10, 20, 30 y 50 Mg ha^{-1}) a los suelos y se incubó por 75 días a 22 ± 2ºC. A los 15 y 75 días se determinó el contenido de materia orgánica (MO), nitrógeno disponible (N), pH, Al extractable, capacidad de campo, densidad aparente y estabilidad de los agregados. La aplicación de lodo incrementó significativamente ($p \leq 0{,}05$) los niveles de nitrógeno y de materia orgánica en ambos suelos, así como el pH, con la consecuente disminución del nivel de Al. Por otro lado, las distintas dosis de lodo no mejoraron significativamente las propiedades físicas de los suelos, a excepción de la estabilidad de los agregados en el suelo serie Gorbea. El menor efecto en las propiedades físicas pudo ocurrir debido a que el periodo de incubación (75 días) no fue suficiente para provocar cambios significativos en las propiedades físicas de los suelos.

INTRODUCCIÓN

La industria chilena de celulosa basada en el proceso Kraft, se ha desarrollado aceleradamente durante las útimas décadas. Este proceso genera grandes cantidades de aguas residuales, las cuales al ser tratadas por procesos biológicos, principalmente aerobios, generan lodos. Estos lodos están compuestos principalmente por compuestos orgánicos y su disposición constituye una preocupación económica y ambiental.

El lodo suele presentar contenidos de sólidos variable entre 0,25 % y 12 %, dependiendo de las operaciones y procesos de tratamiento (Catricala *et al*., 1996). La estabilización de los lodos es el proceso por el cual disminuye la tasa de descomposición de la materia orgánica, dejando el material sin las condiciones necesarias de humedad y temperatura, evitando así una proliferación de microorganismos. Este proceso reduce el volumen del residuo, elimina la presencia de patógenos, reduce los compuestos tóxicos y olores (Winkler, 1986; Jokela *et al*., 1997). La aplicación de lodos a suelos agrícolas degradados puede ayudar a recuperar su productividad por aumento en el pH, aumento en el contenido de materia orgánica y un mejoramiento de la disponibilidad de otros nutrientes tales como N, P y K. Sin embargo, la aplicación de lodos al suelo debe ser controlada, ya que altas dosis pueden provocar una disminución de la densidad aparente y de las propiedades hidráulicas del suelo (Goyal *et al*., 1999) y una eventual acumulación de metales pesados.

En Chile, los estudios sobre la disposición de lodos para fines agrícolas y forestales son recientes, comparados con los realizados en Norte América y Europa. La disposición de lodos en suelos degradados o erosionados es una buena alternativa para Chile, considerando que en nuestro país 46 % del suelo agrícola presenta erosión en tres niveles: seria, moderada y suave. Por otro lado, los suelos derivados de cenizas volcánicas ocupan en Chile un área aproximada a los 4 millones de hectáreas, de las cuales una superficie cercana al millón es arable. Estos suelos se caracterizan por poseer una alta capacidad de intercambio catiónico, alta capacidad de retención de fosfatos, bajo porcentaje de saturación de bases, altos contenidos de Al de intercambio y niveles de pH moderadamente ácidos a fuertemente ácidos (Gallardo *et al.*, 1999; Mora, 1994).

La acidez de los suelos derivados de cenizas volcánicas limita el crecimiento de las plantas debido a una combinación de factores que incluyen, entre otros, elevados niveles de Al de intercambio (Baligar y Fageira, 1999; Gallardo *et al*., 1999).

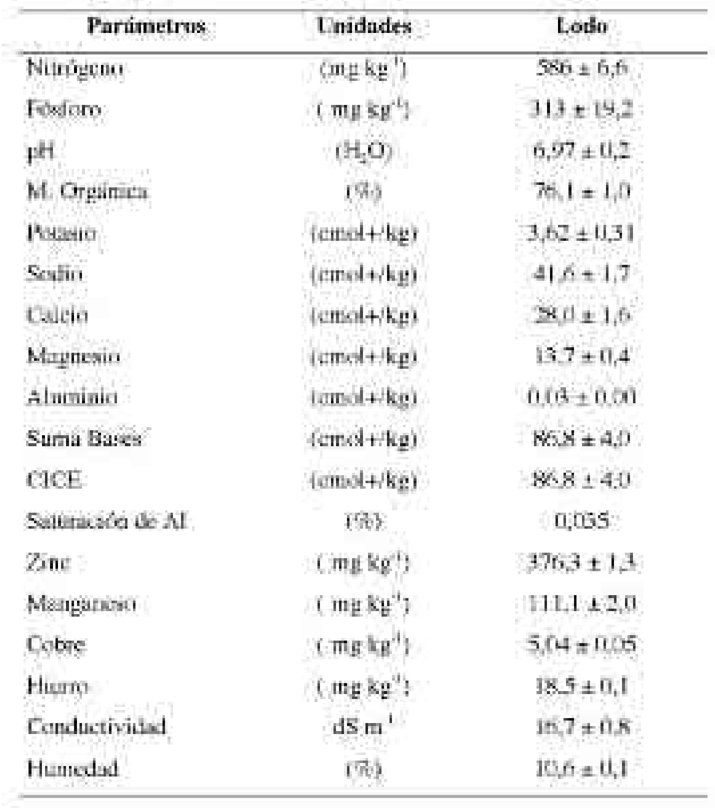
Además, es importante notar que el tratamiento de las aguas residuales en Chile aún no ha llegado a su producción máxima (Marambio y Ortega, 2003) por lo cual sólo se puede estimar la producción de los lodos, e inferir que representará un problema ambiental. El objetivo del presente trabajo fue evaluar el efecto de la aplicación de lodo proveniente del tratamiento de aguas residuales de la industria de celulosa, sobre las propiedades físicas y sobre el nivel de aluminio de intercambio, materia orgánica y nitrógeno en suelos agrícolas derivados de cenizas volcánicas.

MATERIALES Y MÉTODOS

Procedencia del lodo

Se utilizó un lodo proveniente del tratamiento biológico (laguna aireada) del agua residual de una industria de celulosa kraft. El lodo es bombeado periódicamente desde la zona de sedimentación de la laguna a un landfill en donde permanecen alrededor de un año, en proceso de estabilización. Estudios previos realizados por Esparza (2004), demostraron que este lodo se encontraba estabilizado de acuerdo a ensayos de actividad biológica (ensayos de

Cuadro 1: Caracterización física y química del lodo: promedios y error estándar de la media.
Table 1: Physical and chemical characterization of the sludge: average and standard error of the mean.



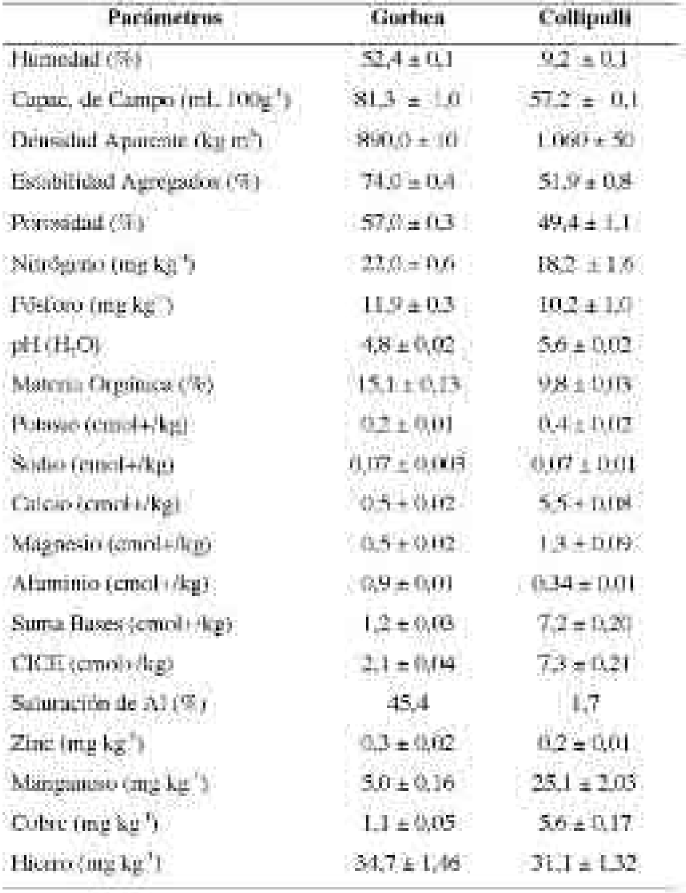
Parámetros	Unidades	Lodo
Nitrógeno	(mg kg^{-1})	586 ± 6,6
Fósforo	(mg kg^{-1})	313 ± 19,2
pH	(H$_2$O)	6,97 ± 0,2
M. Orgánica	(%)	76,1 ± 1,0
Potasio	(cmol+/kg)	3,62 ± 0,31
Sodio	(cmol+/kg)	41,6 ± 1,7
Calcio	(cmol+/kg)	28,0 ± 1,6
Magnesio	(cmol+/kg)	13,7 ± 0,4
Aluminio	(cmol+/kg)	0,03 ± 0,00
Suma Bases	(cmol+/kg)	86,8 ± 4,0
CICE	(cmol+/kg)	86,8 ± 4,0
Saturación de Al	(%)	0,035
Zinc	(mg kg^{-1})	376,3 ± 1,3
Manganeso	(mg kg^{-1})	111,1 ± 2,0
Cobre	(mg kg^{-1})	5,04 ± 0,05
Hierro	(mg kg^{-1})	18,5 ± 0,1
Conductividad	dS m^{-1}	16,7 ± 0,8
Humedad	(%)	10,6 ± 0,1

germinación y actividad respiratoria), indicando que puede usarse con seguridad en mezclas en suelos agrícolas. En el Cuadro 1 se presenta la caracterización fisicoquímica del lodo usado en este estudio. Este material presentó un contenido de materia orgánica de 76%, como también altos contenidos de nutrientes disponibles como N y P, equivalentes a 586 y 313 mg kg^{-1}, respectivamente.

Origen de los Suelos

Los suelos seleccionados fueron suelos de las series Gorbea (Andisol) y Collipulli (Ultisol), muestreados en el horizonte superficial Ap a los 20 cm de profundidad. El suelo Gorbea presenta pH ácido (4,8) y alto contenido de aluminio intercambiable (0,9 cmol+/kg) mientras que el suelo Collipulli presenta un pH menos ácido (5,6)

Cuadro 2: Caracterización física y química de las series de suelo: promedios y error estándar de la media.
Table 2: Physical and chemical characterization of the soil series: average and standard error of the mean.



Parámetros	Gorbea	Collipulli
Humedad (%)	52,4 ± 0,1	9,2 ± 0,1
Capac. de Campo (mL $100g^{-1}$)	81,3 ± 1,0	57,2 ± 0,1
Densidad Aparente (kg m^{-3})	890,0 ± 10	1.060 ± 50
Estabilidad Agregados (%)	74,0 ± 0,4	51,9 ± 0,8
Porosidad (%)	57,0 ± 0,3	49,4 ± 1,1
Nitrógeno (mg kg^{-1})	22,0 ± 0,6	18,2 ± 1,6
Fósforo (mg kg^{-1})	11,9 ± 0,3	10,2 ± 1,0
pH (H_2O)	4,8 ± 0,02	5,6 ± 0,02
Materia Orgánica (%)	15,1 ± 0,13	9,8 ± 0,03
Potasio (cmol+/kg)	0,2 ± 0,01	0,4 ± 0,02
Sodio (cmol+/kg)	0,07 ± 0,003	0,07 ± 0,01
Calcio (cmol+/kg)	0,5 ± 0,02	5,5 ± 0,08
Magnesio (cmol+/kg)	0,5 ± 0,02	1,3 ± 0,09
Aluminio (cmol+/kg)	0,9 ± 0,01	0,34 ± 0,01
Suma Bases (cmol+/kg)	1,2 ± 0,03	7,2 ± 0,20
CICE (cmol+/kg)	2,1 ± 0,04	7,3 ± 0,21
Saturación de Al (%)	45,4	1,7
Zinc (mg kg^{-1})	0,3 ± 0,02	0,2 ± 0,01
Manganeso (mg kg^{-1})	5,0 ± 0,16	25,1 ± 2,03
Cobre (mg kg^{-1})	1,1 ± 0,05	5,6 ± 0,17
Hierro (mg kg^{-1})	34,7 ± 1,46	31,1 ± 1,32

y menor contenido de materia orgánica (9,8%) (Cuadro 2). Se obtuvieron dos porciones de suelo, una fue tamizada por 2 mm y secada al aire para su posterior caracterización y la otra porción se usó para los tratamientos de mezcla con lodos.

Incubaciones

Una vez realizadas las mezclas, las macetas fueron incubadas a 22 ± 2 ºC en cámara de crecimiento adaptadas para este propósito. Todos los suelos se mantuvieron a 50 % de la capacidad de campo. Las evaluaciones se realizaron en dos oportunidades: al día 15 y 75 desde el comienzo de la incubación.

Determinación de las propiedades físicas y químicas

Se determinaron las siguientes propiedades físicas: estabilidad de los agregados (Kemper y Rosenau, 1986), capacidad de campo (Barajas *et al*., 1994), a través del método volumétrico, relacionando el porcentaje de humedad del suelo y la diferencia entre agua retenida y drenada después de 48 h. Además se determinó densidad aparente (Buckman, 1991), analizada por la relación peso-volumen. Los análisis químicos realizados fueron: materia orgánica, N disponible, Al extractable y pH según (Sadzawka *et al*., 2004).

Diseño experimental y análisis estadístico

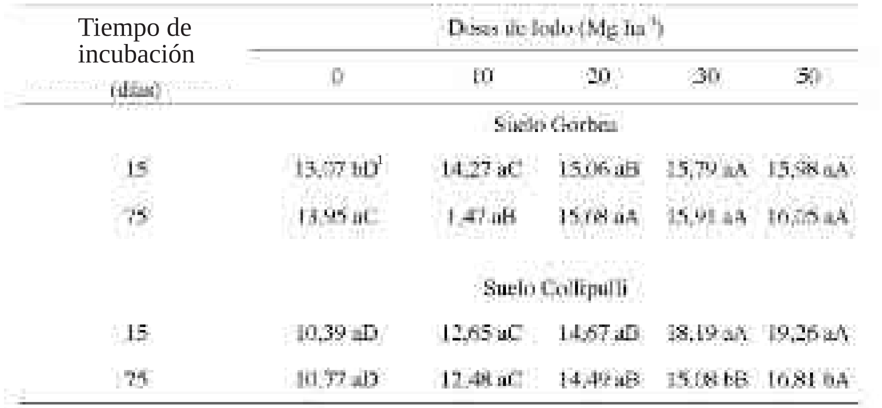
El diseño experimental consistió en un arreglo factorial completamente al azar con cinco niveles de lodo: 0, 10, 20, 30 y 50 Mg ha^{-1} en mezcla con 2 kg de suelo (base seca) y tres repeticiones. Los datos fueron analizados mediante una ANDEVA de una vía, considerando la prueba de comparación de medias de Tukey. También se utilizó la prueba t student para muestras independientes con el objeto de comparar las medias en los tratamientos a 15 y 75 días. Ambas pruebas fueron ajustadas a un nivel de significación de 5 %. El programa estadístico utilizado corresponde a SPSS, V. 10.0.

RESULTADOS Y DISCUSIÓN

En el Cuadro 3 presenta el efecto de la aplicación del lodo sobre el contenido de materia orgánica (MO) en el suelo Gorbea y en el suelo Collipulli. Se observa que este parámetro incrementó significativamente especialmente en el suelo Collipulli por efecto de las dosis aplicadas, no observándose diferencia significativa ($p < 0,05$) en el suelo serie Gorbea en dosis igual o mayor a de 30 Mg ha^{-1}. La aplicación de lodo equivalente a 50 Mg ha^{-1} correspondió a un 54 % del total de MO del suelo Collipulli, por lo cual se observó un mayor efecto comparado con el suelo serie Gorbea en que la aplicación de 50 Mg ha^{-1} correspondió solo a un 17 % del total de MO del suelo. Los incrementos de MO frente a la aplicación de lodo concuerdan con los resultados obtenidos por Diez *et al*., 1996; O'Brien *et al*., 2002; Gallardo *et al*., 2007 y Zhang *et al*., 2004. La materia orgánica junto a otros parámetros químicos como fertilidad del suelo, pH, suma de bases, puede determinar la disponibilidad de los nutrientes presentes en el suelo y en consecuencia el rendimiento potencial de los cultivos (Honorato, 2000).

Cuadro 3: Contenido de materia orgánica (%) de los suelos Gorbea y Collipulli con 0, 10, 20, 30 y 50 Mg ha^{-1} de lodo de celulosa, después de 15 y 75 días de incubación.

Table 3: Organic matter content (%) of Gorbea and Collipulli soils with 0, 10, 20, 30 and 50 Mg ha^{-1} of cellulose sludge, after 15 and 75 days of incubation.

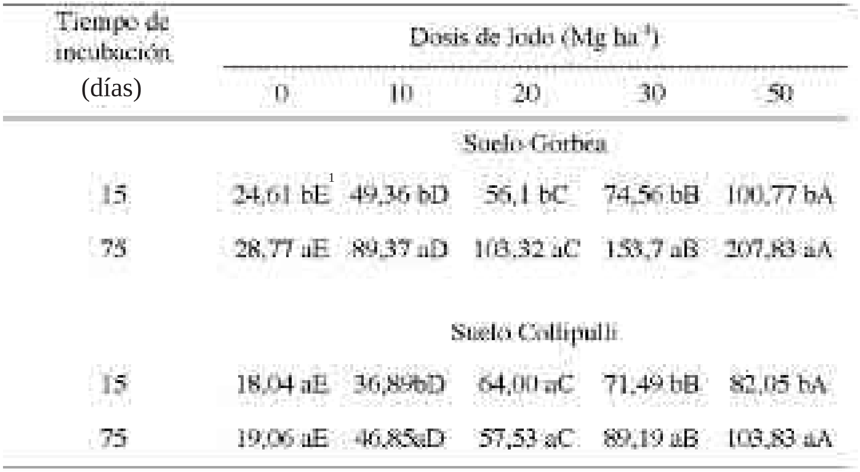


Tiempo de incubación (días)	Dosis de lodo (Mg ha^{-1})				
	0	10	20	30	50
			Suelo Gorbea		
15	13,07 bD[1]	14,27 aC	15,06 aB	15,79 aA	15,98 aA
75	13,95 aC	1,47 aB	15,68 aA	15,91 aA	16,05 aA
			Suelo Collipulli		
15	10,39 aD	12,65 aC	14,67 aB	18,19 aA	19,26 aA
75	10,77 aD	12,48 aC	14,49 aB	15,08 bB	16,81 bA

[1] Para cada suelo por separado, los valores seguidos de distinta letra mayúscula en una misma fila y letra minúscula en una misma columna, presentan diferencias significativas ($p \leq 0,05$).

El contenido de nitrógeno disponible incrementó significativamente con la aplicación de lodo en ambos suelos estudiados, siendo mayor el efecto a medida que se incrementó la dosis de lodo aplicada (Cuadro 4). Se observó además diferencia significativa ($p < 0,05$) entre los valores obtenidos a los 15 y a los 75 días de incubación. El efecto de la adición de lodo fue mayor en el suelo serie Gorbea, obteniéndose un contenido de N de 207,83 mg kg^{-1} al día 75 para el tratamiento de 50 Mg ha^{-1}. Sin embargo, en el mismo periodo de incubación y en la misma dosis de lodo, el valor obtenido para el suelo serie Collipulli fue de 103,83 mg kg^{-1}. Las variaciones entre ambos suelos se pueden deber a variación en la relación C/N durante el período de incubación y a la diferente actividad biológica que presentan ambos suelos (Gallardo *et al.*, 2006). Por otro lado, estudios realizados por Zhang *et al.*, 2004 han determinado que después de dos meses de incubación, existe una disminución significativa de la lignina y de la disponibilidad de C y N.

Cuadro 4: Contenido de nitrógeno (mg kg^{-1}) del suelo Gorbea y Collipulli con dosis de 0, 10, 20, 30 y 50 Mg ha^{-1} de lodo de celulosa, después de 15 y 75 días de incubación.
Table 4: Nitrogen content (mg kg^{-1}) of Gorbea and Collipulli soils with application of 0, 10, 20, 30 and 50 Mg ha^{-1} of cellulose sludge, after 15 and 75 days of incubation.



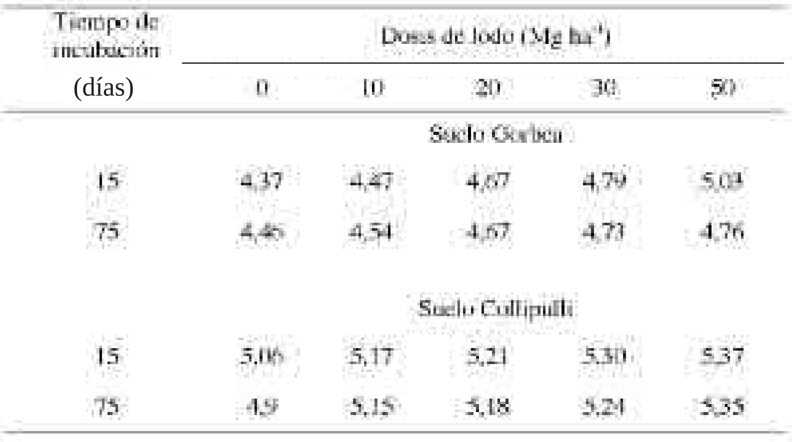
Tiempo de incubación (días)	Dosis de lodo (Mg ha^{-1})				
	0	10	20	30	50
			Suelo Gorbea		
15	24,61 bE[1]	49,36 bD	56,1 bC	74,56 bB	100,77 bA
75	28,77 aE	89,37 aD	103,32 aC	153,7 aB	207,83 aA
			Suelo Collipulli		
15	18,04 aE	36,89bD	64,00 aC	71,49 bB	82,05 bA
75	19,06 aE	46,85aD	57,53 aC	89,19 aB	103,83 aA

[1] Para cada suelo por separado, los valores seguidos de distinta letra mayúscula en una misma fila y letra minúscula en una misma columna, presentan diferencias significativas ($p \leq 0,05$).

El pH en los suelos Gorbea y Collipulli incrementó durante la incubación por efecto de la aplicación de lodo (Cuadro 5). En el suelo Gorbea el pH incrementa de 4,37 a 5,03 después de 15 días de incubación al aplicar lodo de 50 Mg ha^{-1} mientras que se obtiene un valor de pH de 4,76 al cabo de 75 días de incubación con la misma dosis aplicada. Similar situación se observa el en suelo Collipulli, en donde los valores de pH corresponden a 5,37 y 5,35 después de 15 y 75 días de incubación con la dosis de 50 Mg ha^{-1}, respectivamente. Se observa una disminución de los valores de pH en el periodo de incubación de 75 días, lo que concuerda con resultados obtenidos por Tang y Yu (1999), quienes señalan que el pH aumenta inmediatamente después de agregar el residuo, disminuyendo a través del tiempo. El aumento en los valores de pH está asociado al aumento en las bases de intercambio debido al aporte de Na^+, K^+, Mg^{+2} y Ca^{+2} que se encuentran en cantidades apreciables en el lodo utilizado (Cuadro 1). Los cationes desplazan H^+ de los sitios de intercambio en el suelo, aumentando por lo tanto la saturación de bases.

Cuadro 5: Valores de pH del suelo Gorbea y Collipulli con dosis de 0, 10, 20, 30 y 50 Mg ha^{-1} de lodo de celulosa, después de 15 y 75 días de incubación.

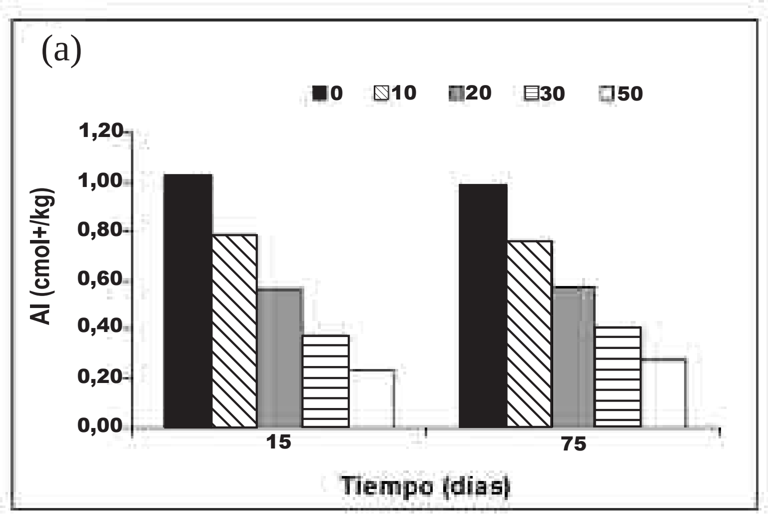
Table 5: pH values of of Gorbea and Collipulli soils with application of 0, 10, 20, 30 and 50 Mg ha^{-1} of cellulose sludge, after 15 and 75 days of incubation.



Tiempo de incubación	Dosis de lodo (Mg ha^{-1})				
(días)	0	10	20	30	50
			Suelo Gorbea		
15	4,37	4,47	4,67	4,79	5,03
75	4,46	4,54	4,67	4,73	4,76
			Suelo Collipulli		
15	5,06	5,17	5,21	5,30	5,37
75	4,9	5,15	5,18	5,24	5,35

El incremento en el pH en suelos volcánicos reviste gran importancia ya que está relacionado con el nivel de Al intercambiable (Al^{+3}) en los suelos, el cual es tóxico para las plantas (Rengel, 2004). En suelos ácidos, el Al es liberado por el complejo de intercambio, debido a la disminución de bases y el aumento de iones hidrógeno. La aplicación de lodo proveniente del tratamiento de las aguas de la industria de celulosa a los suelos Gorbea y Collipulli aumentó los valores de pH con la consecuente disminución del Al de intercambio, tal como se muestra en la Figura 1 (a y b). Se observa que el nivel deAl disminuyó de 1,02 (cmol+/kg) a 0,23 (cmol+/kg) a los 15 días de incubación en el Suelo Gorbea con 50 Mg ha^{-1}. Este suelo presenta un mayor nivel de acidificación que el suelo Collipulli. Sin embargo, la adición de lodo también disminuyó el nivel de Al de intercambio, disminuyendo de 0,35 a 0,07 con la dosis de 50 Mg ha^{-1} después de 15 días de incubación. Resultados similares han sido obtenidos por Carpenter y Fernández (2000) y Zhang *et al.*, (2004) al aplicar lodos de la industria de celulosa, obteniendo aumentos en los valores de pH y disminución en el % de saturación de Al.

Los valores de capacidad de campo para el suelo Collipulli sin adición de lodo, son notoriamente inferiores a los obtenidos para la serie Gorbea (Cuadro 6). Sin embargo, existe un incremento significativo de este parámetro al incorporar dosis superiores a 20 Mg ha^{-1} para el suelo Collipulli. Este aumento se debe particularmente a que la aplicación de lodo como aporte en materia orgánica produce un incremento en la macroporosidad, con formación de agregados de mayor tamaño (ver más adelante), lo que se traduce en una mayor



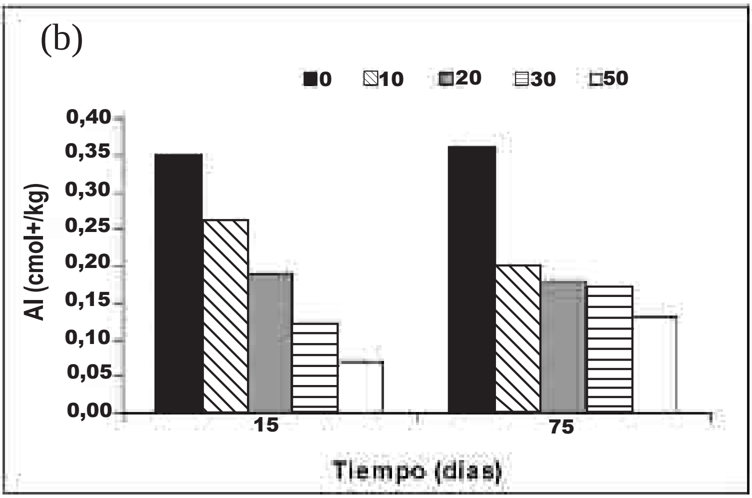


Figura 1: Efecto de la aplicación de lodo de celulosa (0, 10, 20, 30 and 50 Mg ha^{-1}) sobre el nivel de aluminio (cmol+/kg) en los suelos Gorbea (a) y Collipulli (b), después de 15 y 75 días de incubación.
Figure 1: Effect of the cellulose sludge application (0, 10, 20, 30 and 50 Mg ha^{-1}) on aluminium content (cmol+/kg) in Gorbea (a) and Collipulli soils (b), after 15 and 75 days of incubation.

capacidad de retención de agua (Arias, 2003). Estudios similares realizados por Rivero *et al*. (2004), indican que el tiempo de incubación de dos meses no juega un papel fundamental, sin embargo, tiempos superiores permiten observar diferencias más marcadas.

Cuadro 6: Capacidad de campo (mL 100g^{-1}) de los suelos Gorbea y Collipulli, con dosis de 0, 10, 20, 30 y 50 Mg ha^{-1} de lodo de celulosa, después de 15 y 75 días de incubación.
Table 6: Field capacity (mL 100g^{-1}) of Gorbea and Collipulli soils with application of 0, 10, 20, 30 and 50 Mg ha^{-1} of cellulose sludge, after 15 and 75 days of incubation.

Tiempo de incubación	Dosis de lodo (Mg ha^{-1})				
(días)	0	10	20	30	50
			Suelo Gorbea		
15	82,48 bA[1]	82,78 bA	84,74 aA	84,76 bA	85,33 aA
75	83,17 aB	85,9 aA	86,08 aA	86,16 aA	86,24 aA
			Suelo Collipulli		
15	49,71 aAB	46,21 aB	49,68 aAB	52,53 bA	55,17 aA
75	49,91 aB	49,06 aB	50,38 aB	55,02 aA	56,20 aA

[1] Para cada suelo por separado, los valores seguidos de distinta letra mayúscula en una misma fila y letra minúscula en una misma columna, presentan diferencias significativas ($p \leq 0,05$).

La estabilidad de los agregados no varió significativamente ($p < 0,05$) en el suelo Collipulli, con el incremento en la dosis de lodo en ambos periodos evaluados, excepto entre el tratamiento control y la dosis de 50 Mg ha^{-1} a los 75 días de incubación (Cuadro 7). Por otro lado, la estabilidad de los agregados incrementó en el suelo Gorbea a medida que se incorporó lodo como aporte en materia orgánica. Se observó diferencia significativa en el valor de la estabilidad de los agregados al aumentar la dosis de lodo en ambos periodos de evaluación, obteniendose un incremento superior a un 25 % al aplicar 50 Mg ha^{-1} de lodo (Cuadro 7). Sin embargo, no se observó diferencia significativa entre ambos periodos de evaluación al aplicar dosis igual o menor a 20 Mg ha^{-1}. Estudios similares fueron obtenidos por Betancourt *et al.* (1999), donde la materia orgánica presentó correlaciones positivas para la estabilidad de los agregados, presentando un mejoramiento en las condiciones físicas de suelos degradados, principalmente en su estabilidad estructural. Es así como las aplicaciones de lodo generan un aumento en la estabilidad de los agregados. Aportes de hasta un 5 % de lodos urbanos generan aumentos de hasta un 78 % de la estabilidad de agregados respecto a la condición inicial de un suelo con 7,5 g kg^{-1} de materia orgánica (Guerrero *et al.*, 2001), lo que asegura un potencial de protección del suelo ante la erosión (Roldán *et al.*, 1996). La mayor estabilidad se traduciría en un aumento del diámetro medio de los agregados, favoreciendo el movimiento del agua y aire (Trelo-Ges y Chuasavathi, 2002). Además, la redistribución del sistema poroso tendría un efecto positivo, mejorando la capacidad de retención de agua (Muñoz *et al.*, 1999).

Cuadro 7: Estabilidad de los agregados al agua (%) de los suelos Gorbea y Collipulli, con dosis de 0, 10, 20, 30 y 50 Mg ha^{-1} de lodo de celulosa, después de 15 y 75 días de incubación.

Table 7: Water aggregate stability (%) of Gorbea and Collipulli soils with application of 0, 10, 20, 30 and 50 Mg ha^{-1} of cellulose sludge, after 15 and 75 days of incubation.

Tiempo de incubación	Dosis de lodo (Mg ha^{-1})				
(días)	0	10	20	30	50
			Suelo Gorbea		
15	58,42 aD[1]	67,5 aC	68,18 aC	72,52 bB	82,45 bA
75	62,06 aD	69,16 aC	70,16 aC	78,16 aB	84,89 aA
			Suelo Collipulli		
15	61,81 aA	62,11 aA	62,06 aA	62,5 bA	65,05 aA
75	61,98 aB	63,03 aAB	63,21 aAB	64,55 aAB	65,69 aA

[1] Para cada suelo por separado, los valores seguidos de distinta letra mayúscula en una misma fila y letra minúscula en una misma columna, presentan diferencias significativas (p ≤ 0,05).

En general no se observaron variaciones significativas en función de la tasa de aplicación del lodo para la densidad aparente, a excepción del suelo Collipulli con dosis superiores a 20 Mg ha^{-1} después de 75 días de incubación (Cuadro 8). La densidad aparente disminuyó en dosis altas de lodo pero este efecto no se expresó en el suelo Gorbea. Estos resultados contrastan con los obtenidos por Seguel *et al.*, (2003). Según estudios realizados por Goyal *et al.*, (1999), la presencia de materia orgánica afecta considerablemente la densidad aparente en el largo plazo, sin embargo, se debe tener en cuenta que las aplicaciones de enmiendas orgánicas aumentan la agregación y con ello, la porosidad fina. Si esta nueva porosidad no muestra un nivel adecuado de continuidad y funcionalidad, al realizar los análisis de laboratorio, el agua que queda retenida tenderá a provocar una sobreestimación de los valores iniciales de porosidad gruesa. Es fundamental determinar cuales son los efectos, tanto cualitativos como cuantitativos de las aplicaciones de lodos sobre las propiedades físicas y mecánicas de los suelos.

Cuadro 8: Densidad aparente (kg m^{-3}) de los suelos Gorbea y Collipulli con dosis de 0, 10, 20, 30 y 50 Mg ha^{-1} de lodo de celulosa, después de 15 y 75 días de incubación.
Table 8: Bulk density (kg m^{-3}) of Gorbea and Collipulli soils with application of 0, 10, 20, 30 and 50 Mg ha^{-1} s of cellulose ludge, after 15 and 75 days of incubation.

Tiempo de incubación	Dosis de lodo (Mg ha^{-1})				
(días)	0	10	20	30	50
			Suelo Gorbea		
15	0,89 aA[1]	0,88 aA	0,88 aA	0,88 aA	0,87 aA
75	0,88 aA	0,86 aA	0,86 aA	0,83 aA	0,83 aA
			Suelo Collipulli		
15	1,2 aA	1,17 aA	1,14 aA	1,05 aA	1,04 aA
75	1,2 aA	1,13 aA	1,09 aAB	0,97 aB	0,98 aB

[1] Para cada suelo por separado, los valores seguidos de distinta letra mayúscula en una misma fila y letra minúscula en una misma columna, presentan diferencias significativas ($p \leq 0,05$).

CONCLUSIONES

El lodo como enmienda es una alternativa para mejorar las propiedades físicas y químicas en suelos agrícolas. Esto permite predecir un mejor desarrollo del cultivo, teniendo en cuenta el método y tiempo de aplicación, propiedades del lodo y del suelo. La aplicación de lodo mejoró significativamente los niveles de nitrógeno y materia orgánica en ambos suelos, así como, incrementó los valores de pH, con la consecuente disminución del contenido de Al de intercambio. Sin embargo, las distintas dosis de lodo no mejoraron significativamente las propiedades físicas de los suelos, a excepción de la estabilidad de los agregados en el suelo Gorbea, lo cual puede deberse al corto periodo de tiempo en el cual se realizó el ensayo (75 días).

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NOTA

INFLUÊNCIA DA ADIÇÃO DE UM RESÍDUO ALCALINO DA INDÚSTRIA DE PAPEL E CELULOSE NA LIXIVIAÇÃO DE CÁTIONS EM UM SOLO ÁCIDO(1)

Henrique Cesar Almeida(2), Paulo Roberto Ernani(3), Jackson Adriano Albuquerque(3), José Mecabô Junior(4) & Denice Almeida(2)

RESUMO

Os subprodutos alcalinos gerados nas indústrias de papel e celulose podem ser utilizados como corretivos da acidez do solo. Entretanto, eles possuem pouco Mg e médio teor de Na e, por isso, podem afetar negativamente a biodisponibilidade de alguns nutrientes, assim como alguns atributos do solo. Antes de recomendá-los, portanto, é importante avaliar seus efeitos. Este trabalho teve por objetivo quantificar a composição química do solo e a mobilidade vertical de cátions decorrente de formas de aplicação de um desses resíduos em relação ao calcário dolomítico. O experimento foi realizado em laboratório, sobre um Cambissolo Húmico, entre 2005 e 2006, utilizando-se colunas de lixiviação (30 x 10 cm de diâmetro). Os tratamentos consistiram de um fatorial 4 x 2 x 2, incluindo dois valores prévios de pH do solo com uma testemunha cada, dois corretivos de acidez (subproduto industrial ou calcário dolomítico) e dois métodos de aplicação (superficial ou incorporado). Foram realizadas 10 percolações, espaçadas em intervalos de sete dias, num volume de 300 mL de água destilada por semana, totalizando o equivalente a 380 mm de chuva. A incorporação do resíduo industrial ao solo causou a lixiviação de 60 % do Na adicionado, porém essa perda diminuiu para 12 % quando o corretivo foi aplicado sobre a superfície. O resíduo alcalino não ocasionou lixiviação de Ca, Mg ou K, e o calcário dolomítico lixiviou apenas 2,4 % do Ca e 7,2 % do Mg adicionados, comprovando a baixa mobilidade vertical desses cátions quando aplicados por meio de produtos alcalinos a solos com carga variável. A elevação prévia do pH diminuiu substancialmente a lixiviação dos cátions em decorrência do aumento das cargas elétricas negativas no solo. Nas condições pluviométricas da região Sul do Brasil, o Na adicionado pelo resíduo

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industrial lixiviará da camada arável em menos de um ano após sua aplicação e, portanto, não deverá prejudicar os atributos químicos e físicos do solo.

Termos de indexação: lixiviação, sódio, resíduo industrial, calcário.

SUMMARY: *CATION LEACHING FROM AN ACID SOIL AFTER APPLICATION OF ALKALINE BY-PRODUCT FROM THE PULP AND PAPER INDUSTRY*

Alkaline by-products generated in the pulp and paper industry can be used to reduce soil acidity. However, the low Mg and intermediate Na values in these residues can negatively affect the bioavailability of some nutrients and soil properties. Before recommending them, it is therefore imperative that their effects on the soil be evaluated. The objective of this study was to quantify the soil chemical composition and vertical mobility of cations due to application of alkaline industrial residue in different forms, in comparison to dolomitic limestone. The experiment was carried out in a laboratory, with a Haplumbrept, from 2005 to 2006, using leaching columns (30 x 10 cm diameter). The treatments consisted of a 4 x 2 x 2 factorial design, including two previous values of soil pH with one control each, two alkaline compounds (industrial residue or dolomitic limestone) and two application methods (surface applied or soil incorporated). Ten percolations were performed, at weekly intervals, in a volume of 300 mL of distilled water per week, corresponding to a total amount of 380 mm rain. 60 % of the Na added leached from the soil-incorporate by-product, but this leaching decreased to 12 % when it was applied on the soil surface. The addition of alkaline residue did not cause leaching of Ca, Mg or K, and dolomitic limestone leached only 2.4 % of the Ca and 7.2 % of added Mg, demonstrating the low vertical mobility of these cations when applied from basic compounds to variable charge soils. The previous elevation of the soil pH decreased cation leaching substantially due to the increase of the soil negative charges. Given the rainfall conditions in southern Brazil, the amount of Na added will disappear from the plow layer in less than one year after its application, so this product should not negatively affect any chemical or physical soil property.

Index terms: leaching, sodium, alkaline by-product, limestone.

INTRODUÇÃO

Muitos resíduos industriais têm sido utilizados na agricultura como fonte de nutrientes ou como corretivos da acidez, principalmente porque o solo tem grande capacidade de inativar parte dos compostos adicionados por meio de vários mecanismos químicos, sobretudo de adsorção e de precipitação (Sparks, 1995). O descarte de resíduos no solo é uma alternativa interessante porque, ao mesmo tempo que reduz o potencial poluente desses materiais, utiliza-os como insumos agrícolas de baixo custo (Defelipo et al., 1992; Mello & Vitti, 2002). Essa utilização, entretanto, deve ser precedida de estudos relacionados com as possíveis alterações que esses produtos possam ocasionar nas propriedades físico-químicas do solo, assim como no desenvolvimento e na composição das plantas (Ferreira et al., 2003).

Nos últimos anos, no Brasil, tem sido avaliado o efeito no solo e nas plantas de inúmeros subprodutos industriais, incluindo resíduos de curtume, de cervejaria, da exploração carbonífera, de estações de tratamento de esgoto e de indústrias de papel e celulose. Neste último, destacam-se dois resíduos: a lama de cal e o *dregs*. Esses subprodutos são retirados na clarificação e recuperação de produtos químicos obtidos no processo de separação da celulose (Cohn & Ribeiro, 2002). A lama de cal possui coloração clara e é constituída basicamente por carbonatos de cálcio ($CaCO_3$), enquanto o *dregs* possui cor acinzentada e é constituído por carbonatos, hidróxidos e sulfetos, sobretudo de Na e de Ca. O valor de neutralização (VN) desses resíduos normalmente varia de 40 a 70 % para a lama de cal e de 39 a 78 % para o *dregs* (Suzuki et al., 1991; Nurmesniemi et al., 2005). O *dregs* ainda possui aproximadamente 3,0 % de Mg e de 1,0 a 4,0 % de Na (Waldemar & Herrera, 1986; Albuquerque et al., 2002; Nurmesniemi et al., 2005; Almeida et al., 2007), além de pequenas concentrações de Ni, Cd e Pb (Nurmesniemi et al., 2005; Almeida et al., 2007).

Além de possuir alguns nutrientes essenciais às plantas e de ter a capacidade de elevar o pH dos solos, os resíduos alcalinos gerados pela indústria de papel e celulose têm preço muito menor do que os calcários comerciais, quando utilizados na mesma região de localização das unidades geradoras. Isso, sem dúvida, é um atrativo aos agricultores, devido à diminuição do custo produtivo das lavouras. A utilização de grandes quantidades desses produtos pode, no entanto, prejudicar algumas propriedades do solo, em razão da presença de Na.

A adição de Na ao solo pode aumentar a dispersão das argilas e dos colóides orgânicos, com prejuízos em alguns atributos físicos, como a redução da macroporosidade e o incremento do selamento superficial dos agregados (Mcintyre, 1958; Agassi et al., 1981; Reichert & Norton, 1994; Nelson et al., 1998). Esses fenômenos acontecem porque o Na tem um raio hidratado grande, que dificulta sua aproximação das superfícies sólidas carregadas negativamente. Com isso, ele aumenta a espessura da dupla camada elétrica que existe ao redor das partículas do solo (van Olphen, 1977) e favorece a dispersão dos colóides. Esses efeitos negativos podem, entretanto, ser temporários, pois o Na^+, por ser monovalente e ter grande raio hidratado, tem baixa afinidade pelas cargas negativas do solo relativamente aos cátions polivalentes, como Al^{3+}, Ca^{2+} e Mg^{2+}. Dessa forma, o Na presente na solução do solo pode ser lixiviado rapidamente para as camadas subsuperficiais, desde que haja fluxo descendente de água.

Nesse sentido, o presente trabalho teve por objetivo quantificar a mobilidade vertical de cátions no solo em função de métodos de aplicação de calcário ou de um resíduo industrial alcalino a um Cambissolo com acidez previamente corrigida ou não.

MATERIAL E MÉTODOS

O experimento foi realizado em laboratório, no Centro de Ciências Agroveterinárias (CAV) da Universidade do Estado de Santa Catarina (UDESC), em Lages, SC, entre o segundo semestre de 2005 e o primeiro semestre de 2006.

Foram utilizadas amostras de um Cambissolo Húmico Alumínico (CHa) (Embrapa, 1999), coletadas na camada de 0 a 20 cm de profundidade, na localidade de Macacos, em Lages, SC. Após a coleta, o solo foi passado em peneira com malhas de 0,5 cm e analisado. Este solo apresentou 350 g kg^{-1} de argila, 360 de silte, 290 de areia, 60 de matéria orgânica e densidade de partícula de 2,54 g cm^{-3}. A composição química do solo antes e após a aplicação dos tratamentos incorporados, porém antes das percolações, está no quadro 1. Na fração mineralógica havia predominância de caulinita e pequena quantidade de micas, de quartzo e de argilominerais 2:1 com hidróxido de alumínio nas entrecamadas (Almeida et al., 1997).

Os tratamentos foram distribuídos num delineamento inteiramente casualizado, com três repetições, e consistiram de um fatorial 4 x 2 x 2, com dois valores prévios de pH do solo (incluindo uma testemunha para cada caso), dois corretivos da acidez e duas formas de aplicação destes. As unidades experimentais foram constituídas por colunas de lixiviação preenchidas com solo, confeccionadas a partir de canos de PVC, com 30 cm de altura e 10 cm de diâmetro. Cada coluna foi formada por duas porções de solo, separadas por uma tela plástica com abertura de 1,0 mm de diâmetro. A porção superior tinha 15 cm de espessura e 1,2 kg de solo (base seca), enquanto a inferior tinha 10 cm de espessura e 0,8 kg de solo (base seca). Os 5,0 cm superficiais de cada coluna não foram preenchidos com solo, para facilitar a adição de água. Dentro da coluna, o solo apresentava densidade média de 1,02 g cm^{-3} e porosidade total média de 60 %. A base das colunas foi hermeticamente vedada com uma tampa de PVC. Na parte central desta foi feito um orifício com 3,0 mm de diâmetro

Quadro 1. Características químicas de amostras de um Cambissolo Húmico Alumínico (CHa), com e sem correção prévia da acidez, após a incorporação de um resíduo alcalino da indústria de papel e celulose e de calcário dolomítico

Tratamento	$pH\text{-}H_2O$	K^+	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}
		mg kg^{-1}		cmol$_c$ kg^{-1}		
			Sem calagem prévia			
Testemunha	4,4	158	7	1,5	0,9	5,1
Calcário incorporado	6,2	157	10	9,0	6,3	0,0
Resíduo incorporado	6,4	160	197	15,4	1,2	0,0
			Com calagem prévia			
Testemunha	6,2	157	10	9,0	6,3	0,0
Calcário incorporado	7,5	153	11	16,0	13,0	0,0
Resíduo incorporado	7,6	157	140	24,0	7,0	0,0

para permitir a drenagem da solução percolada, sobre o qual, internamente, foi colocada tela plástica com malha de 1,0 mm de abertura, a fim de evitar a passagem de solo. Cada coluna foi envolta com um funil plástico flexível, confeccionado a partir de sacos plásticos transparentes, a fim de evitar a perda de efluente e direcionar a solução percolada para os frascos de coleta, localizados abaixo delas.

A elevação prévia do pH de metade das amostras de solo foi efetuada seis meses antes do preenchimento das colunas. Para isso, 10 g kg^{-1} de calcário dolomítico foram misturados e homogeneizados com as amostras. Os dois corretivos de acidez (resíduo industrial e calcário dolomítico) foram aplicados por ocasião da transferência do solo para as colunas de lixiviação. Cada um deles foi adicionado sobre a superfície das colunas (método superficial) ou misturado (método incorporado) com todo o volume de solo da parte superior delas. No método de aplicação superficial, a fim de evitar a formação de crostas calcárias na superfície do solo, os corretivos da acidez foram misturados manualmente e homogeneizados com 80 g de solo (base seca), cujo volume foi depositado na parte mais superficial de cada coluna e correspondeu a uma camada com 1,0 cm de espessura. As quantidades adicionadas do resíduo industrial (15 g por coluna) ou de calcário dolomítico (12 g por coluna) foram as mesmas para as duas formas de aplicação (superficial ou incorporada) e corresponderam a uma vez a dose (PRNT = 100 %) recomendada pelo método SMP para elevar para 6,0 o pH das amostras sem calagem prévia.

O resíduo industrial utilizado apresentava Ca = 354 g kg^{-1}, Mg = 9,2 g kg^{-1}, Na = 10,2 g kg^{-1}, pH = 10,7, valor de neutralização (VN) = 80 % e eficiência relativa (ER) de 100 % (Almeida et al., 2007). O calcário dolomítico apresentava Ca = 289 g kg^{-1}, Mg = 118 g kg^{-1}, Na = 170 mg kg^{-1}, VN = 99,7 % e ER de 100 %. Os teores de Ca, de Mg e de Na do calcário, além do seu VN e ER, foram determinados de acordo com o método descrito em Tedesco et al. (1995).

Após serem preenchidas com o solo, as colunas foram acondicionadas verticalmente em suportes plásticos, cuja base ficou 20 cm acima da superfície de um balcão. As percolações iniciaram-se uma semana após a transferência do solo para as colunas. Elas foram repetidas a cada sete dias, durante 10 semanas. Em cada percolação, adicionaram-se 300 mL de água destilada sobre a superfície de cada coluna, na velocidade de 2,0 mL por minuto, totalizando o equivalente a 380 mm de chuva durante todo o período experimental. A solução percolada foi coletada no dia seguinte, para determinação do volume e da composição química.

Na solução percolada, foram determinados o pH, a condutividade elétrica (CE) e as concentrações de Ca, Mg, K e Na. No solo da coluna, foram avaliados o pH-H_2O e os teores de Ca, Mg, K, Na e Al trocáveis. As concentrações de Ca e de Mg foram quantificadas por espectrofotometria de absorção atômica; K e Na, por fotometria de emissão; pH, por potenciometria; Al trocável, por titulometria ácido-base; e CE, por condutivimetria. Os métodos utilizados estão descritos em Tedesco et al. (1995).

Os resultados foram submetidos à análise de variância por meio dos modelos geométricos lineares (procedimento GLM). As médias foram comparadas por meio de contraste a 5 % de significância.

RESULTADOS E DISCUSSÃO

Efeitos no sódio

A lixiviação de Na variou com o corretivo da acidez (resíduo industrial ou calcário dolomítico), com a forma de aplicação deste e com o pH prévio do solo (Quadro 2). Ela foi maior com o resíduo industrial do que com calcário, principalmente quando o resíduo foi incorporado ao solo (Figura 1). O calcário não lixiviou Na, independentemente da forma de aplicação e dos valores prévios de pH do solo (Quadro 2), devido à pequena concentração do elemento nesse produto (170 mg kg^{-1}). A dose de calcário utilizada, apesar de alta (10 g kg^{-1} de solo ou 20 g por coluna), adicionou apenas 3,4 mg de Na por coluna, o que equivale a 1,7 mg kg^{-1} de solo. Azevedo et al. (1996) aplicaram doses de até 40 Mg ha^{-1} de calcário dolomítico a um Latossolo Bruno e verificaram que nessa dose a concentração de Na da camada superficial com 20 cm de profundidade aumentou apenas 1,9 $mmol_c$ kg^{-1}.

Grande parte do Na adicionado pelo resíduo industrial lixiviou em pouco tempo, porém a magnitude da lixiviação variou com a forma de aplicação e com os valores prévios de pH (Quadro 2, Figura 1). A maior lixiviação de Na aconteceu quando o resíduo industrial foi incorporado ao solo nas amostras sem calagem prévia. Nesse tratamento, em apenas 10 percolações de água, o resíduo industrial lixiviou 150 mg dos 255 mg de Na adicionados por coluna, totalizando 60 % do aplicado. A maior lixiviação de Na ocorreu na oitava percolação, cuja concentração máxima atingiu 154 mg L^{-1} no efluente percolado (Figura 2). Considerando que a precipitação média anual no Planalto Catarinense é de aproximadamente 1.550 mm, estima-se que todo o Na adicionado pela dose de 20 Mg ha^{-1} do resíduo seja lixiviado em menos de um ano, caso o produto seja incorporado ao solo, pois neste trabalho as percolações equivaleram a uma precipitação total de 380 mm de chuva. Quando o resíduo industrial foi aplicado nas amostras de solo que já tinham recebido calagem, a lixiviação de Na diminuiu 22 % em relação ao solo sem correção prévia de pH, devido, provavelmente, ao aumento do número de cargas elétricas negativas geradas pelo aumento do pH (Albuquerque et al., 2000).

Quando o resíduo industrial foi aplicado sobre a superfície do solo que não havia recebido correção

Quadro 2. Análise da diferença entre os valores acumulados de Na, K, Ca e Mg após 10 percolações em amostras de um Cambissolo Húmico com dois valores prévios de pH em conseqüência da aplicação de um resíduo industrial da indústria de papel e celulose ou de calcário dolomítico

Contraste	Na	K	Ca	Mg
	mg			
Calcário Inc x Calcário Sup(1) (s/c)	ns	ns	*(+)	*(+)
Resíduo Inc x Resíduo Sup (s/c)(2)	*(+)	ns	ns	ns
Calcário Inc x Resíduo Inc (s/c)	*(-)	*(+)	*(+)	*(+)
Calcário Sup x Resíduo Sup (s/c)	ns	ns	ns	ns
Testemunha x Calcário Inc (s/c)	ns	*(-)	*(-)	*(-)
Testemunha x Calcário Sup (s/c)	ns	ns	ns	ns
Testemunha x Resíduo Inc (s/c)	*(-)	ns	ns	ns
Testemunha x Resíduo Sup (s/c)	ns	ns	ns	ns
Calcário Inc x Calcário Sup (c/c)	ns	ns	ns	ns
Resíduo Inc x Resíduo Sup (c/c)	*(+)	ns	ns	ns
Calcário Inc x Dregs Inc (c/c)	*(-)	ns	ns	ns
Calcário Sup x Resíduo Sup (c/c)	ns	ns	ns	ns
Testemunha x Calcário Inc (c/c)	ns	ns	ns	*(-)
Testemunha x Calcário Sup (c/c)	ns	ns	ns	ns
Testemunha x Resíduo Inc (c/c)	*(-)	ns	ns	*(-)
Testemunha x Resíduo Sup (c/c)	ns	ns	ns	ns
(s/c) x (c/c)	*(+)	*(+)	*(-)	*(-)
	Resumo da análise de variância do procedimento GLM			
R^2	0,92	0,98	0,93	0,98
CV (%)	42	7,3	17	17

(1) inc: produtos incorporados ao solo; sup: produtos aplicados sobre a superfície do solo. (2) s/c: solo sem correção prévia do pH; c/c: solo com correção prévia do pH. *: significativo a 5 % pelo teste de Student, segundo análise de contraste. Valores positivos mostram maior diferença significativa do grupo à esquerda do contraste, enquanto os valores negativos mostram maior diferença significativa do grupo à direita do contraste; ns: não-significativo.

prévia de pH, a perda de Na foi de apenas 12 % do adicionado, ou seja, cerca de cinco vezes menos do que no tratamento incorporado (Figura 1). O efeito mais lento proporcionado pela aplicação superficial fez com que a maior perda de Na ocorresse somente entre a oitava e a décima percolação, com concentração máxima de 50 mg L^{-1} na solução percolada (Figura 2). Na média dos tratamentos com o resíduo industrial (com e sem correção prévia de pH), a incorporação desse subproduto alcalino lixiviou 92 mg a mais de Na por coluna em relação aos tratamentos com aplicação sobre a superfície do solo (Figura 1), o que representa 36 % do Na adicionado. Quando aplicado sobre a superfície do solo, o produto precisa percorrer um caminho mais longo até atingir o fundo da coluna, sendo, portanto, fortemente dependente da quantidade de água que percola através do perfil do solo, ou seja, da intensidade e da quantidade das chuvas.

O Na remanescente no solo após o término das percolações variou com a forma de aplicação do resíduo industrial. Nas amostras de solo coletadas da parte superior da coluna (15 cm), a adição do resíduo industrial numa quantidade equivalente a 20 Mg ha^{-1} manteve uma concentração de Na de 138 mg kg^{-1} quando o produto foi incorporado e de 230 mg kg^{-1} quando ele foi aplicado sobre a superfície do solo, na média das amostras com e sem calagem prévia. Na testemunha e nos tratamentos com calcário dolomítico, a concentração de Na foi de 7 e de 10 mg kg^{-1}, respectivamente (dados não mostrados).

Efeitos no cálcio e no magnésio

Os dois corretivos da acidez provocaram pouca lixiviação de Ca e de Mg (Quadro 2, Figuras 3 e 4). A adição de calcário dolomítico, numa dose equivalente a 20 Mg ha^{-1} (10 g kg^{-1}), lixiviou somente 2,4 % do Ca e 7,2 % do Mg adicionados. Essa pequena lixiviação se deve à baixa solubilidade dos calcários agrícolas, aliada às pequenas quantidades de seus ânions que permanecem na solução do solo após a correção da acidez (Ernani et al., 2001; Miranda et al., 2005). É necessário considerar, entretanto, que a quantidade de água percolada pelas 10 adições foi relativamente pequena – o equivalente a um total de 380 mm de chuva.

A lixiviação desses dois cátions foi tão pequena a ponto de a adição de 25 Mg ha^{-1} (12,5 g kg^{-1}) do resíduo industrial, que tem 354 g kg^{-1} de Ca, não ter afetado

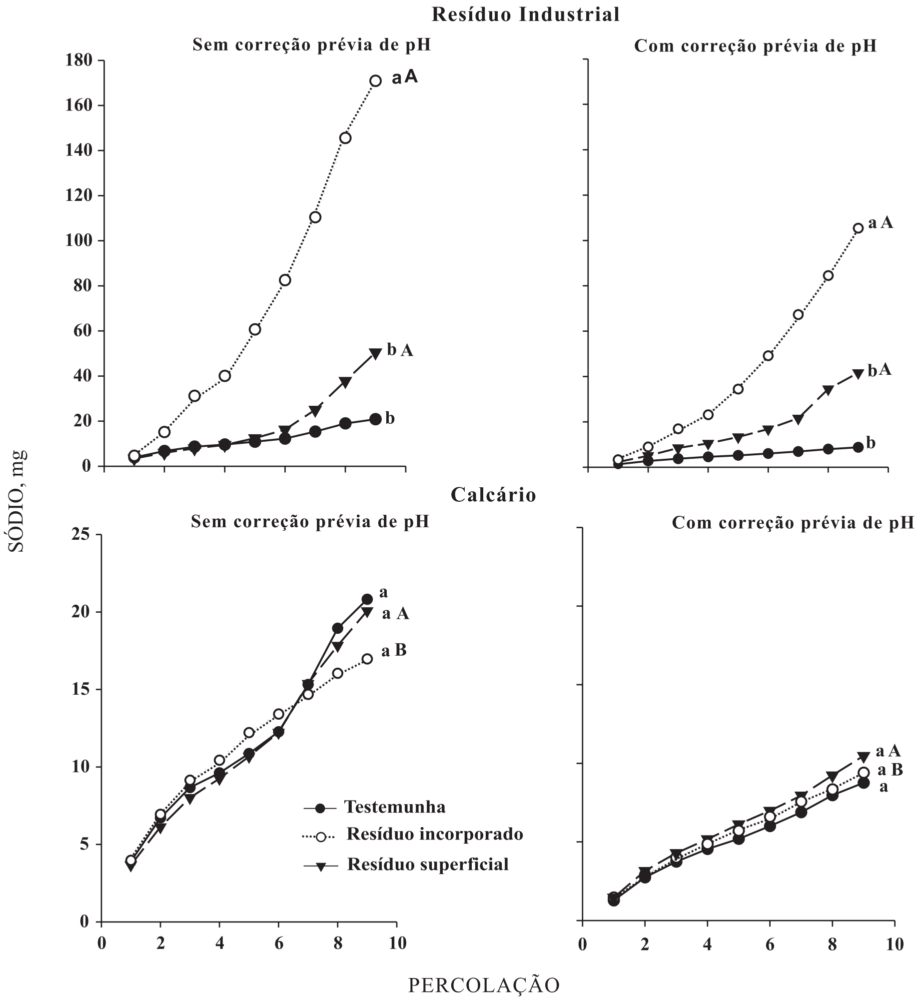

Figura 1. Perdas acumuladas de sódio após 10 percolações com água destilada em conseqüência da aplicação de calcário ou de um resíduo industrial em amostras de solo com e sem correção prévia de pH. (Letras minúsculas comparam as formas de aplicação de cada corretivo com a testemunha dentro de cada pH; letras maiúsculas comparam esses mesmos tratamentos entre os corretivos da acidez, dentro do mesmo pH. Ausência de letra significa inexistência de diferença estatística pela análise de contraste a 5 %).

a perda desse nutriente, independentemente da forma de aplicação, em relação ao tratamento em que ele não foi aplicado (Quadro 2). Na média dos tratamentos, aqueles com correção prévia da acidez foram os que causaram maior lixiviação de Ca e de Mg (Quadro 2), em razão da existência de maiores concentrações desses dois cátions, tanto nas cargas negativas como na solução do solo (Ciotta et al., 2004). Além disso, os tratamentos com correção prévia da acidez possuíam distribuição uniforme de calcário dolomítico em toda a extensão da coluna, o que facilita a lixiviação desses íons. Nos tratamentos sem calagem prévia, os corretivos foram aplicados na superfície do solo ou incorporados nos 15 cm superficiais, dependendo do tratamento, e, para atingirem o fundo da coluna, teriam que percorrer pelo menos mais 10 cm de solo. Como a coluna tinha 25 cm de solo e o resíduo industrial foi aplicado sobre a superfície ou misturado com os 15 cm da parte superior, verifica-se, portanto, que a mobilidade vertical do Ca originário desse resíduo industrial foi inferior a 10 cm. Esses dados confirmam a baixa mobilidade dos cátions adicionados pelos corretivos da acidez, constantemente verificada nos solos do Sul do Brasil (Ernani et al., 2001, 2004).

A incorporação dos dois corretivos da acidez (resíduo alcalino ou calcário dolomítico) às amostras com correção prévia de pH lixiviou aproximadamente 30 mg a mais de Mg do que de Ca (Figuras 3 e 4). A maior solubilidade do $MgCO_3$ em relação ao $CaCO_3$ presentes no calcário dolomítico adicionado previamente nessas amostras e a menor preferência do Mg em relação ao Ca pelas cargas negativas (Ernani & Barber, 1996) provavelmente foram as responsáveis pela maior lixiviação do Mg ao longo da coluna de solo. As constantes de solubilidade (K_{ps}) do $CaCO_3$ e do $MgCO_3$ são, respectivamente, de $4,8 \times 10^{-9}$ e $2,6 \times 10^{-5}$ (Weast, 1972).

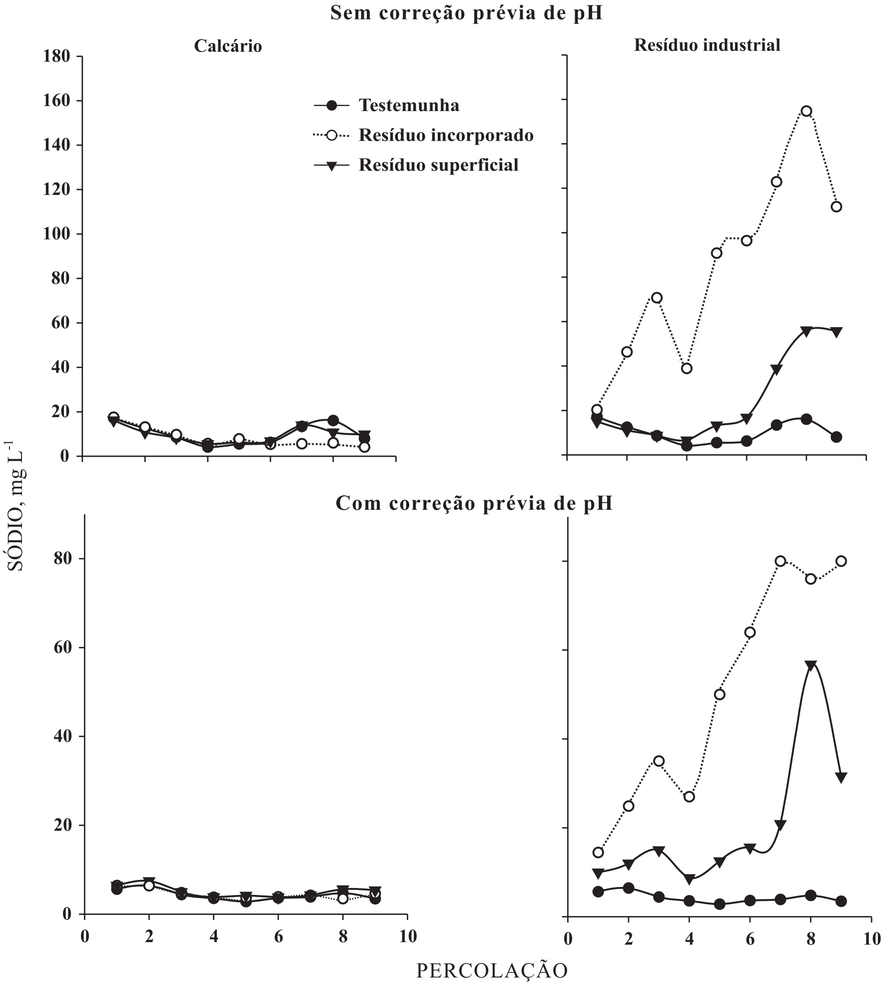

Figura 2. Flutuação temporal da concentração de sódio na solução percolada em cada uma das 10 percolações com água destilada em função de formas de aplicação de calcário ou de um resíduo industrial em amostras de solo com e sem correção prévia de pH.

Efeitos no potássio e no pH

A maior lixiviação de K ocorreu nas amostras de solo sem prévia elevação do pH (Quadro 2), numa média de 36 mg por coluna a mais do que nas amostras que receberam calcário previamente (Figura 5), onde foram retidos, em média, cerca de 130 mg kg^{-1} de K. Como a elevação do pH aumenta o número de cargas elétricas negativas do solo (Albuquerque et al., 2000), parte do K da solução passa a ser adsorvida eletrostaticamente às cargas criadas e se torna menos suscetível à lixiviação (Ernani et al., 2001, 2007). Em virtude da diminuição da concentração de K na solução, decorrente do aumento das cargas negativas, a nova tabela de adubação dos Estados do Rio Grande do Sul e de Santa Catarina considera a capacidade de troca de cátions (CTC) do solo como um fator na avaliação da disponibilidade de K às plantas (CFSRS/SC, 2004).

Relativamente à testemunha, nenhum tratamento com o resíduo industrial ocasionou lixiviação de K. O calcário dolomítico, entretanto, somente lixiviou K quando foi incorporado ao solo nos tratamentos sem prévia elevação do pH (Quadro 2, Figura 5). A concentração de Na presente no resíduo industrial não afetou, portanto, o equilíbrio do K no solo, nas condições experimentais utilizadas no presente estudo. A maior lixiviação de K provocada pelo calcário dolomítico em relação ao resíduo industrial se deveu, provavelmente, à maior quantidade total de cátions divalentes (Ca + Mg) no calcário, os quais possuem maior afinidade pelas cargas negativas do solo em relação aos cátions monovalentes. Quando os corretivos da acidez são aplicados ao solo, esses dois cátions descem até profundidades maiores do que aquelas onde ocorre elevação do pH (Ernani et al., 2004). Com isso, parte dos átomos de Ca e de Mg que atinge as profundidades onde o pH não foi afetado desloca K das

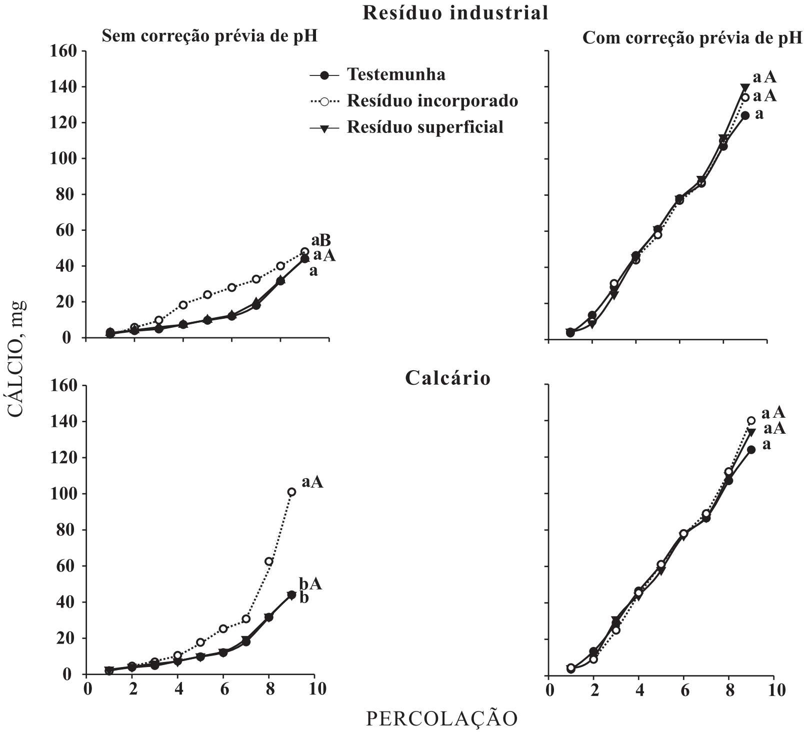

Figura 3. Perdas acumuladas de cálcio após 10 percolações com água destilada em decorrência da aplicação de calcário ou de um resíduo industrial em amostras de solo com e sem correção prévia de pH. (Letras minúsculas comparam as formas de aplicação de cada corretivo com a testemunha dentro de cada pH; letras maiúsculas comparam esses mesmos tratamentos entre os corretivos da acidez, dentro do mesmo pH. Ausência de letra significa inexistência de diferença estatística pela análise de contraste a 5 %).

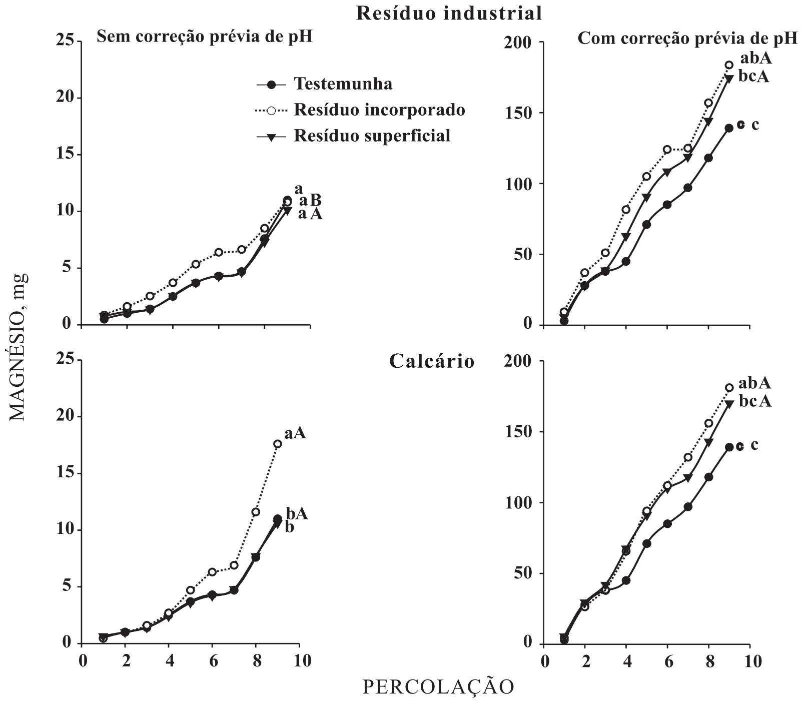

Figura 4. Perdas acumuladas de magnésio após 10 percolações de água destilada em conseqüência da aplicação de calcário ou de um resíduo industrial em amostras de solo com e sem correção prévia de pH. (Letras minúsculas comparam as formas de aplicação de cada corretivo com a testemunha dentro de cada pH; letras maiúsculas comparam esses mesmos tratamentos entre os corretivos da acidez, dentro do mesmo pH. Ausência de letra significa inexistência de diferença estatística pela análise de contraste a 5 %).

cargas elétricas dessa região para a solução do solo, facilitando sua lixiviação. Ernani et al. (2004) verificaram resultados semelhantes com o deslocamento do Al^{3+} nas camadas de solo abaixo dos locais de aplicação de calcário. Nos tratamentos em que o pH do solo foi corrigido previamente esse fenômeno não aconteceu, devido à uniformidade na distribuição do calcário em toda a extensão da coluna de solo. A concentração de K tanto no calcário quanto no resíduo alcalino foi inferior a 1,5 mg kg^{-1}.

O pH do efluente percolado das colunas de solo, na média das 10 percolações, não foi afetado pela adição dos corretivos da acidez (calcário e o resíduo industrial) nem pelos métodos de incorporação destes (superficial ou incorporado). A incorporação dos corretivos da acidez nas amostras de solo aumentou o pH de 4,4 para 6,3, nos tratamentos sem calagem prévia, e de 6,2 para 7,55, naqueles com calagem prévia (Quadro 1). O pH da solução percolada não foi afetado pelos tratamentos porque o efeito alcalino exercido pelos corretivos da acidez na parte superior da coluna foi contrabalanceado pelo efeito acidificante ocasionado pela hidrólise do Al^{3+}, retirado das cargas negativas do solo abaixo das regiões corrigidas pelo Ca e pelo Mg (Ernani et al., 2004).

CONCLUSÃO

A lixiviação do Na adicionado ao solo pelo resíduo alcalino da indústria de papel e celulose diminuiu com o aumento do pH e foi afetada pela forma de aplicação. Ela variou de 12 a 60 % do total adicionado, respectivamente quando esse subproduto industrial foi adicionado sobre a superfície ou incorporado na camada superficial do solo. Por sua vez, o resíduo não lixiviou K, Ca e Mg. Com base nessas avaliações laboratoriais, presume-se que esse produto possa ser utilizado como corretivo da acidez para solos ácidos sem ocasionar efeitos negativos nas propriedades químicas e físicas.

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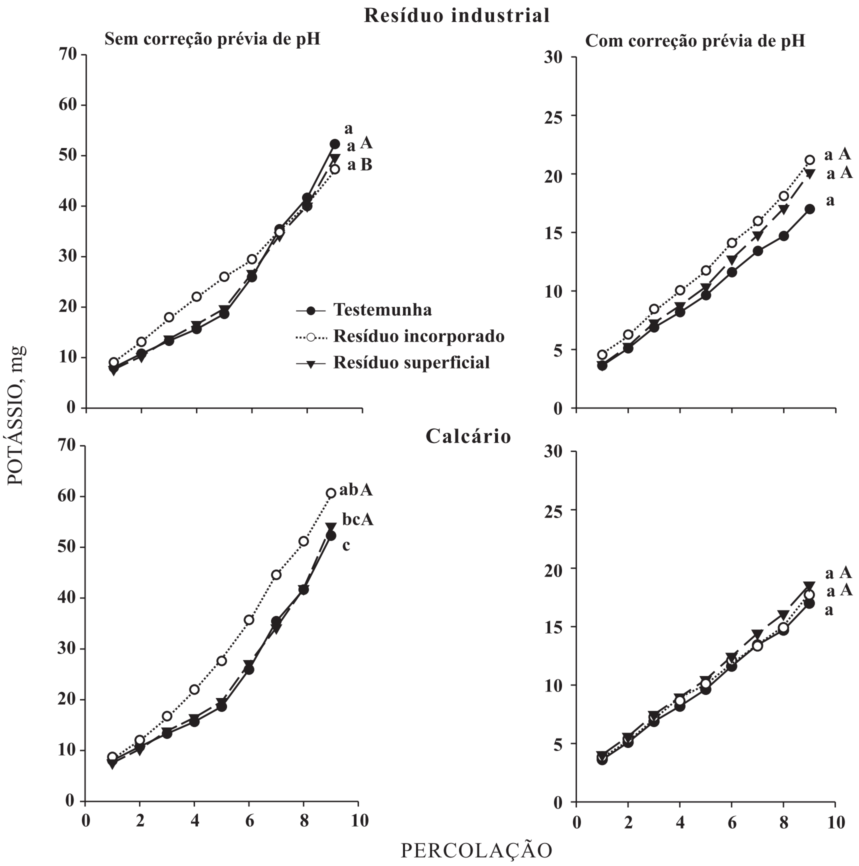

Figura 5. Perdas acumuladas de potássio após 10 percolações com água destilada em virtude da aplicação de calcário ou de um resíduo industrial em amostras de solo com e sem correção prévia de pH. (Letras minúsculas comparam as formas de aplicação de cada corretivo com a testemunha dentro de cada pH; letras maiúsculas comparam esses mesmos tratamentos entre os corretivos da acidez, dentro do mesmo pH. Ausência de letra significa inexistência de diferença estatística pela análise de contraste a 5 %).

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ACIDS SOILS' PH AND NUTRIENT IMPROVEMENT WHEN AMENDED WITH INORGANIC SOLID WASTES FROM KRAFT MILL

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ABSTRACT

Kraft mill generates a large amount of dregs (D) and grits (G) as solid wastes due to the causticizing process. The disposal of these wastes is expensive in terms of land requirement and maintenance. On the other hand, solid wastes have alkalinity and buffer properties, which make them appropriate for use as amendments to acidic soils.

The goal of this work was to determine the physical, chemical, toxicity and hazardousness characteristics of D & G. Additionally, the effect on acidic soils' physical properties after mixing with these wastes as well as potential leach properties were evaluated.

Hazardousness (inflammability, reactivity, corrosivity) and toxicity (due to inorganic compounds) assays on D & G indicated that their values are below the EPA Standard. Additionally, physicochemical characterization (pH (12.76), Ca (26.5%), Mg (1.5%), P (0.28%) and K (0.20%)) confirms their potential use in degraded solids.

To study the amended soils' leaches, the behavior of a series of columns with acid soils and D&G (1:1) at rates of 2 and 6 g kg^{-1} was evaluated during 86 d. The physicochemical characteristics of the amended soils were improved by D&G incorporation.

Keywords: Acid soils; Dregs; Grits; Industrial wastes.

1. INTRODUCTION

Kraft pulping process generates solid wastes, such as slaker grits (G) and dregs (D). Grits are unreacted lime particles, and dregs are light, fluffy black material composed by carbon, iron, silica, potassium, calcium, alumina, magnesium, and some sulfides (Rabas, 1988). Dregs are removed from the green liquor clarifier inserted in the re-causticizing process where they have accumulated, generating environmental and economic impacts. Moreover, mass balance in a kraft Chilean mill, indicated that the causticizing process generates 10 and 3 tons day^{-1} of the D and G, respectively (Zambrano et al., 2003). These solid wastes could be beneficially re-used in acidic soil for various reasons: the mineral content provides calcium carbonate as a liming agent decreasing acidification of acidic soils, and the clay can improve a soil's cation exchange capacity and slow down water percolation on fast-draining soil.

Ground agricultural limestone has been the traditional material for liming acid soils in the Southeastern U.S. Farmers usually refer to it as "lime", although its technical name is "ground limestone" or "ag limestone". There are two fundamental reasons for using aglime: (1) to neutralize soil acidity (increase soil pH) and (2) add calcium and magnesium to the soil. Ground limestone does this well since it is mostly $CaCO_3$ or $CaCO_3$ + $MgCO_3$. However, since carbonates are not very soluble in water, limestone must be ground very finely and mixed with the soil to be effective at neutralizing soil acidity. Although ground limestone may have 100% calcium carbonate equivalency (CCE) (pure $CaCO_3$), it may only be 67% effective at neutralizing soil acidity due to coarse particles. Most soil testing laboratories take this into consideration when making soil liming recommendation outlines.

There are many other products and by-products which may also be used to neutralize soil acidity and supply Ca, Mg, and other plant nutrients. However, the mill sludge is often disposed in large amounts in the neighborhood surrounding the factories, causing serious environmental problems. Therefore, recycling of D & G could increase the productivity of the widespread acidic soils, acting as a significant source of the nutrients P, K, Mg, Ca and lime (Ohno and Erich 1990; Etiegni et al., 1991; Huang et al., 1992). D & G's agronomic benefits both as a nutrient source and a liming agent for agricultural soils are well documented (Clapham and Zibilske, 1992; Krejsl and Scanlon 1996).

South Chilean Andisols have high organic matter (20%), acidity (5 < pH < 6), high aluminum saturation (5-30%), and high pluviometry (1200 mm year^{-1}·m^{-2}). Consequently, the application of D & G should improve soil fertility. This could be a promising method to recycle D & G and improve the agricultural acid soils (Voundi et al., 1998).

The goals of this work were to determine the physical, chemical, toxicity and hazardousness characteristics of D & G. Additionally, the effect of D & G application on the physical properties in the acid soil and potential leaches properties were evaluated.

2. Materials and methods

Dreg and grits was obtained from the causticizing process of a Chilean kraft-pulp mill, where *Pinus radiata* is the principal raw material.

The acid soil samples were taken in a profile of 20 – 40 cm (soil series Gorbea (IX Region – Chile), dried to environmental temperature, and sieved through a 2-mm mesh-size sieve.

Commercial lime was utilized to correct the acidity of the degraded soils. Its chemical characterization, showed a content of $CaCO_3$ (91%), $Ca(OH)_2$ (5%) and 2% of S and Mg.

Batch incubation was performed to determine the D&G (1:1) application dose for the acid soil. Acid soil samples were incubated, and different D&G concentrations (5, 9, 14, 18 and 30 g kg^{-1}) were applied to the acid soil. This incubation was carried out in capsules dampened under field capacity moisture conditions at 60°C for 24 hours. After of the incubation period, the soil's pH was measured. The soil - pH was determined following Mora and Barrow (1996).

For the continuous leaching experiences, eight PVC columns (external diameter 16 cm, length 50 cm) were arranged, two of them in duplicate containing a mixture of acid soil + D&G (5 g kg^{-1} and acid soil + D&G (14 g kg^{-1}). The other four corresponded to control samples of acid soil, normal soil, acid soil + lime (2 g L^{-1}), and finally a column with a D&G (1:1). The different substrates were arranged in each one of these columns, to a height of 40 cm. To study the leaching, the annual precipitation of the IX Region (Chile) was simulated (1,200 mm year^{-1} m^{-2}) by passing distilled water through the columns. A volume of 60 mL day^{-1} was fed by controlled pumping. The leaching was collected every two days for the entire study period (86 days), and the volume and pH were determined. Additionally, the N, P, and Ca content and the Chemical Organic Demand (COD) were determined. Finally, the compacting and filtration curves during all the leaching procedure were determined.

D, G and soil characterization were performed following the Analytical Methods recommended for Chilean Soils (Commission of Normalization and Chilean Accreditation Company of Soil Sciences). Whereas the toxicity and danger characteristics were performed according to US EPA Standard, CFR PART 261 "Identification and hazardous waste listing" and corresponded to the following analysis: flammability, Method: SW-846, Method 1010, Reactivity: Method: SW-846, Method 9010-9030, Corrosive: Method: SW-846, Method 1110. Additionally, inorganic toxicity was determined following Method: SW-846, Method 1311, analyzing the presence of the following elements: Ar, Ba, Cr, Pb, Hg, and Cd. The pH in batch incubation was performed following the methodology indicated by Mora and Barrow (1996). The field capacity and density were measured according to Barajas et al. (1994).

Nitrogen, P, Ca and COD determinations in the leaching were carried out according to APHA-AWWA-WPCF (1985).

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3. RESULTS AND DISCUSSION

Determinations of hazardousness (flammability, reactivity, corrosivity) and toxicity essays to D & G indicated that their values are below the EPA Standard.

Table 1 presents the D, G, and D&G characterization. The results indicate alkaline properties due to carbonate hydrolysis to calcium oxide with the corresponding hydroxides, confirming in this way the possibility of using these solid wastes for land application. Additionally, D, G and D&G could also influence the soil's water and nutrient retention capacity (Zambrano et al., 2003, Ceppi, et al., 2005).

Table 1. Dregs and grits characterization.

Parameter	Dreg	Grit	D & G
pH (in H_2O)	12.78	12.73	12.4
Apparent density (kg m^{-3})	760	755	753
Humidity (%)	50.79	23.39	40.04
Organic matter (%)	3.53	0.53	1.79
S (%)	2.40	0.41	1.40
Ca (%)	23	30	27
Mg (%)	2.95	0.33	1.50
K (%)	0.33	0.11	0.20
P (%)	0.28	0.30	0.28
Fe (mg L^{-1})	0.98	0.11	0.52
Mn (mg L^{-1})	0.82	0.015	0.47
Cu (mg L^{-1})	0.035	0.0005	0.015
Zn (mg L^{-1})	0.14	0.0004	0.007
Al (mg L^{-1})	1.12	0.26	0.66
Na (%)	3.55	0.92	2.21
B (mg L^{-1})	0.0004	0.0004	0.0004
CO_3 (%)	47	57	59
granulometer*(%)	30	57	45

*0.850 mm of open diameter. [#] D:G as 1:1.

D & G are also a source of essential plant nutrients (K, P, Mg and Ca), and the concentration of the last two is very similar to the values found in commercial lime (Etiegni et al., 1991).

Figure 1 shows the pH effects due to different D&G (1:1) rate in acid solids. The leach analysis during the incubation period presented the following effects: the filtering distilled water had an initial pH of 5, increasing to values of 7.36 and 8.23 for the concentration of D&G in the acid soil of 5 and 30 g kg^{-1} respectively. These values were higher than the values observed in the leaches collected from the commercial lime + acid soil (2 g L^{-1}) column (see Table 2), which was probably due to the fraction of CaO present in the solid wastes which is more reactive than pure $CaCO_3$ present in the commercial lime.

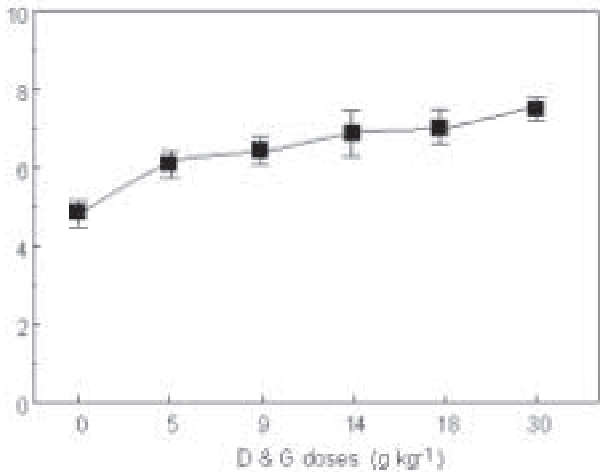

Figure 1. D & G (1:1) doses to add to acid soils.

Moreover, Table 2 shows that D&G have a better effect on the increment of Mg and Ca in the acid soil than observed with the commercial lime (Zambrano et al., 2003).

Table 2. Chemical characteristics of the mix: acid soil – solid waste and witness samples after three months of incubation under simulation of local pluviometry conditions.

Parameter	Acid soil	Natural soil	Acid soil + lime (2 g kg^{-1})	Acid soil + D&G(1:1) (5 g kg^{-1})	Acid soil + D&G(1:1) (14 g kg^{-1})
N (mg L^{-1})	23	11	20	20	27
P (mg L^{-1})	7	5	11	12	12
K (mg L^{-1})	47	78	70	78	90
Ca (mg L^{-1})	186	1434	676	1148	3226
Mg (mg L^{-1})	0.30	1.15	4.74	6.32	8.12
pH	4.87	6.23	5.39	5.81	6.76
Organic matter (%)	16	9	11	14	13
Basis (meq 100^{-1} g^{-1})	1.47	8.76	4.06	6.79	17.71
CICA (meq 100^{-1} g^{-1})	0.3	1.15	4.28	6.84	17.73
Al saturation (%)	43.46	0.03	5.14	0.73	0.11
B (mg L^{-1})	0.35	0.33	0.52	0.54	0.52
Zn (mg L^{-1})	0.16	0.4	0.29	0.36	0.96
Mn (mg L^{-1})	1.32	0.33	2.82	3.23	5.31
Cu (mg L^{-1})	0.87	0.71	1.68	2.33	3.22
Fe (mg L^{-1})	18.76	16.28	44.41	46.11	51.43
Mn (mg L^{-1})	1.32	0.33	2.82	3.23	5.31
S (mg L^{-1})	8	11	20	29	26

Therefore, it is 1.8 times more reactive in comparison with pure calcium carbonate, and could be almost 3 times more effective at neutralizing soil acidity compared to ground limestone (Vondi et al., 1997), which is the highly reactive, caustic lime used by the steel industry, paper industry, and construction industry where a highly caustic, alkaline material is needed. When oxide lime comes in contact with water, an intense, exothermic reaction occurs. Oxide lime may be used to rapidly increase soil pH (Campitelli et al., 2003).

Probably for this reason, the increase in soil pH (5.8) with the application of 5g kg^{-1} solid waste (D & G, 1:1) was higher than the commercial lime (5.4) at the same concentration. This phenomenon was also observed in the final values of the Al saturation, with 0.73 (5 g kg^{-1} D&G) and 5.14% (commercial lime) and in cation exchange capacity (CEC) with 6.84 y 4.28% respectively (Campitelli et al., 2003). For the application of 14 g kg^{-1} of D&G (1:1), the observed values were logically higher with an increased soil pH of 6.8, the Al saturation decreased to 0.11%, and there was an increase in the final soil nutrient content such as Ca, K y Mg reflected in an increased CEC with a value of 17.7%.

Leach evolutions are shown in the Figure 2. The D & Column G produced the leaches with highest pH (Figure 1a), while the leaches with lowest pH were produced by column with acid soil. The D&G effect on the acid soil-pH can be evaluated comparing the columns with 2 g D&G kg^{-1} and 6 g D&G kg^{-1}. The average pH value ranged between 6.7 and 7.9 and between 7.9 and 8.5 for the 2 g D&G kg^{-1} and 6 g D&G kg^{-1} columns, respectively.

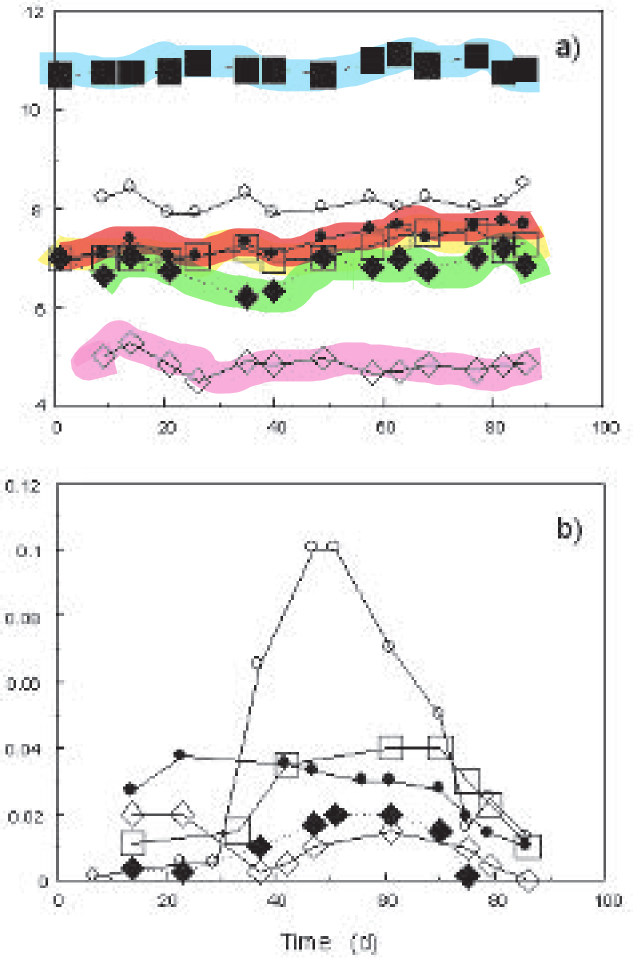

Figure 2. Leach characterization arising from continuous column with lime (♦), D&G (■), natural soil (□), acid soil (◇), acid soil+ 2 g D&G kg^{-1} (1:1) (•), acid soil + 6 g D&G kg^{-1} (1:1) (○). Evolution of a) pH and b) phosphorous (mg L^{-1}).

Figure 1b shows the evolution of the phosphorus. The concentration of this parameter was higher at the beginning, probably due to the particle size of the solid wastes, and then it decreased due to phosphorous' typically low mobility in the soil. However, between 40 and 60 days, concentration was 0.1mg L^{-1} in the leaches coming from column with 6 g D&G kg^{-1}.

The case of nitrogen content in the leaches is different because there is no nitrogen in industrial solid waste, and as a result the leaches' nitrogen concentration is probably due to the incremental activity of nitrogen fixing bacteria resulting from the leaches' better pH condition.

Figure 3 shows the leaches-COD evolution. The tendency of the concentration curves in all cases decreased over time. In almost all of the cases, the highest concentration at the beginning was 40 mg L^{-1} of COD, except in the leaches coming from column 6 g D & G kg^{-1}. However, even in these leaches, the tendency was to decrease from 450 to 128 g L^{-1} of COD.

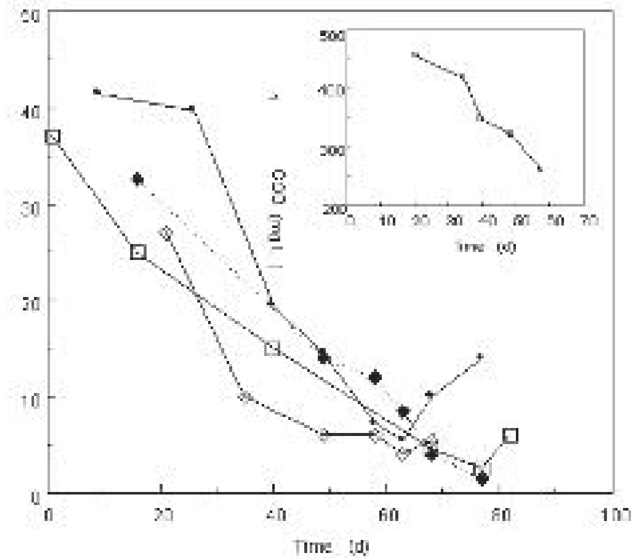

Figure 3. COD-leach evolution arising from continuous column with lime (♦), D&G (■), natural soil (□), acid soil (◇), acid soil+ 2 g D & G kg^{-1} (1:1) (•), acid soil + 6 g D&G kg^{-1} (1:1) (○).

On the other hand, the leaches' calcium concentration was between 20 and 120 mg L^{-1} and it decreased slowly (data not shown). This is cation has a high mobility at low pH values (<5.8), which explains their following decrease.

Due to above, D&G show alkaline characteristics that allowing them to increase the pH of acid soil. Additionally, its mineral content provides calcium carbonate and calcium oxide as a liming agent, and the clay incorporated can improve a soil's cation exchange capacity and slow down water percolation. Indeed, nutrient measurements in leaching show that the amount lost due to the desorption effect is of little importance (17 and 8 mg L^{-1} of Ca and N respectively, 20 mg L^{-1} of organic matter and 0.01 mg P L^{-1}). Because of this, D&G application to the acid soil at a rate of 5 and 14 g kg^{-1} increased the soil pH to values of 5.8 and 6.8 (Al saturation of 0.73 and 0.11%), respectively. It also increased the soil's final Ca, Mg, K and P content, which is reflected in a higher CEC (6.84 and 17.7 %) (Mora and Barrow, 1996).

The effect in the application of the commercial lime to the acid soil (2 g L^{-1}) did not have a significant effect on the increase in the soil pH nor does it make an important nutrient contribution (contrasting with the waste application at the same concentration (Zambrano et al., 2003). The leaches' analysis shows that there is no significant effect on the leaches' elemental leakage and there is no negative effect on the underground water.

CONCLUSIONS

D&G coming from kraft mill are not hazardous (flammability, reactivity, corrosivity) or toxic, and their values are below the EPA Standard.

Physical characteristics such as granulometry and density improve soil water retention and compactation. Furthermore, D&G's chemical characteristics, such as pH, elements as Ca, Mg, P and K and some essentials microelements (Cu, Zn, B), are useful for plants and confirm the potential use on agricultural degraded soils.

The D&G (1:1) application on degraded soils at the rate of 5 g D&G kg^{-1} increased the pH from 4.87 to 5.81 and CEC from 2.6 to 6.84 meq 100 g^{-1}. Also, essential elements such as Ca, P among others for plant were increased. On the other hand, low nutrient concentrations were measured in the leaches.

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Wastes from pulp and paper mills - a review of generation and recycling alternatives

(Resíduos da produção de papel e celulose - uma revisão da geração e alternativas de reciclagem)

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Abstract

The production of pulp and paper is increasing worldwide, and wastes are therefore being generated in appreciable amounts. Various materials are generated in pulp and paper mills, such as ash, dregs, grits, lime mud and pulp mill sludge. Over the years, these wastes have typically been sent to landfills or incinerated. However, with increased environmental awareness new alternatives have been investigated, especially the valorization of these materials. In this review, the characteristics of the manufacturing process, generated wastes, main destinations and recycling alternatives are addressed. The state of the art indicates that dregs are useful in agriculture as soil amendments, while lime mud can be used in agriculture and in environmental technology, mainly in wastewater treatment. Grits are commonly employed in construction, and pulp mill sludge shows applications in agriculture, construction and energy processes. In conclusion, this review shows several successful cases of recycling wastes from pulp and paper mills.

Keywords: paper, pulp, waste management.

Resumo

A produção de papel e celulose está aumentando em todo o mundo e consequentemente a geração de resíduos. Vários materiais são gerados neste processo, tais como cinzas, dregs, grits, lama de cal e lama de ETE. Ao longo dos anos, esses resíduos foram normalmente enviados para aterros ou incinerados. No entanto, com maior consciência ambiental, novas alternativas foram investigadas, especialmente na valorização desses materiais. Nesta revisão, as características do processo, os resíduos gerados e as principais alternativas de reciclagem são abordados. O estado da arte indica que os dregs e lama de cal podem ser usados na agricultura (corretivos de solo) e em tecnologias ambientais, principalmente no tratamento de águas residuais. Os grits são comumente empregados na construção e as lamas de ETE são aplicadas na agricultura, construção e processos energéticos. Em conclusão, esta revisão mostra vários casos bem-sucedidos na reciclagem de resíduos da produção de papel e celulose.

Palavras-chave*: papel, celulose, gestão ambiental.*

INTRODUCTION

The concept of sustainability has been applied over the years in all manufacturing activities, including pulp and paper mills, which represent an important worldwide economic activity and cause remarkable environmental impact [1]. In this context, waste management plays an important role in a modern management system [2] and becomes one of the requirements for attenuation of the generated impact, not only from the environmental stance but also from the economic and social points of view. According to the European Commission (EC) and the United States Environmental Protection Agency (USEPA), residues are classified as wastes and by-products [3, 4]. The Resource Conservation and Recovery Act (RCRA) §1004(27) of the USEPA defines solid waste as any garbage, sludge from a wastewater or water treatment plant, or any other discarded material (solid, liquid, semisolid, or contained gaseous material) resulting from industrial activities, commercial, mining, or agricultural operations or from communities. Likewise, a by-product is defined by RCRA §261.1(c) (3) [4] as a material that is not one of the primary products of a production process and is not solely or separately produced by the production process. A by-product may include most wastes that are not spent materials or sludge. The Directive of EC 2008/98/CE defines a by-product as any residue whose subsequent use without

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any further processing other than ordinary industrial practice is assured. The Directive of EC cites the appropriate legal actions to ensure that the waste category can be changed and be considered a by-product by environmental protection agencies. In this sense, studies on waste recycling to transform waste into by-products and generate minimal amounts of tailing are extremely important for sustainability.

Pulp and paper mill production is growing every year worldwide. As a consequence, the amount of generated waste is increasing, along with increasing concern and the importance of this topic. In 2013, world paper production reached 403 Mt, while pulp production reached 179 Mt [5], with the USA, China, Canada, Brazil, Sweden, Finland, Japan, Russia, Indonesia and Chile being the top ten pulp producers [6]. Kinnarinen *et al.* [7] estimate that waste production is most likely over one million metric tonnes per year. Currently, various inorganic and organic substances are generated in pulp and paper mills, such as ashes, green liquor dregs, slaker grits, lime mud and pulp mill sludge of waste water treatment plants (WWTP) [8, 9]. When improperly disposed of, these wastes can have a significant impact on the environment, damaging the water, soil and air. The high organic matter content in wastewater treatment sludge can increase BOD levels in water and, in the worst-case scenario, cause the eutrophication of lakes, ponds and other hydric bodies. In soils, some undesirable elements, e.g. heavy metals, can harm the nutrient dynamics. Regarding air, the control of emissions in incinerators is essential to preserving the quality of life for the people. Thus, the waste must be intensely researched to mitigate the negative impacts and enhance the benefits of their use.

In many countries, the use of such waste has gained notoriety and importance. In the USA and China, for example, lime mud has been used in environmental technology [10, 11]. Finland generates energy from wood waste and biological sludge [12]. In Brazil, green liquor dregs and lime mud have been used in agriculture as soil amendments [13, 14]. Other wastes have been used in construction [15]. The focus of these studies is developing environmentally friendly processes and products. Based on this goal, a review of the generation of pulp mill wastes and recycling alternatives plays a major scientific and technologic role, taking into account cleaner production and therefore sustainability. Biomass ashes are not included in this review because they are also generated by other production processes. Therefore, many studies are specifically related to this waste in the literature [16-23]. Thus, this work reviews the efforts of the pulp and paper production process to improve the productive performance and to reduce the use of natural resources.

MANUFACTURING PROCESS AND WASTE GENERATION

Kraft process; the primary source of fibers for paper production is wood (coniferous and deciduous) [24]. In addition to cellulose fibers, wood is composed of carbohydrates and lignin [12] that can be separated by mechanical or chemical processes [25]. The most widely used chemical route is the Kraft process (Fig. 1), which employs active chemical agents, such as sodium hydroxide (NaOH) and sodium sulfide (Na_2S) [26]. The process is divided into six main stages: pulping, washing, evaporation, combustion, clarification and causticizing [27]. The first step of the Kraft process is pulping, where lignin is removed in a cooking chemical solution called white liquor [24]. The pulp from the digester (black liquor) undergoes a washing process (second step) to separate the fibers (pulp) from the chemical inputs and waste. The pulp fibers pass through several steps (dilution, refining and chemical addition) for the production of paper [26, 28], while the remaining black liquor is subjected to the recovery process of the inputs. In the recovery of the white liquor, the solution undergoes evaporation and combustion to increase the solids content. In combustion, the black liquor is burned to produce a mix of dissolved salts (mainly sulfides, carbonates, sulfates and sodium and potassium chlorides) known as smelt, whose wash generates green liquor [29]. The green liquor passes through two steps: i) clarification, where dregs are produced [30], and ii) causticizing (Eq. A) to regenerate the white liquor with the production of lime mud [28, 29]. The lime mud is usually calcined for the regeneration of CaO [31], representing 90% of the needed lime for the causticizing step [32]. The use of the recovered lime, coming from a lime kiln, is dissolved in water in a series of reactors, and the insoluble material removed is called grits [9, 12, 29]. Frequently, these industries run power generation units by burning surplus biomass and organic-rich wastes generated in the process (e.g., sludge from the wastewater treatment process, or WWTP), and ash and sand are the wastes associated with this activity [2].

$$Ca(OH)_{2(l)} + Na_2CO_{3(l)} \rightarrow CaCO_{3(s)} + 2\ NaOH_{(l)} \qquad (A)$$

Characteristics of the wastes: pulp and paper mills produce large amounts of waste with compositions that vary in a wide range of values [2, 33]. Some wastes are rich in nutrients that can be returned to the environment, reducing the amount disposed of in landfills [34]. In general, these wastes are considered non-hazardous wastes [24, 32, 35] and show high alkalinity, typically with pH >10 (Table I). The grits are sandy in appearance and gray in color [28] and consist of sand, gravel, limestone ($CaCO_3$), impurities that concentrate the unreacted components in the process, and residual amounts of CaO, $Ca(OH)_2$ and Na_2CO_3 [36]. Grits may also contain portlandite [$Ca(OH)_2$], pirssonite [$Na_2Ca(CO_3)_2.2H_2O$], larnite (Ca_2SiO_4) and brucite [$Mg(OH_2)$] [29]. Grits, green liquor dregs and lime mud represent the largest fraction of solids among all of the waste generated at pulp mills. The composition of grits varies widely, containing crystalline phases such as calcite [29] and several metal ions such as barium, chromium, copper, lead, nickel and zinc [8]. Chemical and mineralogical compositions reported in other studies [15, 29, 37] confirm that $CaCO_3$ is the major component of lime mud; CaO

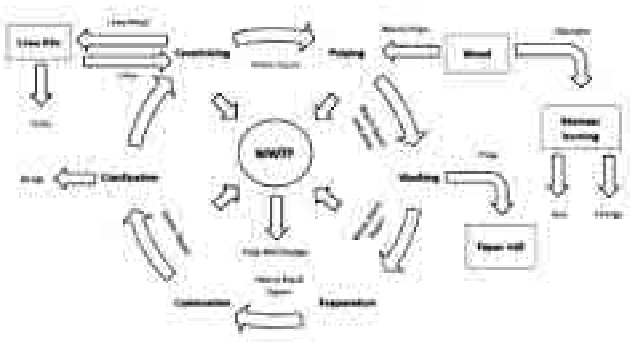

Figure 1: Kraft process and generated waste: green liquor dregs, lime mud, slaker grits, ash and pulp mill sludge of wastewater treatment plant - WWTP.

[Figura 1: Processo Kraft e geração dos resíduos: dregs, lama de cal, grits, cinzas e lama de ETE.]

and $Ca(OH)_2$ are compounds also commonly detected, together with Mg, K, Na, Cr, Mn and Fe trace elements. According to [38], dregs show high amounts of Na, K, Mn, Mg and Zn, and the main crystalline phase is pirssonite [$Na_2Ca(CO_3)_2 2H_2O$]. This Ca predominance in dregs, lime mud and grits, registered in the literature, is shown in Table I. Other physical and chemical characteristics (moisture content and pH) of these wastes are also shown.

The first step in WWTP is primary clarification, which generates the primary sludge. Primary clarification is usually carried out by sedimentation and sometimes by dissolved air (flotation) [39]. The generated wastewater is sent to the secondary (biological) treatment, where microorganisms convert soluble organic matter into carbon dioxide and water, consuming oxygen and reducing the level of biochemical oxygen demand (BOD) [12, 39]. These two treatments produce sludge with different characteristics. The sludge from WWTPs is predominantly composed of water (>50 wt%) and shows a pH ranging from 6.6 to 8.2 (Table II). Therefore, this sludge must be totally or partially dehydrated prior to any management action being implemented [25]. The sludge composition generally comprises organic matter, nitrogen and phosphorus, which can be used as macronutrient fertilizers in agriculture [32]. Table II shows the predominance of organic matter in pulp mill sludge (primary and secondary) according to the literature. The primary sludge is composed of low biodegradable organic matter (mainly cellulose fibers) [40] and by fillers (kaolinitic clay, calcium carbonate and titanium dioxide) but might show low amounts of K, Mg, Na and several toxic metals [25, 41]. This sludge possesses high C/N ratios (150 to 250) [40]. In some cases, ash and inert materials, which were rejected during the recovery process of the chemical products, are also found in the primary sludge [2, 39]. The biological sludge is produced from treatment with microorganisms and is typically composed of activated sludge, cake from the filter press and sludge from the secondary decanters and thickeners [2]. This sludge presents a higher nutrient content compared to primary sludge [25], resulting in a low C/N ratio (5 to 30) [40]. In many cases, both sludges are mixed to facilitate handling and may be dried to decrease their volume [12, 39]. Fig. 2 shows the appearance of the typical wastes produced from a Kraft process from a Brazilian pulp and paper mill, i.e. green liquor dregs, lime mud, slaker grits and pulp mill sludge.

Table I - Physical and chemical characteristics of dregs, lime mud and grits.

[Tabela I - Características físicas e químicas dos dregs, lama de cal e grits.]

Waste	Moisture (%)	pH	Ca (wt%)	Ref.
Dregs	-	10.7	35.4	[13]
	50.0	12.0	23.0	[49]
	-	12.2	25.0	[30]
	48.0	11.0	29.8	[53]
	-	-	32.4	[29]
	57.0	10.4	26.9	[54]
Lime mud	-	13.0	-	[58]
	32.4	12.6	38.5	[53]
	-	-	36.0	[29]
	-	12.0	59.0	[37]
	45.6	-	32.7	[64]
	1.1	12.1	-	[67]
	-	-	37.4	[65]
	-	11.5	35.4	[15]
Grits	-	12.6	41.7	[30]
	16.0	-	36.8	[26]
	-	-	53.0	[36]
	-	-	34.6	[29]
	7.0	12.8	42.0	[27]
	-	-	68.7	[35]

Table II - Physical and chemical characteristics of pulp mill sludge.

[Tabela II - Características físicas e químicas da lama de ETE.]

Pulp mill sludge	Moisture (%)	pH	Organic matter (wt%)	Ref.
Primary	-	6.6	-	[79]
	-	6.6	36.0-47.0	[25]
	77.1	6.7	47.8	[73]
	67.0	8.0	-	[2]
Secondary	-	7.7	-	[79]
	-	7.2	35.0-45.0	[25]
	-	7.0	76.1	[80]
	52.7	6.8	58.8	[72]
	-	8.2	63.6	[82]

Figure 2: Wastes of Kraft process: A - dregs, B - lime mud, C - grits, and D - pulp mill sludge.
[Figura 2: Resíduos do processo Kraft: A - dregs, B - lama de cal, C - grits e D - lama de ETE.]

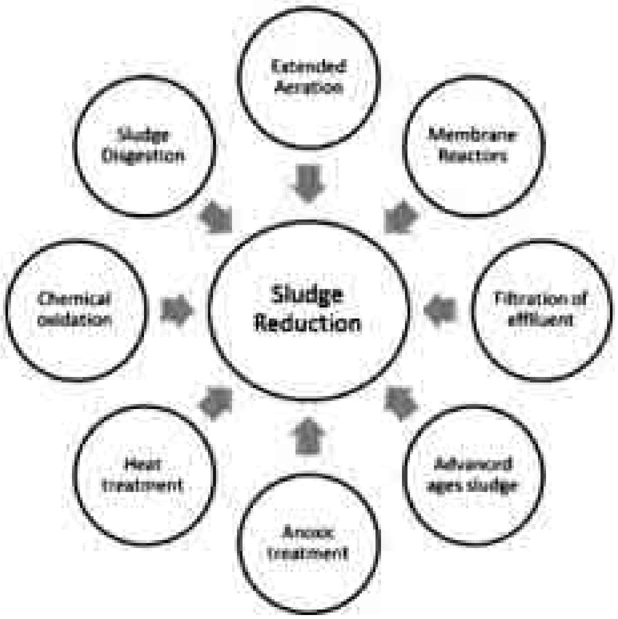

Figure 3: Outline of sludge reduction technologies.
[Figura 3: Esboço das tecnologias de redução de lama de ETE.]

FINAL DESTINATION AND RECYCLING

When analyzing the waste disposal alternatives in a particular industry, the generated quantity should be considered, and changes in the production that minimize waste generation are decidedly welcome [42]. For instance, the continuous improvement of waste management in a plant in Finland reduced waste generation from 43 to 6 Mt (wet weight) between 1994 and 2004 [12]. Taking into account more rigid environmental legislation and increasing disposal costs, adopting new treatment technologies or implementing process changes are gaining importance minimizing waste generation. One of the challenges in the management of pulp and paper mill waste is the low solids content of several streams. According to [43], 60% of the costs involved in wastewater treatment are related to the disposal of the produced sludge. Fig. 3 shows the main changes in the WWTP and post-treatment steps conducted to reduce the amount of sludge.

Extended aeration and generation of smaller bubbles are possible changes to be implemented in wastewater treatment because organic matter degradation may be improved, and therefore less sludge may be generated. The use of membrane bioreactors, effluent filtration and sludge with advanced ages improve effluent quality and also decrease the volume of the generated waste. Introducing an anoxic treatment step to promote denitrification has also been reported in the literature, and the sludge volume can be reduced by means of heat or chemical treatments. Moreover, drying, pelletizing/granulation and heat treatment processes can be used to adapt the waste for further valorization while minimizing its volume [34, 44]. Worldwide, landfilling is the most common destination for such wastes, but the high (and increasing) volumes involved and the possible presence of hazardous elements in some streams impose environmental constraints to this practice. As already mentioned, legislation is also becoming more restrictive and costs are increasing [45]. Any potential recycling alternative requires the full determination of relevant characteristics of the waste. For landfilling, the composition and leaching behavior must also be known [12]. As will be detailed later, agriculture, construction, energy generation, and environmental technology are the most explored fields for recycling such wastes [46, 47]. Table III lists some work conducted in these fields.

Table III - Works on reuse of pulp and paper mill wastes.
[Tabela III - Trabalhos de reuso dos resíduos do processo de obtenção de papel e celulose.]

Waste	Agriculture	Construction	Energy	Environmental technology
Dregs	[13, 14, 27, 30, 34, 49-52]	-	-	[12, 27, 53, 54]
Lime mud	[15, 27, 34, 58, 59]	[61, 62]	-	[9, 37, 67]
Grits	-	[28, 35, 36, 69]	-	-
Pulp mill sludge	[25, 32, 72-75, 77-82, 102]	[83, 45, 24, 84, 85, 86, 2, 41, 87, 63, 44]	[42, 90, 94, 98, 99]	-

Green liquor dregs

Green liquor dregs have been mostly applied in agriculture and environmental technology fields (Table III).

Agriculture: the use of alkaline waste in agriculture to correct soil acidity and fertilizer has been widely investigated. Medeiros *et al.* [14] evaluated the physical and chemical changes caused by the addition of dregs in aluminic soil (*Humic Cambisol*) for a wheat crop. The results were compared to those obtained with a conventional corrective (limestone). The increased waste content of the mix increased the pH values to 6 and improved the soil chemistry properties. Pértile *et al.* [48] evaluated the development of a type of pine (*Pinus taeda L.*) and the variation of the physical and chemical properties of an acidic soil. The results showed an improvement in the soil fertility and reduced acidity. The increased base saturation was found to be similar to that reached with limestone, and no adverse effects were found on the average diameter of the plants. In addition to the liming effect, Almeida *et al.* [13] reported that dregs can be a source of calcium and micronutrients for the plants. Productivity rates were found to be similar to those obtained using commercial limestone. However, some negative aspects must be taken into consideration in relation to this practice, as cited in [49]. The authors determined the influence of dregs in the soil chemical properties and the leaching of phenolic compounds. The analysis of the leachate showed that the application of the dregs increased the content of these compounds to values above the limit allowed by law. In other works, similar positive results were found using dregs in the soil. Zambrano *et al.* [50] showed that the physical and chemical characteristics of the waste are useful for plants, and the research confirmed their potential use on degraded soils in Chile. In Sweden, Österås *et al.* [51] concluded that in a long-term perspective the use of such wastes does not increase the accumulation of heavy metals in plants. Lu *et al.* [52] showed that the phytotoxicity is not a problem for land application in Taiwan. These authors also reported the use of dregs combined with WWTP sludge in composting. High CO_2 production rates and accentuated losses of the total volatile compounds were obtained after 3 days of composting, and a stable compound was produced after 7 days.

Environmental technology: in this field, most studies tried using dregs in wastewater treatment or as a landfill cover component. In wastewater treatment, dregs have been applied for neutralizing acidic waters in Finland [12]. Pöykiö [27] and Manskinen *et al.* [38] showed the effects of liming with 34.2 and 39.6 wt% Ca, respectively, similar to commercial lime (38 wt% Ca). The heavy metal contents measured in the tested dregs were well below the limits for fertilizers used in forestry [38]. The dregs were mostly composed of carbonates and were strongly alkaline (pH 11.7). Pöykiö [27] also related increased heavy metal content in the sludge generated from wastewater treatment, confirming the high retention of such species by the dregs. The use of dregs as an alternative material to create landfill covering layers is possible due to their high buffering capacity. By assuring high pH values for longer periods, they improve the immobilization of chemical elements at very low contents (up to ppb) in the waste [53]. Mäkitalo [54] studied the use of dregs as a sealing material for preventing acid mine drainage in Sweden because the waste has a low hydraulic conductivity and high alkalinity. The water retention capacity proved to be as good as that assured by clay-based layers, normally used for this purpose, allowing the sealing to be saturated even in times of drought. This result means greater difficulty for oxygen penetration and therefore lower oxidation of tailings. The alkalinity of the dregs showed a direct effect on the stability of certain elements, extending the benefits of using this potential waste. Mäkitalo *et al.* [55] also evaluated the long-term efficiency of green liquor dregs sealing layers along the years. Green liquor dregs fresh and aged (3 to 13 years) were collected and analyzed to determine how aging affects its chemical and physical properties. The results showed no significant effect of aging on the evaluated properties in a sealing layer.

Lime mud

The composition of lime mud can vary depending on the raw materials but mainly depends on the operational conditions. The lime mud might contain distinct (but normally low) amounts of toxic compounds, and some recycling routes are also limited by the presence of chlorides [56, 57]. Table III summarizes the recycling attempts already reported, which include agriculture, construction and environmental technology.

Agriculture: the use of lime mud as a corrective and soil fertilizer has been investigated in agriculture. He *et al.* [58] investigated the liming effect of the mud (four distinct charges: 2.25, 4.51, 9.01, 22.50 t/ha) in soils used to grow *Lolium perenne L.* ryegrass in the USA. The pH of the soil initially increased due to the application of lime mud but then declined over the 6-week testing period. Concentrations between 4.51 and 9.01 dry t/ha were found to be more beneficial for the growth of the grass. The effects of lime mud as a buffering agent and provider of inorganic nutrients for the anaerobic digestion of food waste were investigated in China [59]. Higher process stabilization and efficiency were obtained using sludge contents ranging from 6 to 10 g/L because the release of alkaline substances favors the methanogenic process. High CH_4 production (273 mL/g SV) was obtained using sludge and volatile solid contents of 10.0 to 19.8 g/L, respectively, with a final pH of 8.4. Zhang *et al*. [60] used lime mud to increase the efficiency of sewage sludge digestion. Batch tests were performed at 55 °C with different lime mud concentrations (1.25 to 5.00 g/L). The best result was achieved for 2.50 g/L of lime mud, with CH_4 production of 146 mL/g SV and 42.4% of volatile solid reduction.

Construction: in this sector, the use of lime mud has gained visibility in recent years. The compositional similarity between this waste and commercial $CaCO_3$ was the primary motive for exploring the substitution of the primary resource with the waste in several building materials. Buruberri *et al.* [61] replaced $CaCO_3$ with lime mud in the manufacture of clinker, while Modolo *et al.* [62] evaluated the properties (fresh and hardened condition) of mortars containing lime mud in Portugal. The use of lime mud as an aggregate tends to change the rheology of the mortar. In general, the fluidity decreases due to the improved cohesion between particles, but this effect is easily corrected. In the hardened state, the relevant properties of the mortars are not strongly affected by the waste addition. In Turkey, Sutcu and Akkurt [63] produced porous and lightweight bricks that showed lower thermal conductivity but suitable compression strength. Mixtures containing up to 30 wt% waste were prepared. The density of the bricks (1.28 g/cm^3) was reduced by up to 33%; the total shrinkage was lower (1-2%) than that of the reference bricks (3%) and the thermal conductivity was <0.4 W/m.K, approximately half that of the reference bricks (0.8 W/m.K). These authors concluded that the waste is an interesting pore-forming additive. Qin *et al.* [64] used lime mud and fly ash as raw materials to produce anorthite ceramics in China. Samples using 36, 40, 50 and 60 wt% lime mud were analyzed. The formulations were pressed and sintered between 900 and 1250 °C for 2 h. The results showed that the best lime concentration and temperature were 36 wt% and 1100 °C, respectively, forming only anorthite phases in the samples. Increased lime mud content increased the water absorption values while decreasing the compressive strength. In conclusion, using lime mud and fly ash as raw materials to produce anorthite-based ceramics is a feasible approach to recycle such waste.

Environmental technology: in this field, studies have explored the high alkalinity of the waste [56] and its major component ($CaCO_3$) to precipitate heavy metals [9, 65], remove phosphorus [66], stabilize sewage sludge [10], and immobilize heavy metals [10, 11]. The lime mud could be activated with sulfuric and hydrochloric acids, creating tunable microporous structures suitable for adsorption of organic matter from wastewater [57]. Sthiannopkao and Sreesai [67] reported the combined use of lime mud and biomass ash in wastewater treatment from metallurgy industries in Thailand. These streams are normally strongly acidic and contain relatively high solids load, including Cr, Cu, Pb and Zn components. The heavy metals are removed by precipitation and adsorption processes. Optimal removal rates of 93% Cr, 99% Cu, 96% Pb and 99% Zn were obtained for a 45 min reaction time. The precipitation of heavy metals in wastewater with lime mud was also investigated by Wirojanagud *et al.* [9] using a jar-test. Lab-prepared solutions were made for each of the following heavy metals: lead (1,434 mg Pb^{2+}/L), chromium (507 mg Cr^{3+}/L), cadmium (1,095 mg Cd^{2+}/L), and mercury (9.4 mg Hg^{2+}/L). Additionally, a real wastewater sample containing 74.5 mg Cr^{3+}/L and a COD of 683 mg Hg^{2+}/L was tested. High removal efficiency was obtained for Pb, Cd and Hg (90%) and for Cr (100%). However, the Hg-COD removal reached only 67%.

Slaker grits

Grits are a solid waste rich in calcium carbonate that can be substituted for primary calcareous resources [35], mainly in building materials (Table III).

Construction: most works have focused on the use of grits in road paving [36], as an aggregate (sand replacement) in mortar formulations [68] and as a raw component of clinker [26]. Miranda *et al.* [28] produced soil-cement bricks containing different amounts of grits (0, 25, 50, 75 and 100 wt%), and the best results were obtained for the addition of 50 wt% grits. The waste-containing bricks developed compressive strength at 28 days of curing that was always above the limit defined by the standard (≥2 MPa). The strength tends to increase for higher grit levels in the formulations. Another work [69] on similar products confirmed these observations, and the optimal formulation, established according to the (maximum) compression strength and the (minimum) water absorption values, was the mix with 62.5 wt% grits. The replacement of Portland cement with grits in the production of soil-cement blocks was also studied in [35]. For up to 20 wt% replacement levels, the relevant properties of the product are not significantly affected, proving that grits might constitute a secondary source of calcite as filler in the mix.

Pulp mill sludge

Like some of the previous waste streams, the recycling routes explored for sludge (see Table III) include agriculture and building materials. The higher content of organic and combustible compounds present in the sludge supports their use for energy and power generation [70, 71]. Fig. 4 summarizes the processes discussed in this review.

Agriculture: some studies reported the use of sludge for composting. In some cases, a fertilizer was added to increase the nutrient content of the produced humus. Although the need for large areas to implement this solution represents the main disadvantage, the overall costs are relatively lower than for other routes [72-74]. Gea *et al.* [72] studied the composting of sludge samples at laboratory scale in Spain using samples from the de-inking process (PCS) and biological sludge (BS). Despite its poor characteristics (high C/N ratio and low organic matter content and moisture), PCS showed excellent behavior in the composting. Thermophilic temperatures were achieved and maintained for more than seven days; thus, complete hygienization was obtained. Complete stabilization of the material was demonstrated by respiration tests, corroborating the other results. Hackett *et al.* [73] used mixes of primary and secondary sludge (70:30 wt%) and fly ash for compost in Canada. Samples were mixed to yield a 50:50 (v/v) mixture of sludge and ash. The moisture content was maintained above 50 wt%, and the final compost showed a pH of 8.5, high nutrient contents and a C:N ratio of 43:1. All of the metal contents, PCBs, PAHs and chlorophenol were below the levels required by local regulations. Over the first 8 weeks

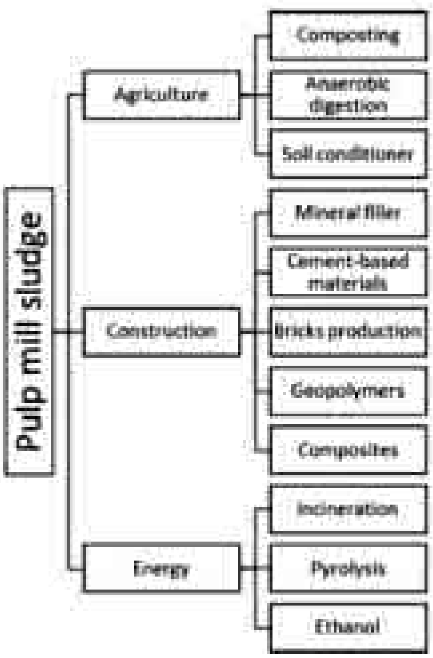

Figure 4: Fields of application of pulp mill sludge suggested in the literature.
[Figura 4: Campos de aplicação da lama de ETE sugeridas na literatura.]

of the composting period, the dioxin contents decreased by 45% and the application of the compost improved the soil characteristics. The authors concluded that the compost produced is acceptable as a low-cost soil conditioner to be used on sod farms and golf courses and for the recovery of land reclamation sites. Anaerobic digestion has been widely researched in recent years, mainly for secondary sludge, although the average generation of primary sludge is greater than the biological sludge [74-77]. Puhakka *et al.* [78] studied the anaerobic digestion of secondary sludge in pilot-scale trials in Finland. The results showed a median removal of volatile solids (VS, ~40%) for the median biogas production of 220 L/kg VS_{added} or 570 L/kg $VS_{removed}$. Anaerobic digestion of primary sludge and co-digestion with secondary sludge were also studied in continuously stirred tank reactors (CSTR) and under thermophilic conditions. At the temperatures used in the work [79], the results showed a potential methane production of 210 and 230 $m^3/t\ VS_{added}$ for primary sludge at 35 °C, and 50 and 100 $m^3/t\ VS_{added}$ for secondary sludge at 55 °C.

Primary sludge, secondary sludge and a mixture of the two may determine the soil basicity and then achieve an interesting liming effect. Southern European countries, such as Portugal and Spain, have a special interest in this evidence. Most of these countries' soils are acidic and have low organic matter content. Additionally, rainfall is generally low and irregular, and risks of erosion are strong. One of the main reported problems is the leaching of nitrates and the concomitant groundwater contamination. Other concerns are the presence of chlorine in the sludge and the potential formation of organochlorine compounds that may impair the soil. Conversely, in northwestern Europe, the soil and rainfall characteristics are opposite and the composting is not required (as much). Thus, incineration is the common practice for the disposal of sludge in this region [25]. Gallardo *et al.* [80] studied soils of volcanic origin in Chile (*Andisol - Gorbea Series* and *Argisol - Collipulli Series*) and evaluated the effects of secondary sludge addition. Sludge loads of up to 50 t/ha were applied. The results showed that the microbial and enzyme activity significantly increased when the sludge rate was enhanced. This significant increase was statistically confirmed with a p-value of $(P) < 0.05$. The maximum levels of biological activity were found to occur between 15 and 30 days after sludge application for loads between 30 and 50 t/ha. Gallardo *et al.* [81] reported that secondary sludge improves the soil properties, increases the organic matter content and increases phosphorus. Thus, an improvement in the biological properties and the nutrient dynamics may be achieved, which proves the potential of using sludge as a soil conditioner. In Belgium, Nkana *et al.* [82] studied the effects of secondary sludge on the soil nutrient dynamics using columns of mixed samples from three tropical soils (*Kandiudult*). The soil columns were leached for 90 days with deionized water in amounts equivalent to the annual local precipitation. For all of the soils, the application of sludge increased the Ca, Mg, SO_4, dissolved organic carbon (DOC) and inorganic carbon concentrations. Compared to liming, the application of wastes reduced NO_3 leaching due to the high C/N ratio of the sludge. With respect to nutrients, even after leaching, the most significant change was a substantial increase of Ca in the treated soil, associated with enhanced soil retention.

Construction: in the building sector, the use of sludge as filler is widely adopted. Ahmadi and Al-Khaja [83] used paper waste sludge as a sand replacement in concrete mixes. Five compositions containing up to 10 wt% wastes were prepared at the ratio of 1:3:6 by weight of cement, sand and aggregate, respectively. The results revealed that the elevation of the waste content increases the amount of water needed to prepare and knead the mixture because the sludge particles have increased water uptake. Sand for sludge substitution of up to 5 wt% can successfully be applied to the concrete mix. Values of the compressive strength (8 MPa) and water absorption (11.9%) were compatible with the reference samples. Several other studies investigated the addition to cement-based materials, for example, to produce fiber-cement structures. This type of material is commonly used in covering roofs but can be applied in diverse construction products. Modolo *et al.* [2] replaced 25% of the VLFP with primary sludge. The chemical characterization of the sludge did not show undesirable compounds, and the measured properties of the produced bodies are compatible with the product requirements. Yadollahi *et al.* [84] investigated WWTP sludge-containing cements. Compositions containing 40, 50 and 60 wt% sludge were prepared, and the results showed that the bending strength decreased with the relative amount of sludge. Values of approximately 22.7 kPa were obtained for samples containing

40 wt% waste. The influence on the mechanical properties was related to the possible interference of this waste in the cement hydration process. The water absorption and consequent thickness swelling significantly increased with the sludge level in the mix. Other authors have evaluated the use of sludge in geopolymers. The properties of fresh and hardened geopolymeric mortars were successfully evaluated by Yan and Sagoe-Crentsil [85]. The average compressive strengths at 91 days of curing using 2.5 to 10 wt% of de-inking sludge were 92% and 52%, respectively, of the reference value (60.6 MPa). Shrinkage upon curing decreased by approximately 34 and 64%, respectively, for the mentioned samples. The water absorption at room temperature also decreased when the sludge content increased. With some improvements in the properties, namely, decreasing the water absorption values due to the presence of residual organic matter and cellulose fibers in the samples, the authors concluded that sludge might be used for some applications in the building sector. Martínez *et al.* [86] used sludge from WWTP and waste from cleaning the pulp in ceramic materials. Increased linear thermal expansion and water absorption values of the fired samples were observed when the waste level increased, while the mechanical strength decreased but still satisfied the required standards. The pozzolanic activity of de-inking calcined sludge was determined in [44]. Samples were calcined at distinct times and temperatures and then mixed with Portland cement (CEM I 52.5N, 10 wt% sludge/90 wt% cement). The sludge was mostly composed of calcite and kaolinite and revealed high pozzolanic reactivity. Optimal preparation conditions were reached at 700 °C for 2 h. The produced blends complied with the physical-chemical specifications of the corresponding European standard (EN 197-1, 2011). The compressive strength at 7 days increased by approximately 10% when sludge was added to the cement compared to the values obtained with pure cement [24].

In brick production, the addition of 5-15 wt% sludge improves product properties as well as the manufacturing process. The porosity is enhanced by increasing the fiber content in the formulations, hence, lighter bricks are obtained. Sludge helps to save fuel in the kiln and decrease the firing time. Moreover, the cracking resistance during the drying and firing steps is improved [45]. Recently, studies have demonstrated the potential use of primary sludge (PS) as a reinforcing agent (fibers) and of secondary sludge (SS) as a binder in wood-plastic composites. The effect of different SS:PS ratios on the mechanical properties of this composite was studied. PS and SS were obtained from three different pulping processes: thermo-mechanical (TM), chemical-thermo-mechanical (CTMP) and Kraft processes. In this study, two SS:PS ratios (1:9 and 3:7) were used to obtain the mixtures. Three contents of those mixtures (20, 30 and 40 wt%) were added to a high-density polyethylene (HDPE) matrix. The results showed that the Kraft process sludge is the most suitable candidate for producing composites with better mechanical properties due to its higher pulp fiber content and longer fibers. Lower values of tensile strength, bending and impact were obtained with the mixture containing a 3:7 ratio compared to the 1:9 ratio. Water absorption and swelling increased with increased mixture content in the composites, and the bending strength and tensile strength improved [87]. Donmez Cavdar *et al.* [88] studied the obtainment of wood cement boards (WCB) using pulp mill sludge. A 1:3 wood:cement ratio was used for the replacement of wood by the sludge at up to 20 wt%. The results were considered acceptable according to the limits stablished by European standard EN 634-2 for up to 10 wt% wood replacement by the pulp mill sludge.

Energy: incineration and pyrolysis are the common combustion methods used to produce energy from wastes. With pyrolysis (or destructive distillation), the organic matter is heated in the absence of oxygen to produce a mixture of liquid and gaseous fuels and a solid material (mainly carbon). This technology was developed for waste with high carbon contents, such as wood, plastic and oil, but is not yet sufficiently developed for pulp sludge. However, some investigations are being conducted to adapt this technology for this type of waste [8, 71]. Although some problems and impacts associated with incineration have been reported [70], some authors [89, 90] defend its use as an appropriate solution instead of landfilling. In Japan, Matsuto [91] and Tomita *et al.* [92] demonstrated that a volume reduction of 80-90% can be achieved through waste incineration. The produced ash would then be landfilled or, preferably, used in building materials. However, some authors highlighted the possible presence of chlorine in the waste, which can lead to problems of corrosion and air contamination due to the formation of organochlorine compounds upon heating. The admissible chlorine content for use as a building material is also very low (<0.1 wt%) [61]. The contents of metals and organochlorine compounds were analyzed in the fuel, ash and exhaust gas generated in the incineration of secondary sludge [70]. The metal concentration showed a positive correlation with the formation of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), demonstrating that incineration requires special control to minimize the potential environmental impacts. Nurmesniemi *et al.* [12] argued that this type of waste-to-energy process is eco-efficient because the energy content of the waste is used in the form of heat and electricity, thus preventing the extraction and use of virgin energy resources. However, some industrial wastes present high contents of inorganic compounds (that generate ash) or expressive moisture levels, which reduce their calorific potential. The fluidized bed technology has become the best alternative for burning such waste-derived fuels, producing electricity and steam [90, 93].

Some authors also studied the conversion process of fibers present in the primary sludge into ethanol [94-96]. Duff *et al.* [97] studied the hydrolysis and fermentation of primary sludge resulting from four distinct production processes (acid bisulfite pulping, Kraft, TM and Alpulp) in Canada, and approximately 60 wt% sludge was transformed into ethanol. In a similar direction, Lark *et al.* [98] successfully converted 72% of the cellulose present in the sludge into ethanol in the USA. Chen *et al.* [99] studied primary sludge from four US plants (virgin pulp production and paper recycling). The conversion to ethanol was found to be more efficient when sludge from virgin pulp production is used. Moreau *et al.* [100] studied the conversion of cellulose present in sludge in ethanol, hydrogen and others compounds by the microorganism Clostridium thermocellum. Results showed that sludge was capable of supporting the growth of C. thermocellum, when used as a carbon source. Microorganism used was able to produce final products with similar concentrations than would be achieved with pure cellulose. After 60 h of fermentation, 8.5 mol/m^3 of acetate, 11.3 mol/m^3 of ethanol, 8.75 mol/m^3 of lactate, 0.27 mol/m^3 of formate, 11.2 mol/m^3 of hydrogen and 18.41 mol/m^3 of carbon dioxide were produced.

Mixtures of wastes

Recycling alternatives for waste mixtures from pulp and paper mills and from other industries are also cited in the literature. Again, the agriculture and construction sectors are the most common.

Agriculture: Cabral *et al.* [30] followed plant growth on soils containing mixtures of ash, primary sludge, dregs and grits; limestone was used as a reference. The correct combination of wastes shows liming potential and might be a substitute for the primary commercial limestone. Potassium and phosphorus concentrations tend to be higher when the waste mix is used, meaning higher fertilizing potential. At the same time, the leached levels of heavy metals are acceptable. Mäkeläa *et al.* [101] combined blast furnace slag, or steel slag, with ash, sludge and dregs from pulp and paper mill production. The blends were applied in the soil for acid amendments. In particular, mixtures of blast furnace slag with sludge seem to be very promising to replace commercial fertilizers. The high levels of total Cr and V found in steel slag are the main limitation. Jordan and Rodriguez [102] also combined ash, dregs and primary sludge with soil, wood bark and other nutrients and tested the growth of several plants, Monterey pines (*Pinus radiata*), *Eucalyptus globulus*, rice (*Oryza sativa cv.* ‘Diamante’) and duckweed *(Lemna minor)*, in greenhouse and *in-vitro* conditions. The use of ash and dregs seems to favor the growth of Monterey pines and the germination of eucalyptus seed. The primary sludge and ash promoted the growth of rice.

Construction: silicates and calcium carbonate present in ash behave similarly to the raw materials that are normally used to produce clinker and/or cement. Upon clinkering, the organic fraction of the waste is burned while the mineral fraction is incorporated into the final product [45]. According to Monte *et al.* [8] and Rajamma *et al.* [103], the fly ashes from biomass combustion are rich in SiO_2 (28-41 wt%) and contain smaller amounts of Fe_2O_3 (2.2-2.6 wt%) and Al_2O_3 (6.2-9.3 wt%). The lime mud consists essentially of calcium carbonate, while the biological sludge can be viewed as an interesting secondary fuel due to its high organic material content. Moreover, biological sludge contains small amounts of oxides also compatible with clinker composition (SiO_2, Al_2O_3, $CaCO_3$ and Fe_2O_3). In this sense, Buruberri *et al.* [61] prepared blends of such wastes and produced belitic and Portland clinkers. The belitic cements showed satisfactory mechanical strength and no signs of deterioration after long periods (strong durability). These cements are (more) environmentally friend than Portland cement because the CO_2 emissions are lower. Simão *et al.* [104] also used pulp and paper mill waste (lime mud, pulp mill sludge and biomass fly ashes) in the production of clinker, achieving results of ~16 and ~21 MPa in 7 and 28 days of curing, respectively. Castro *et al.* [26] carried out clinker production field tests, incorporating 0.1 wt% dregs and 0.25 wt% grits into the raw mix composition. No negative environmental effects were observed, and such minor incorporation amounts did not alter the current processing conditions. Gemelli *et al.* [68] studied the influence of ash, fibers, dregs and grits on the properties of mortars formulated with Portland cements CPI-S-32 or CPII-Z-32. Ash and dregs partially replaced the cement, while fibers and grits were substituted for sand. The curing time of the samples ranged from 7 to 28 days, and the results showed that the type of cement and curing time significantly influenced the development of microstructure and the compressive strength. The best results were obtained at 28 days for samples prepared with cement CPI-S-32, ash (10 wt%) and grits (10 wt%). Martínez-Lage *et al.* [105] studied the use of green liquor dregs and biomass fly ash to fabricate mortars and concrete. Different mortars were fabricated replacing 10, 20 or 30 wt% of cement by biomass fly ash and dregs. The compressive and tensile splitting strength increase when 10 wt% of cement is replaced by biomass fly ash and decrease in all other cases.

CONCLUSIONS

This work presented a review of case studies about management and proper disposal of waste from pulp and paper mills. The generation and recycling alternatives for ash, lime mud, pulp mill sludge, dregs and grits were evaluated. The assessed studies show that pulp and paper mills are approaching the ‘zero waste’ goal. Such a situation can be achieved primarily by reducing waste generation and encouraging internal recycling, which is a desirable situation considering the cleaner production concept. However, such wastes can be suitably processed into by-products and then sent to external recycling agencies. Thus, these materials can be used in agriculture, construction, energy and environmental technology. The studies showed that dregs can be used in agriculture as soil amendments, while lime mud can be used in agriculture as well as in environmental technology, mainly in wastewater treatment. Grits can be used in construction. Finally, applications in agriculture, construction and energy use were found to be the main alternatives for pulp mill sludge (primary and secondary). In addition to the physical and chemical characteristics of the wastes, the relationship between supply and demand must also be taken into consideration. For example, soil improvement materials are not needed in countries having fertile soils. In this sense, one can conclude that the best destination for the wastes from pulp and paper mills is the one that best adapts to the environmental, economic and social conditions of the region where it is produced. In this context, the construction industry plays an important role because the world's mineral reserves will not be enough to meet future demands. Several limitations interfere with the use of these wastes, highlighting social, political and even bureaucratic issues. New governmental politics should encourage the recycling of these materials to change this scenario. The pulp and paper mill industry has shown a high potential for sustainability.

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APPLICATION OF ALKALINE WASTE FROM PULP INDUSTRY TO ACID SOIL WITH PINE(1)

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ABSTRACT

In Brazil extensive areas are covered with pine forests, planted for pulp and paper production. This industry generates solid alkaline waste, such as dregs. The application of this dregs to forest soils is an alternative for soil acidity correction and plant nutrient supply, as well as a solution for its proper disposal. The purpose of this study was to compare the residual effect of surface application of dregs and dolomitic lime on (a) changes in the physical and chemical properties of an acidic soil and (b) pine tree development. The experiment was carried out in 2004 in Bocaina do Sul, Santa Catarina, consisting of the application of increasing dreg and lime rates to a *Pinus taeda* L. production area, on a Humic Cambisol, in a randomized block design with four replications and 10 x 10 m plots. The treatments consisted of levels of soil acidity amendments corresponding to the recommendations by the SMP method to reach pH 5.5 in the 0–20 cm layer, as follows: no soil amendment; dregs at 5.08 (1/4 SMP), 10.15 (1/2 SMP) and 20.3 Mg ha^{-1} (1 SMP); and lime at 8.35 (1/2 SMP) and 16.7 Mg ha^{-1} (1 SMP). Soil layers were sampled in 2010 for analyses of soil chemical and physical properties. The diameter at breast height of the 6.5 year old pine trees was also evaluated. Surface application of dregs improved soil chemical fertility by reducing acidity and increasing base saturation, similar to liming, especially in surface layers. Dregs, comparable to lime, reduced the degree of clay flocculation, but did not affect the soil physical quality. There was no effect of the amendments on increase in pine tree diameter. Thus, the alternative to raise the pH in forest soils to 5.5 with dregs is promising for the forestry sector with a view to dispose of the waste and increase soil fertility.

Index terms: dregs, lime, alkaline front, soil physical quality, *Pinus taeda* L.

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RESUMO: *APLICAÇÃO DE RESÍDUO ALCALINO DA INDÚSTRIA DE CELULOSE EM SOLO ÁCIDO CULTIVADO COM PÍNUS*

No Brasil existem extensas áreas com plantio de pínus para a produção de papel e celulose, processo que gera resíduos sólidos alcalinos, como o dregs. O uso desse resíduo em solos florestais é uma alternativa para correção da acidez do solo, fornecimento de nutrientes às plantas e seu próprio descarte. O objetivo deste trabalho foi avaliar o efeito residual da aplicação superficial de dregs, comparando-o com o calcário dolomítico, nos atributos físicos e químicos de um solo ácido e no desenvolvimento de pínus. O experimento foi implantado em 2004 em Bocaina do Sul, SC, em um Cambissolo Húmico alumínico, constituindo da aplicação superficial de doses crescentes de dregs e calcário em uma área de produção de Pinus taeda *L. O delineamento experimental utilizado foi em blocos ao acaso com quatro repetições e parcelas com dimensão de 10 x 10 m. Os tratamentos consistiram de níveis de corretivos da acidez do solo correspondentes à recomendação indicada pelo método SMP para atingir pH 5,5 na camada de 0–20 cm, sendo: sem corretivo; dregs nas doses de 5,08 (1/4 SMP), 10,15 (1/2 SMP) e 20,3 Mg ha^{-1} (1 SMP); e calcário nas doses de 8,35 (1/2 SMP) e 16,7 Mg ha^{-1} (1 SMP). Amostras de solo em camadas foram coletadas em 2010 para análise de atributos químicos e físicos do solo. O diâmetro à altura do peito das plantas de pínus com 6,5 anos também foi avaliado. A aplicação superficial de dregs melhorou a fertilidade química do solo, com diminuição da acidez e aumento da saturação por bases de forma semelhante ao calcário, principalmente nas camadas superficiais. O dregs, assim como o calcário, diminuiu o grau de floculação da argila, mas não prejudicou a qualidade física do solo. Quanto ao crescimento em diâmetro do pínus, não houve efeito dos corretivos. Assim, a aplicação de dregs em solos florestais para elevar o pH a 5,5 é uma alternativa para o setor florestal, como forma de descarte do resíduo e aumento da fertilidade do solo.*

Termos de indexação: dregs, calcário, frente de alcalinização, qualidade física do solo, Pinus taeda *L.*

INTRODUCTION

Santa Catarina is one of the largest pulp and paper producers in Brazil. An area of 169 thousand hectares of the State is covered with planted forests, of which 90 % consist of *Pinus* sp. (ABRAF, 2010). The ease of adaptation of pine to acid soils, which cover most areas in the south of the country, indicate the species for planting in extensive areas, making it an important source of raw material (Kronka et al., 2005).

This high suitability for forestry is the basis of an important industrial center for pulp and paper in Santa Catarina. But the great quantity of waste generated by the pulp and paper factories causes environmental problems (Rodrigues, 2004), due to the incomplete recovery of the chemical reagents used to digest the wood fiber (Cohn & Ribeiro, 2002). An alternative disposal of these dregs is application to the soil, which can serve as a medium to clarify these dregs due to its physical, chemical and biological characteristics (Bellote et al., 1998).

Among the waste products generated by the pulp and paper industry are dregs (Bellote et al., 1998), i.e., dregs consisting of the removed impurities, e.g., carbon, mud particles, metal hydroxides and sulfates, and iron, silica, calcium and aluminum salts (Cohn & Ribeiro, 2002). It was shown that dregs can be used as soil amendments in forest plantations (Almeida et al., 2007), because they raise the pH and increase nutrient availability (Bellote et al., 1998). These factors are important for southern Brazil where soils are, with few exceptions, highly acidic and little fertile, limiting even forestry activities. In addition, waste from the pulp and paper industry is less expensive than commercial lime when used in the same region as the generating units (Almeida et al., 2008).

In contrast to dolomitic lime, dregs have a low magnesium and high sodium content (Almeida et al., 2007) and their use may therefore have a negative influence on plant growth. The high Ca/Mg ratio may induce Mg deficiency in plants if applied at high quantities to soils with low Mg availability (Miotto, 2009), due to the competition between Ca and Mg for the soil adsorption sites and root uptake (Medeiros et al., 2008). The application of a high Na quantities, in turn, may increase the dispersion of clay and organic colloids (Albuquerque et al., 2002). This can affect some physical properties, e.g., reduce macroporosity and increase surface sealing (Reichert & Norton, 1994). Sodium has a large hydrated radius, which prevents it from approaching negatively charged solid surfaces (Sposito, 1989; Almeida et al., 2008).

Although pine is not very demanding in terms of soil fertility (Ferreira et al., 2004), different yield levels have been observed when planted on different soils (Ferreira et al., 2004; Morales et al., 2010). Moreover, since forest plantations are not destined for human food consumption, there are some advantages to the application and use of waste products.

The purpose of this study was to evaluate the residual effect of the surface application of dregs in comparison to dolomitic lime on (a) changes in the physical and chemical properties of a Humic Cambisol as well as on (b) the growth of *Pinus taeda* L.

MATERIAL AND METHODS

The experiment was carried out in Bocaina do Sul, SC (27º 44' 40" S; 49º 56' 40" W, 860 m asl). The climate at this location is humid mesothermal with mild summers (Cfb), according to the Köppen classification. Rains are well distributed throughout the year and mean annual rainfall and temperature are 1,500 mm and 15.6 °C respectively (Santa Catarina, 2011).

The soil is a Humic Cambisol (Embrapa, 2006) with a clay loam texture with 410 g kg^{-1} sand, 240 g kg^{-1} silt and 350 g kg^{-1} clay. Prior to the experiment, the area had been covered by native vegetation, without previous acidity amendment or fertilization. The main soil chemical properties are described in table 1.

The experiment was set up in November 2004 and consisted of surface application of increasing dregs and lime rates to a *Pinus taeda* L. production system with 6-month-old trees, spaced 2.0 x 2.5 m. A randomized experimental block design was used with four replications and 10 x 10 m plots. Treatments consisted of soil amendment levels based on the recommendation of the SMP method to achieve pH 5.5 in the 0–20 cm layer (CQFSRS/SC, 2004). The following treatments were established: without amendment; dregs rate of 5.08 Mg ha^{-1} (1/4 SMP); dregs rate of 10.15 Mg ha^{-1} (1/2 SMP); dregs rate of 20.3 Mg ha^{-1} (1 SMP); dolomitic lime rate of 8.35 Mg ha^{-1} (1/2 SMP); and dolomitic lime rate of 16.7 Mg ha^{-1} (1 SMP). Soil amendments were applied by hand to the surface of the whole area, without incorporation. No fertilization for soil amendment nor fertilization at planting were performed for the pine trees.

The soil amendment rates were determined from the initial SMP index of the soil (4.3), resulting in the need for 15 Mg ha^{-1} $CaCO_3$, with an effective neutralizing power (ENP) of 100 %. The following amendments were used: dolomitic lime (filler) with ENP of 90 % and dregs derived from a pulp and paper industry located in the municipality of Correia Pinto (SC), with the following characteristics: neutralizing value (NV) 80 %; moisture 22 %; pH 10.7; 300 g kg^{-1} Ca; 10 g kg^{-1} Mg, and 34 g kg^{-1} Na.

During the first year of the experiment, weeding was done mechanically. Treatments were reapplied in October 2006, at the same rates applied in 2004. Again the soil amendments were applied by hand to the soil surface of the whole area, without incorporation. This reapplication only two years after the first rates and, consequently, above the need for soil amendment, had the purpose of simulating practices commonly used by the producers in the region, testing whether higher dregs rates would cause problems for the soil or pine tree growth.

In October 2010, disturbed and undisturbed soil samples were collected for chemical and physical analyses. The chemical analyses (layers 0–5; 5–10; 10–20 and 20–40 cm) determined and calculated the following properties: pH in water, contents of exchangeable K^+, Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+}, extractable P, total organic carbon, effective CEC,

Table 1. Chemical analysis of the 0–20 cm layer of the Humic Cambisol. Bocaina do Sul, SC

Layer	pH_{H_2O}	Al	Ca	Mg	P	K	TOC
			$cmol_c$ kg^{-1}		mg kg^{-1}		g kg^{-1}
0–20 cm	4.7	6.0	1.8	1.5	2.4	204	46

pH_{H_2O}: pH in water; Al: exchangeable aluminum; Ca: exchangeable calcium; Mg: exchangeable magnesium; P: extractable phosphorus; K: exchangeable potassium; TOC: total organic carbon. Analyses performed according to Tedesco et al. (1995).

base saturation, Al^{3+} saturation and Na^+ saturation. The pH in water was determined at a 1:1 ratio by potentiometer reading; exchangeable Na^+ and K^+ and extractable P were extracted by the double acid extraction method (Mehlich-1) with acid solution of 0.05 mol L^{-1} HCl and 0.0125 mol L^{-1} H_2SO_4, Na^+ and K^+ were quantified by flame photometry and P quantified by UV-VIS spectrophotometer absorbance; exchangeable Ca^{2+}, Mg^{2+} and Al^{3+} were extracted with a neutral saline solution of 1 mol L^{-1} KCl, Ca^{2+} and Mg^{2+} were determined by atomic absorption spectrophotometry and Al^{3+} quantified by acid-base titration with 0.0125 mol L^{-1} NaOH (Tedesco et al., 1995). Organic carbon was determined by the Walkley & Black method modified by Tedesco et al. (1995), by oxidation with 1.25 mol L^{-1} $K_2Cr_2O_7$ in a concentrated acid medium of H_2SO_4 and titration with 0.25 mol L^{-1} $FeSO_4$. Effective CEC, base saturation, Al^{3+} saturation, and Na^+ saturation were calculated according to Embrapa (1997). To calculate base saturation, potential non-exchangeable acidity was extracted with a 0.5 mol L^{-1} $Ca(CH_3COO)_2$ buffer solution at pH 7.0 and quantified by acid-base titration with 0.0125 mol L^{-1} NaOH (Embrapa, 2009).

The soil physical analyses (layers 0–5; 5–10 and 10–20 cm) determined the following properties: total porosity, macroporosity, soil density, flocculation degree, aggregate stability and soil penetration resistance. For these analyses, two undisturbed samples were collected in metallic rings (volume 141.4 cm^3, height 5 cm, diameter 6 cm) per layer and plot. These samples were saturated, subjected to a tension of 6 kPa on a sand tension table and dried in a laboratory oven at 105 °C. Total porosity was determined by the moisture difference between the saturated soil and the dry soil; macroporosity by the moisture difference between the saturated soil and at a tension of 6 kPa (Embrapa, 1997); and soil density by the volumetric ring method according to Blake & Hartge (1986). Disturbed soil samples were collected to determine the flocculation degree by the pipette method (Gee & Bauder, 1986) through dispersion in NaOH for determination of the total clay content, and in water for water dispersible clay. Wet aggregate stability was determined by wet sieving of subsamples (diameter 4.76 to 8.00 mm) according to Kemper & Chepil (1965), and the results expressed as mean geometric diameter. Soil penetration resistance was determined by an electronic soil compaction meter (Falker) to a depth of 20 cm, measuring 20 resistance values in this layer (1 measurement cm^{-1}) at five sampling points per plot, with a cone (diameter 12.82 mm) and maximum measuring speed of 50 mm s^{-1}, manually controlled. These resistance measures were grouped in layers, obtaining a mean resistance value.

At the time of soil sampling, the diameter at breast height of the pine tree plants at 6.5 years of age was determined with a tree calipers for six plants per plot.

Results were subjected to normality analysis by the Shapiro-Wilk test and, when necessary, transformed before analysis of variance by the F test ($p < 0.05$). The quantitative factor (amendment rate) was analyzed per soil layer, with adjustment of linear or quadratic regression equations for the dregs rates and linear equations for the lime rates. The zero rate treatment was used as control for both soil amendments. Differences between amendments at equivalent rates were analyzed by linear contrasts. The models PROC REG and PROC GLM of the statistical program SAS 9.1.3 (SAS, 2007) were used for the regressions and contrasts respectively.

RESULTS AND DISCUSSION

Soil chemical properties

Chemical properties were affected by surface application of amendments (dregs and lime). Significant differences were observed in increases in pH, exchangeable Ca^{2+} and Mg^{2+} content, Ca/Mg ratio, base saturation and effective CEC, and in the reduction of Al^{3+} content and saturation, with more intense effects at higher amendment rates and in surface layers.

Increasing amendment rates raised the soil pH linearly down to a depth of 10 cm. Soil amendment by dregs and lime reached the 5–10 cm layer (Figure 1). The highest dregs rate raised the soil pH to 7.2 in the 0–5 cm layer and to 5.3 in the 5–10 cm layer (Figure 1a) and by lime to 7.4 in the 0–5 cm layer at rates corresponding to 1 SMP. The pH level was higher than recommended in the surface layer due to amendment reapplication at doses exceeding the requirement and to the accumulation of amendments on the soil surface.

In a study of lime surface application to two soils of Rio Grande do Sul (with 380 and 580 g kg^{-1} clay), Pöttker & Ben (1998) found an increase in pH only in the 0–5 cm layer after 36 months. Rheinheimer et al. (2000) however observed a pH increase to approximately 5.5, down to a depth of 15 cm 48 months after the application of 17 Mg ha^{-1} lime to a Gray Argisol (Plinthaquult medium texture). Lime leaching in the profile depends on the lime rate and type, the soil physical properties, organic matter content, water regime of each region (Caires et al., 1998; Rheinheimer et al., 2000; Amaral et al., 2004) and the crop system. In addition, there is no migration of liming effects into the soil profile when the quantity applied to the surface is less than that necessary to neutralize Al^{3+} in the surface layers (Rheinheimer et al., 2000).

With the increasing rates, the dregs reduced the exchangeable Al^{3+} content linearly down to a depth of 10 cm (Figure 1c), while with lime the effect was observed down to 20 cm (Figure 1d). The highest rates reduced the exchangeable Al^{3+} contents to nearly zero $cmol_c\ kg^{-1}$ in the surface layer. In many studies with surface application of lime (Caires et al., 1998; Pöttker & Ben, 1998; Rheinheimer et al., 2000) and dregs (Albuquerque et al., 2002; Medeiros et al., 2009) similar results were reported.

When the amendment is not incorporated, an alkaline front is generated at the soil surface. This has been attributed to the descending movement of the fine particles when the soil physical characteristics are favorable to the movement of the basic anions resulting from dissolution of the amendment (Amaral & Anghinoni, 2001). An adequate rainfall volume also supports the dissolution of lime particles, as well as of ion leaching (Amaral et al., 2004). In forests, leaf interception reduces the rainfall that effectively reaches the soil surface. On the other hand, preservation of the soil structure favors formation of macropores, which contribute to water percolation and incorporation of components of the amendments.

The exchangeable Ca^{2+} contents increased linearly, down to the 10–20 cm layer, with increasing amendment rates (Figure 2a,b). Lime also increased the exchangeable Mg^{2+} content down to a depth of 20 cm (Figure 2d). Dregs, with only 10 g kg^{-1} Mg, increased the exchangeable Mg^{2+} content in the 5–10 cm layer (Figure 2c); nevertheless, increases in soil Mg content are not expected from application, due to the low Mg content of this element in the waste. In a Brown Latosol (Haplohumox), Ciotta et al. (2004) concluded that the reapplication of lime rates of 4.5 and 3.0 Mg ha^{-1} (in two growing seasons) raised the pH down to a depth 15 cm and the Ca^{2+} and Mg^{2+} contents down to a depth of 20 cm after 12 years. Rheinheimer et al. (2000), however, found increased Ca^{2+} and Mg^{2+} contents down to a depth of 10 cm after 48 months of application of 8.5 Mg ha^{-1} lime.

The application of amendments on the soil surface creates an alkaline front, where the adsorption of Na^+, K^+, Ca^{2+} and Mg^{2+} increases due to the creation of variable negative charges generated with the raising pH (Teixeira, 2003). However, the mobility of the basic cations in the soil profile may be favored by the formation of ionic pairs with inorganic compounds from the products of dissolution of the amendment (Amaral & Anghinoni, 2001) or through

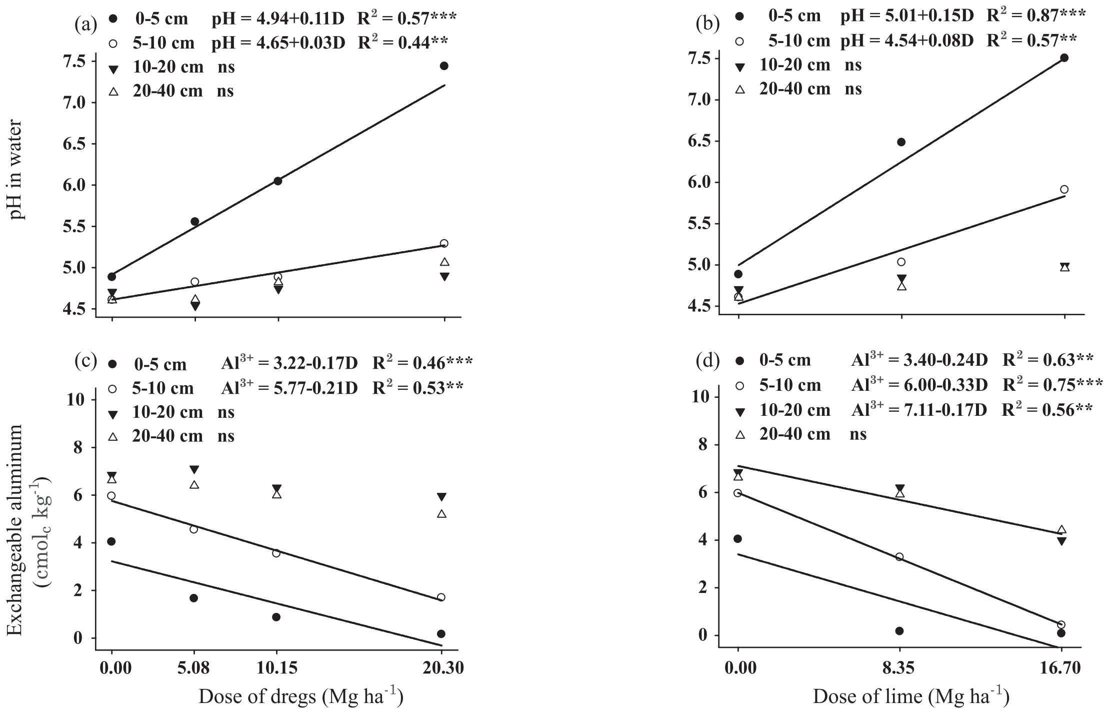

Figure 1. pH in water and exchangeable aluminum (Al^{3+}) in the layers of a Humic Cambisol amended with doses (D) of dregs (a, c) and lime (b, d), applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2010. (*, **, * and ns: significant at 5, 1, 0.1 % and not significant, respectively).**

hydrosoluble organic compounds originating from decomposition of plant dregs deposited on the soil surface (Rheinheimer et al., 2000).

The Ca/Mg ratio was not altered with the application of increasing rates of dolomitic lime, remaining near 1 in all layers (Figure 2f). Nevertheless, dregs increased the Ca/Mg ratio down to the 20–40 cm layer (Figure 2e), reaching nearly 7 in the surface layer at the highest dose. According to the Southern Brazilian Committee for soil Chemistry and Fertility (CQFSRS/SC, 2004), most crops are not affected by Ca/Mg ratios from 0.5 to over 10, provided that neither of the two nutrients are deficient in the soil. In soils with adequate exchangeable Ca and Mg contents, the interaction between these two cations in plant uptake is weak or non-existent (Miotto, 2009).

The increase of dregs and lime rates linearly raised the effective CEC, with effects down to a depth of 10 cm with the application of dregs (Figure 3a) and down to 20 cm by liming (Figure 3b). Albuquerque et al. (2002) also found an increase in effective CEC in the 0–5 cm layer two months after surface application of dregs to a Latosol and Cambisol. Liming increases the effective CEC in acid soils with predominance of variable charge (Albuquerque et al., 2000), as is the case of most soils in southern Brazil.

With the increase of basic cations in the soil, base saturation (V) increased with the doses, with linear increases down to a depth of 40 cm for both amendments (Figure 3c,d). Base saturation in the surface layer increased at the highest rates of dregs and lime, to 89 and 96 %, respectively. In the

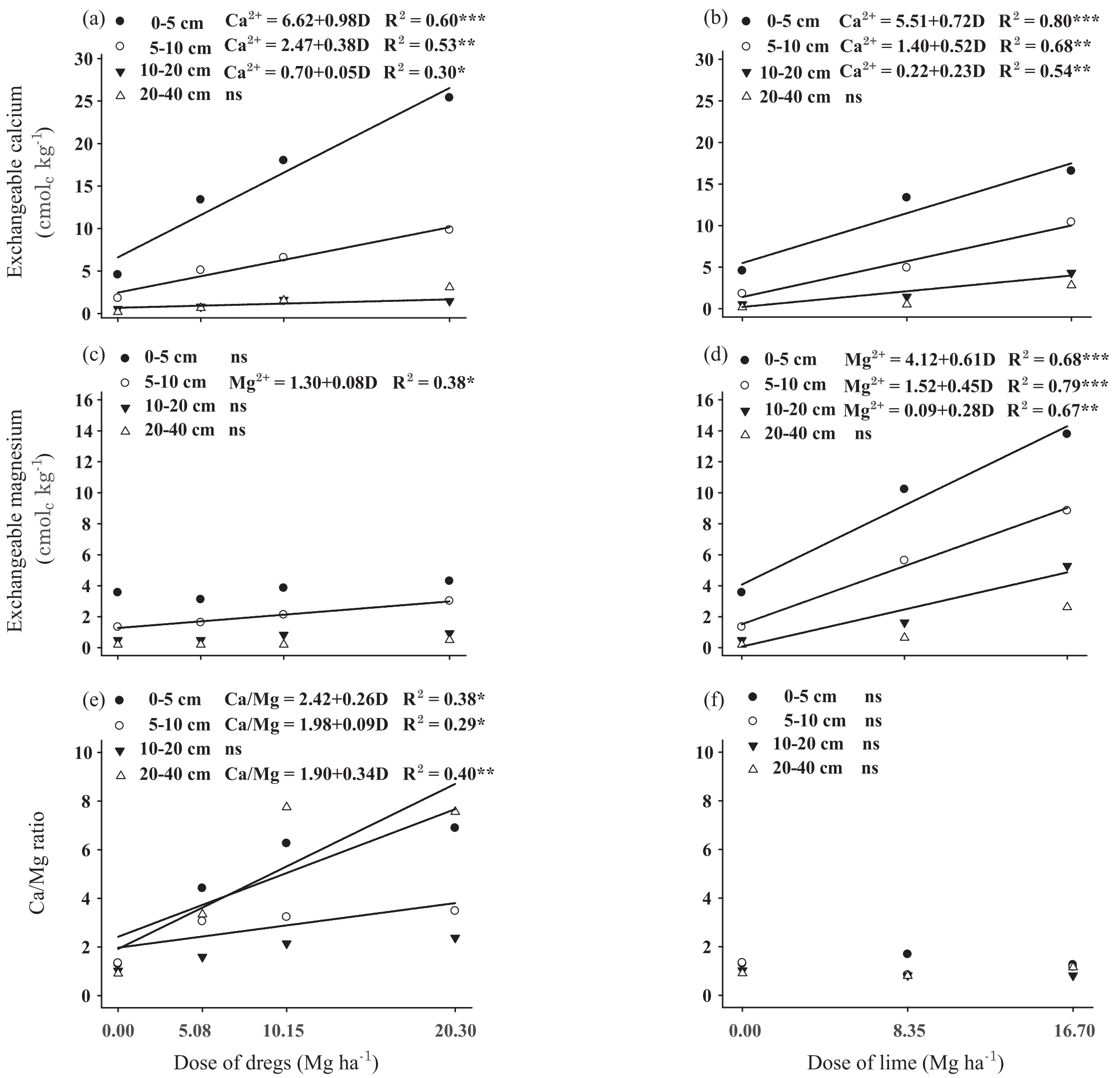

Figure 2. Exchangeable calcium and magnesium (Ca^{2+}, Mg^{2+}) and Ca/Mg ratio in the layers of a Humic Cambisol amended with doses (D) of dregs (a, c, e) and lime (b, d, f) applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2010. (*, **, * and ns: significant at 5, 1, 0.1 % and not significant, respectively).**

mean values of layers to a depth of 20 cm, V was greater at the full rate of lime than of dregs, with around 56 %. The Southern Brazilian Committee for Soil Chemistry and Fertility (CQFSRS/SC, 2004) recommends a V of 65 % for a satisfactory development of most crops.

Aluminum saturation (m) decreased down to the 20–40 cm layer with increasing rates of both amendments (Figure 3e,f). Al^{3+} saturation decreased to below 10 % down to a depth of 5 cm at rates corresponding to 1/2 and 1 SMP of dregs and lime, and down to 10 cm only at the highest lime rate.

There was a significant linear increase in the exchangeable Na^+ content down to a depth of 10 cm with increasing dregs rates. The highest rate raised the Na^+ content in the 0–5 cm layer to 104 mg kg^{-1} (Figure 4a). Lime also raised the Na^+ content linearly in the 0–5 cm layer, with a maximum content of 57 mg kg^{-1} (Figure 4b). In the study of Albuquerque et al. (2002), the Na^+ content in the 0–5 cm layer increased to 108 and 170 mg kg^{-1} with dregs rates equivalent to 1/2 SMP, respectively, in a Latosol and a Cambisol, two months after surface application. At the same rate, Na^+ also increased in the 5–10 cm layer to 16 mg kg^{-1} in the Latosol and to 21 mg kg^{-1} in the Cambisol.

The increase in the soil Na^+ content did not raise sodium saturation (Sat_{Na}), remaining from 1.2 to 2.4 % down to a depth of 40 cm (Table 2). This occurred because 71 months after the first application and 48 months after reapplication of the soil amendments, there was a relevant increase in the effective CEC and leaching of much of the Na^+ to layers below those evaluated.

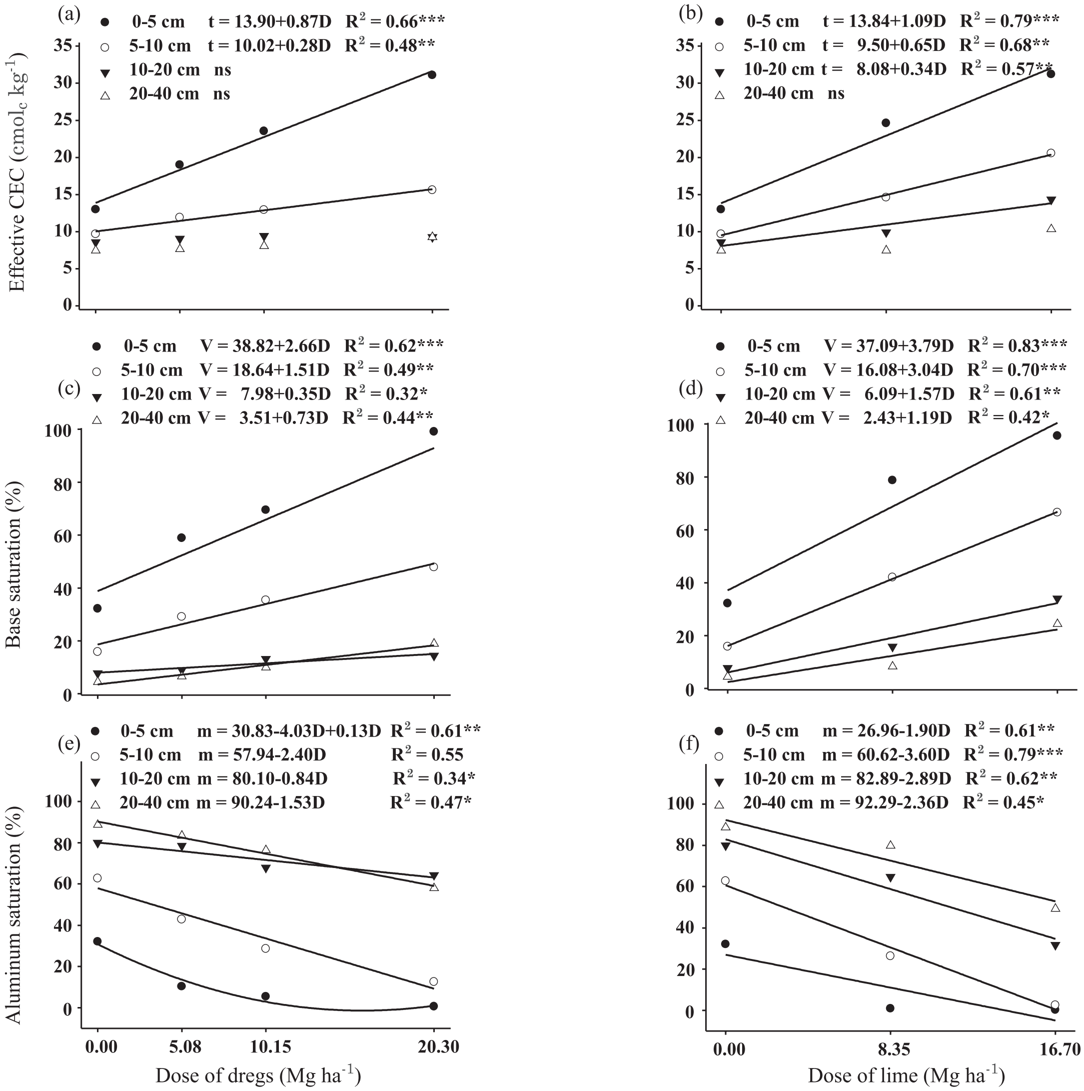

Figure 3. Effective CEC (t), base saturation (V) and aluminum saturation (m) in the layers of a Humic Cambisol amended with doses (D) of dregs (a, c, e) and lime (b, d, f), applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2009. (*, **, * and ns: significant at 5, 1, 0.1 % and not significant, respectively).**

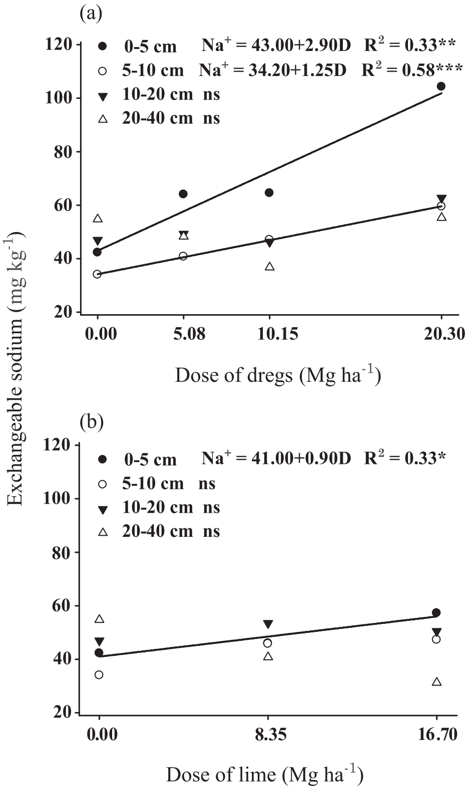

Figure 4. Exchangeable sodium (Na^+) in the layers of a Humic Cambisol amended with doses (D) of dregs (a) and lime (b) applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2010. (*, **, * and ns: significant at 5, 1, 0.1 % and not significant, respectively).**

The contents of P, K^+ and total organic carbon (TOC) did not differ among the treatments (Table 2). The mean contents of P and K^+ in the 0–20 cm layer were 2.0 and 210 mg kg^{-1}, respectively. For the soil under study, the K^+ content was considered 'very high' (CQFSRS/SC, 2004) and P 'very low'. With regard to TOC, the contents were highest in the surface layers, which is common in systems with little or no degree of soil mobilization.

Since the nutrient contents were adequate for plant growth, with the exception of P (CQFSRS/SC, 2004), it was concluded that surface liming 48 months after reapplication of the soil amendments was efficient down to 5 cm at the highest dregs rate (20.3 Mg ha^{-1}) and down to 10 cm only for the highest lime rate (16.7 Mg ha^{-1}). The effect of liming on highly buffered soils is normally restricted to a few centimeters (Ernani, 2008); in addition, rainfall on forest soils is decreased by leaf interception (Balbinot et al., 2008).

Linear contrasts among corresponding dregs and lime rates are shown in table 3. The pH and K^+ and TOC contents did not differ between dregs and lime. In the contrasts between lime and dregs at the 1/2 SMP dose (L50 and D50, respectively), differences were only observed for Mg^{2+} content in the 0–5 and 5–10 cm layers, with higher contents in the lime treatment and for the Ca/Mg ratio in all layers, due to high Ca and low Mg addition in the dregs treatment. Nevertheless, at 1 SMP, other properties also differed between lime and dregs treatments (L100 and D100, respectively). Dregs increased Na^+ and the Ca/Mg ratio and the Sat_{Na} down to a depth of 40 cm, and Ca^{2+} and P in the 0–5 cm layer. Lime in turn increased the Mg^{2+} contents throughout the profile and Ca^{2+}, V and effective CEC contents in the 10–20 cm layer, as well as Al^{3+} saturation.

A comparison between the soil amendments for changes in soil chemical properties shows a similar efficiency of both, but some drawbacks to the application of dregs, e.g., a low Mg^{2+} content and high Ca/Mg ratio and Na^+ contents.

Soil physical properties

Of the physical properties analyzed, the flocculation degree (FD) decreased linearly in the 0–5 cm layer with the surface application of increasing dregs and lime rates to the soil (Figure 5). FD decreased from 84 to 75 % at the highest dregs

Table 2. Mean value of chemical properties per layer of a Humic Cambisol amended with dreg and lime rates applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2010

Treatments	Layer	P	K	Sat_{Na}	TOC
	cm	mg kg^{-1}		%	g kg^{-1}
Mean value	0–5	4.7[1]	245	1.2	54
	5–10	2.1	221	1.5	50
	10–20	0.7	188	2.3	41
	20–40	0.0	93	2.4	27

[1] Mean value of 24 observations; P: extractable phosphorus; K: exchangeable potassium; Sat_{Na}: sodium saturation; TOC: total organic carbon.

Table 3. Estimate⁽¹⁾ of the linear contrasts between treatments for chemical properties of a Humic Cambisol amended with dregs and lime rates applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2010

Contrasts	pH	Al	Ca	Mg	Ca/Mg	P	K	Na	CEC_{ef}	V	m	Sat_{Na}	TOC
			—— $cmol_c\ kg^{-1}$ ——				——— $mg\ kg^{-1}$ ———		$cmol_c\ kg^{-1}$		——— % ———		$g\ kg^{-1}$
0–5 cm Layer													
L50 x D50	0.4^{ns}	-0.7^{ns}	-4.6^{ns}	6.4^{**}	-4.6^{*}	-0.7^{ns}	55.5^{ns}	-18.5^{ns}	1.1^{ns}	9.2^{ns}	-4.6^{ns}	-0.3^{ns}	3.7^{ns}
L100 x D100	0.2^{ns}	-0.1^{ns}	-8.8^{*}	9.5^{***}	-5.6^{*}	-4.4^{***}	-98.8^{ns}	-47.0^{*}	0.2^{ns}	6.0^{ns}	-0.3^{ns}	-0.6^{ns}	3.7^{ns}
5–10 cm Layer													
L50 x D50	0.1^{ns}	-0.3^{ns}	-1.7^{ns}	3.5^{**}	-2.4^{**}	-0.1^{ns}	36.0^{ns}	-1.3^{ns}	1.7^{ns}	6.6^{ns}	-2.3^{ns}	-0.1^{ns}	-1.5^{ns}
L100 x D100	0.6^{ns}	-1.3^{ns}	0.6^{ns}	5.8^{**}	-2.3^{**}	-0.1^{ns}	-47.5^{ns}	-12.3^{ns}	5.0^{ns}	18.7^{ns}	-10.0^{ns}	-0.8^{*}	4.4^{ns}
10–20 cm Layer													
L50 x D50	0.1^{ns}	-0.1^{ns}	-0.2^{ns}	0.8^{ns}	-1.3^{*}	0.2^{ns}	-17.3^{ns}	7.3^{ns}	0.5^{ns}	2.7^{ns}	-3.3^{ns}	0.2^{ns}	-3.6^{ns}
L100 x D100	0.1^{ns}	-2.0^{*}	2.9^{**}	4.3^{**}	-1.6^{*}	0.5^{ns}	-35.8^{ns}	-12.3^{ns}	5.1^{***}	19.6^{**}	-32.6^{**}	-1.3^{**}	6.9^{ns}
20–40 cm Layer													
L50 x D50	-0.1^{ns}	-0.1^{ns}	-1.0^{ns}	0.5^{ns}	-7.0^{*}	0.0^{ns}	12.8^{ns}	4.0^{ns}	-0.6^{ns}	-1.7^{ns}	3.4^{ns}	0.4^{ns}	-2.4^{ns}
L100 x D100	-0.1^{ns}	-0.8^{ns}	-0.3^{ns}	2.1^{**}	-6.4^{**}	0.0^{ns}	28.8^{ns}	-24.0^{**}	1.1^{ns}	5.4^{ns}	-8.8^{ns}	-1.2^{**}	0.7^{ns}

(1) Absolute difference in the value of the property between the treatments (positive values indicate a higher value in the first treatment); L50: lime rate of 1/2 SMP; L100: lime rate of 1 SMP; D50: dregs rate of 1/2 SMP; D100: dregs rate of 1 SMP; pH: pH in water; Al: exchangeable aluminum; P: extractable phosphorus; K: exchangeable potassium; Na: exchangeable sodium; Ca: exchangeable calcium; Mg: exchangeable magnesium; Ca/Mg: Ca/Mg ratio; CEC_{ef}: effective CEC; V: base saturation; m: aluminum saturation; Sat_{Na}: sodium saturation; TOC: total organic carbon; *, **, *** and ns: significant at 5, 1, 0.1 % and not significant, respectively.

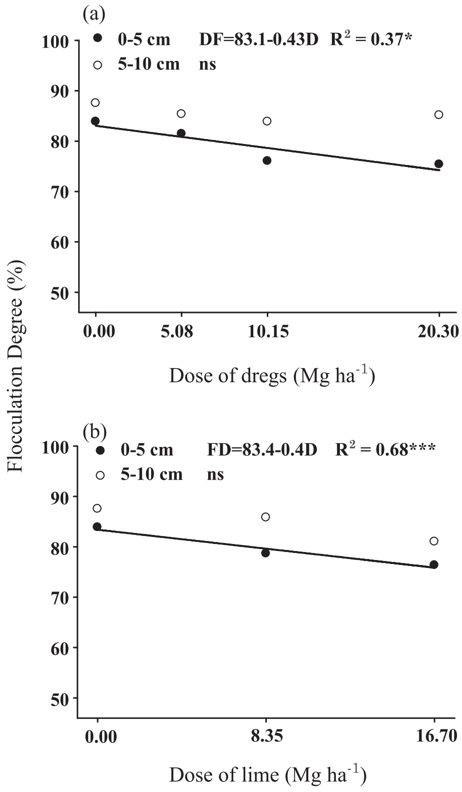

Figure 5. Flocculation degree (FD) in the layers of a Humic Cambisol amended with doses (D) of dregs (a) and lime (b) applied to the soil surface in 2004/2006. Bocaina do Sul, SC, 2010. (*, **, * and ns: significant at 5, 1, 0.1 % and not significant, respectively).**

and lime rates. Clay dispersion and FD reduction with an increase in pH were observed in soils of the Santa Catarina Plateau (Albuquerque et al., 2000, 2002; Medeiros et al., 2009) The reason may be the greater repulsion among soil particles through the increase of net negative charge and the thickness of the electric double layer caused by the substitution of Al^{3+} by Ca^{2+} and Mg^{2+}, due to the application of soil amendments (Fontes et al., 1995).

The other soil physical properties did not differ according to the amendment rates (Table 4). The high total organic carbon (TOC) content contributed to decrease soil bulk density (BD), to a mean value of 0.90 Mg m^{-3}. The low values of soil penetration resistance (PR) (Table 4) coincide with the low BD. The clay content and high organic matter content are also responsible for the high soil aggregate stability, as already stated by Bertol et al. (2000) for soils of the Santa Catarina Plateau.

The contrasts between equivalent amendment rates on soil physical properties are shown in table 5. There was a difference only for the PR with the application of dregs or lime. The addition of dregs reduced the PR in greater intensity than liming down to a depth of 20 cm, for both the dose corresponding to 1/2 SMP (D50) and the dose corresponding to 1 SMP (D100). These results indicate that the influence of the surface application of corresponding dregs and lime rates on the soil physical quality did not differ very much six years after the beginning of the experiment. The

Table 4. Mean value of physical properties per layer of a Humic Cambisol amended with dregs and lime rates applied to the surface in 2004/2006. Bocaina do Sul, SC, 2010

Treatments	Layer	BD	TP	Macro	MGD	PR (θ=0,37 m^3 m^{-3})
	cm	Mg m^{-3}	m^3 m^{-3}		mm	kPa
Mean value$^{(1)}$	0–5	0.88	0.70	0.23	4.3	366
	5–10	0.92	0.67	0.19	5.2	704
	10–20	0.91	0.68	0.19	4.7	819

(1) Mean value of 24 observations; BD: soil bulk density; TP: total porosity; Macro: macroporosity; MGD: aggregate mean geometric diameter; PR: soil penetration resistance; θ: soil moisture.

Table 5. Estimate[1] of the linear contrasts between treatments for physical properties of a Humic Cambisol amended with dreg and lime rates applied to the surface in 2004/2006. Bocaina do Sul, SC, 2010

Contrasts	BD	TP	Macro	FD	MGD	PR
	Mg m^{-3}	m^3 m^{-3}		%	mm	kPa
			0–5 cm layer			
L50 x D50	0.01^{ns}	0.00^{ns}	0.00^{ns}	2^{ns}	0.2^{ns}	118^{***}
L100 x D100	-0.02^{ns}	0.02^{ns}	-0.01^{ns}	1^{ns}	-1.1^{ns}	400^{***}
			5–10 cm Layer			
L50 x D50	0.01^{ns}	0.00^{ns}	0.00^{ns}	2^{ns}	0.1^{ns}	78^{ns}
L100 x D100	0.01^{ns}	0.00^{ns}	-0.02^{ns}	-4^{ns}	-0.3^{ns}	374^{***}
			10–20 cm Layer			
L50 x D50	-0.06^{ns}	0.01^{ns}	0.02^{ns}	.	-0.1^{ns}	489^{***}
L100 x D100	0.00^{ns}	0.01^{ns}	-0.02^{ns}	.	0.3^{ns}	370^{***}

(1) Absolute difference in the value of a property between treatments (positive values indicate a higher value in the first treatment); L50: lime rate of 1/2 SMP; L100: lime rate of 1 SMP; D50: dregs rate of 1/2 SMP; D100: dregs rate of 1 SMP; BD: soil bulk density; TP: total porosity; Macro: macroporosity; FD: flocculation degree; MGD: aggregate mean geometric diameter; PR: soil penetration resistance; *, **, *** and ns: significant at 5, 1, 0.1 % and not significant, respectively.

difference between the amendments was evident only for PR, reducing the physical barriers for roots with the application of dregs.

Pine tree growth

There was no difference in the diameter at breast height of the pine trees resulting from the application of increasing dregs and lime rates, with a mean value of treatments of 16.6 cm (data not shown). There was also no difference between the corresponding dregs and lime doses.

Although the nutritional demand of pine trees is considered low, some authors observed that pine productivity is affected by changes in the soil physical and chemical properties, such as pH, organic matter, exchangeable bases, and water retention capacity (Rodrigues, 2004; Morales et al., 2010). Nevertheless, according to Gonçalves (1995), pine trees are not very sensitive to acid soil, and can grow adequately in soils with high Al levels, in agreement with the data obtained. In addition, the soil under study has no physical barriers to root development, which allows water and nutrient uptake from a greater soil volume, and consequently, an excellent plant development.

CONCLUSIONS

1. Surface application of dregs to acid soil improved the chemical fertility by reducing the acidity and increasing base saturation similarly to lime, mainly in the surface layers. However, dregs increased the sodium content and Ca/Mg ratio.

2. Dregs, comparable to lime, reduced the degree of clay flocculation by the increase of pH, but did not

affect aggregate stability and the other soil physical properties.

3. No effect of the soil amendments on diameter of pine trees was observed.

4. The application of dregs to forest soils to raise the pH to 5.5 is an alternative for the forestry sector of the Santa Catarina Plateau as a form of waste disposal and to increase soil fertility.

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CHEMICAL FRACTIONS OF Al IN VOLCANIC SOIL AMENDED WITH CELLULOSE WASTE

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ABSTRACT

The cellulose industry generates a great volume of organic and inorganic waste, one of these wastes are called dreg (D) and grits (G). These residues have a high content of calcium carbonate, positioning them as potential bleachers in acid soils. Due to the important content of Al in the residues, a sequential extraction was done to establish the metal chemical fractions such as exchangeable, adsorbed, organic carbonated, and the ones associated to sulfurs, in incubated samples (2, 4, 8, and 32 days at 60ºC) of an Andisol amended soil with Grits, Dregs + Grits and lime in 1, 2 and 3 ton/ha doses. The results revealed that there was a significant increase in the amount of Al in all fractions, in comparison to the control soil. On the other hand the incorporation of these residues through a Dregs (70%) + Grits (30%) mixture provoked a pH increase, always higher than the commercial lime.

Finally, the Al present on amended soils was mostly distributed in the residual and carbonated chemical fractions, which would constitute less labile chemical forms to the soil-solution.

Keywords: sequential extraction, chemical fractions, cellulose waste (*Dregs*, *Grits)*, volcanic soil, waste disposal.

INTRODUCTION

The cellulose industry generates organic and inorganic waste, especially in the bleached and causticizing process, known as *Dregs* (D) and *Grits* (G) [1]. These wastes have an alkaline character, since *D* are generated in a clarification process called green liquor (Na_2CO_3 + Na_2SO_4 + Na_2S + $Fe(OH)_2$), while *G* are solid inorganic wastes. Both have high $CaCO_3$ and heavy metals content, due to the different processes of paper manufacturing [2, 3]. Consequently, these wastes have already been considered as possible soil bleaching agents. In this context, preliminary studies of the waste application on acid soils have evidenced that the toxicity and dangerousness of *D* and *G* are above the EPA (Environmental Protection Agency) regulations [4] and above the limits established for forestry utilization [5]. Besides, it was observed that the use of these wastes in soil amendment improves the chemical availability of nutrients through pH increase and also increases the water retention in soils used for *Pinus radiate* growing [6]. In Brazil the wastes from this industry are used for forest plantations of the country, using dregs and grits mixtures as a replacement of lime to improve soil pH [7]. On the other hand, the use of waste such as sludge or biosolids from the paper and cellulose industry as pH improvers in acid soils has proved to be useful [8]. Also, studies exist that attempt to assess the use of these wastes in the cement and structural concrete industry, using waste from the bins, as well as in composting [9, 10].

In Chile previous studies exist concerning the use of these wastes from the Kraft cellulose fabrication process for the vegetal productivity in Chile, where a pH improvement in amended soils was observed [11].

Considering the geographic zone of the cellulose plants in Chile, volcanic materials derived soils are considered as optimal candidates to dump this kind of waste. These soils are around the 70% of the arable land in Chile. Also, these are acid and show considerable quantities of iron oxides and organic matter, while its variable charge, which is pH and ionic strength dependent, is one of its singular features. Furthermore, they possess a high cationic exchange capacity (CEC) and a high accumulation of P as phosphate [12]. As mentioned above, these soils present acidity problems. One primarily responsible is Al^{3+} released to the soil-solution with a consequent acid-base equilibrium shift in aqueous solution, product of climatologic factors and agricultural management. Despite the importance of Al presence, scarce studies exist [13] regarding this kind of soil amended with these wastes, particularly Al, related to its incorporation and possible associations due to the content of this metal in cellulose residuals.

Consequently, it is necessary to study the different fractions or association of Al in amended soils with different cellulose residuals, establishing the importance of the use of these wastes as pH improver or bleacher in agricultural soils.

MATERIALS AND METHODS

Sampling

Samples of the surface horizon (0-0.15 m) of one volcanic soil located in southern Chile were used. The Andisol (Santa Barbara, *Ashy, medial, mesic Typic Dystrandept*) was collected, sieved at 2 mm, and stored at field moisture content. The industrial residues from a cellulose plant near to Santa Fe city were used. The residues were dried, crushed, and sifted through a 0.250 mm (60 mesh) sieve to improve soil interaction. The residues considered in this study were Grits (G) and Dregs (D). In addition, commercial lime was included in this study to be used as a comparison parameter in contrast to the rest of the amendments. The used amendments were i) Grits (G); ii) Mix of *D* and *G* in 70%-30% proportion, respectively (D-70 + G-30). The quantity of residue and lime added to the soil was worked out considering an equivalent amendment of 1, 2 and 4 ton ha^{-1} of $CaCO_3$. Four different conditions were considered: (a) control soil, (b) control soil with G (1, 2 and 4 ton ha^{-1}), (c) control soil with D-70 + G-30, (1, 2 and 4 ton ha^{-1}), and (d) control soil with lime (1, 2 and 4 ton ha^{-1})

Incubation procedure

A "fast incubation" procedure was utilized [14]. All the amended samples were packed and wetted up to 50% of its water-holding capacity. Then, the samples were taken to the incubator in the darkness at 60ºC during 2, 4, 8 and 32 days. All the samples were taken in triplicate, according to the conditions and dose described above.

Characterization

Santa Barbara soil was characterized for organic matter (OM) content using the Walkley-Black method (Allison 1965) adapted to Chilean soils [15], pH, electrical conductivity (1:2.5 w/v soil:water). The CEC was estimated as a total amount of Ca-Na-K-Mg exchanged in soil. Besides, the sand-lime-clay distribution, using the pipette method [16], and the bulk density were established [17]. In all incubated samples the pH was determined using the aforementioned method.

Al chemical fractions

The chemical fraction of Al was obtained utilizing the Sposito et al. (1982) sequential extraction procedure [18] carried out in triplicate. Al fractionation involves exchangeable, adsorbed, organic, carbonate, and residual fractions. Samples (2 g) were sequentially treated with 25 mL of the following reagents: 0.5 mol L^{-1} KNO_3 maintained in contact for 16 h (F1); deionized water for 2 h (3 times, the extracts are combined) (F2); 0.5 mol L^{-1} NaOH for 16 h (F3); 0.05 mol L^{-1} Na_2EDTA for 6 h (F4); and 4 mol L^{-1} HNO_3 at 80 ºC for 16 h (F5). After each extraction the suspension was centrifuged and the supernatant filtered through a 0.45 mm membrane filter. The Al content in each extract was determined by ICP-OES spectrometry on an Optima 2000 DV Perkin Elmer instrument.

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RESULTS AND DISCUSSION

Characterization

The soil used for the assay belongs to the Andisol series, which is classified as a volcanic soil with silty-loam texture. The pH of this soil has acid characteristics with low electric conductivity and density, and low quantities of exchangeable Ca, Na, K, and Mg (see Table 1).

The OM content was important. Andisols are rich in OM and its accumulation is probably associated with mineralogy, dominated by low crystalline compounds [19]

Table 1. Santa Barbara soil chemical and physical properties

Characteristics	Santa Barbara
Soil Order	Andisol
Soil Class	*Ashy, medial, mesic Typic Dystrandept*
Latitude Longitude Altitude (m) Rainfall (m/year) Annual mean temp. (ºC)	71º55´W 36º50´S 400-1100 1.5-2.0 13.5
Bulk density (g/mL) EC (mS/cm) OM(wt%) pH-H_20	0.79 0.15 16.2 5.58
Sand (%) Lime (%) Clay (%)	23.4 56.0 20.6
Exchangeable cations (mEq/100 g) Ca Na K Mg	 5.98 0.04 0.78 0.44
Exchangeable Al (mEq/100 g)	0.21

The pH of the residues has alkaline characteristics, with similar contents of CaO in D and G, which are lower than in commercial lime. Comparatively, D has a higher MgO content, *i.e.* is advantageous to use this residue in Mg-low-content soils and in those with acidity problems. The Al content in D and G residues was high, and therefore, this analyte deserves a more in-depth study. The chemical features of commercial lime are those reported by the manufacturer, showing a minimum and maximum content for CaO and MgO. Table 2 shows the characteristics of residues and commercial lime.

Table 2 – Chemical characteristics of residues and commercial lime.

Characteristics	Dregs	Grits	Commercial lime
pH-H_2O	12.69	12.96	---
CE [mS cm^{-1}]	39.00	27.9	---
$CaCO_3$ [%]	79.52	75.05	91.0-93.5
CaO [%]	44.53	42.03	50.4-52.4
MgO [%]	2.10	0.43	0.8 – 1.1
Al [mg/kg]	6877[1]	7077[1]	---

[1] Chemical analysis from cellulose plant

Since both residues and commercial lime have alkaline pH, their addition to soils caused a pH increase as compared to the soil control, it is directly proportional to the applied dose of any of the used bleaching materials. In general, for equivalent doses of 1, 2 and 4 ton $CaCO_3$/ha, the pH increase is higher when the mixture D+G is used rather than G and lime. As for pH variations, related to incubation time, for all the amended samples pH stabilization occurs after 16 days of incubation. Soils amended with G, show a similar behavior as those amended with lime. However, when the D+G mixture is utilized a higher initial increase than the observed in other amendments ocurred. Hence, when pH variation is analyzed in relation to the doses and incubation days; as for residues, Fig 1 shows that the use of the D+G mixture is the most appropriate.

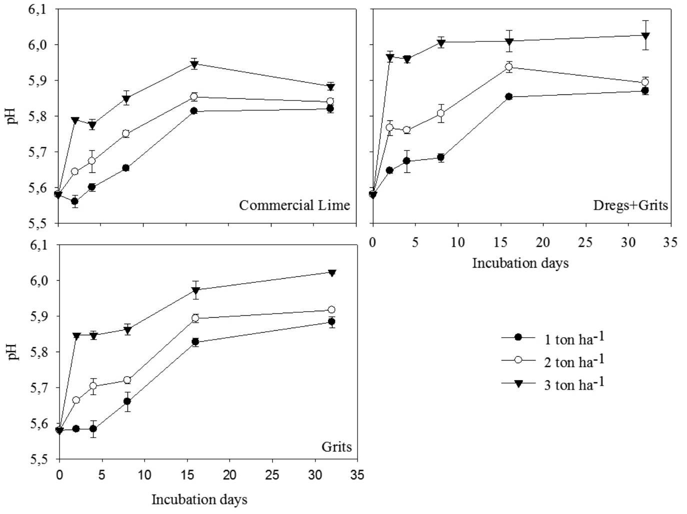

Figure 1 – pH variation of Santa Barbara amended soil – Dose and incubation

An important consequence of this pH change is the likely increase of the negative superficial charge, considering the isoelectric point of this soil (IEP: 3.4). In soils with variable surface charge, when pH increases the negative surface charge increases and, consequently, the CEC of soils; thus, the adsorption of metals (Al) may be also enhanced, as a consequence of the amendment process. According to the well-known buffer capacity of volcanic soils, the pH of amended samples goes down to the control soil pH after an incubation period of 2 months. Therefore, in amended Chilean volcanic soils, after some time the CEC or the excess of previously adsorbed metals may be released to the soil solution [12].

Al chemical fractions

Following Sposito et al. 1982, the exchangeable, sorbed, organic, carbonate, and sulfide fractions of trace metals are assumed to correlate well with the amount extracted by KNO_3, H_2O, NaOH, EDTA and HNO_3. Nevertheless, in this study the Al fractionation will be reported according to the extracting reagent employed, instead of the expected soil solid-phase fraction.

From the analysis of different chemical fractions of Al obtained for the control soil using no incubation, it was found that Al was mostly distributed in the residual fraction than in the fraction associated to organic components, *i.e.* Al would be found mostly as oxide and sulfide with a minor number of forms associated to carbonates. Finally, the more labile fractions that would reveal how leachable or exchangeable the analyte is, are the lowest, being not detectable in its soluble form (see Fig. 2).

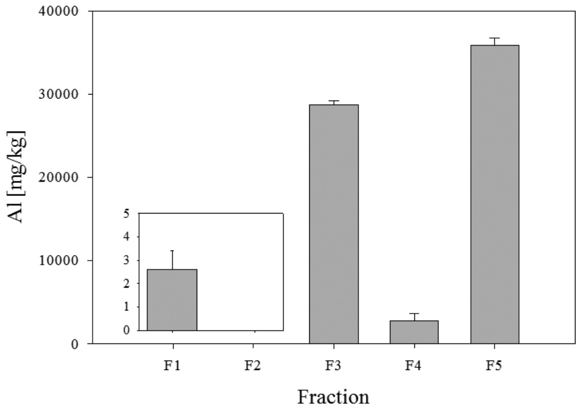

Figure 2 – Chemical fractionation of Al in Santa Barbara soil (no incubation)

Lime

Samples amended with commercial lime, after two days of incubation, the control soil presented higher levels of Al in the adsorbed and organic fraction as compared to soils amended with lime (see Fig. 3). Although in non-incubated soil Al was not detected in F2, in F3 28742,82±455,91 mg kg^{-1} was found, a lower value than 49362,60±545,36 mg kg^{-1} found in F3 of the control soil after two days of incubation. However, the values of Al that were determined in these two fractions stabilize through incubation time, which would imply that this sudden Al increase in the mentioned fractions, is because of the applied temperature during the incubation procedure. This Al content in F2 and F3 decreased due to lime amendment in the three applied doses, exhibiting lower values than the control soil. On the other hand, F1, F4, and F5 bleached soil fractions have no important changes as compared to the control soil. Then, after 4 days, a stabilization of the five fractions was observed, with respect to control soil and soil amended with lime using different doses.

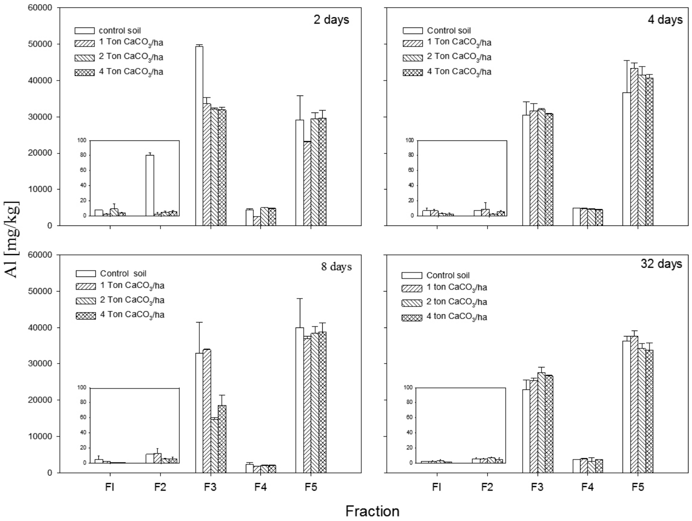

Figure 3 – Commercial lime: Al chemical fractions based on days of incubation and dose.

Only in F1 and F4 it is observed a slight diminution of exchangeable and carbonated Al because of pH increase that lime amendment causes in large doses. Lime amendment exhibits not Al incorporation in significant amount since not increases or decrease occurred after four days of incubation.

After eight days of incubation, an Al change is observed associated to organic components in soils amended with 2 and 4 ton, probably caused by pH increase to 5,85±0,02. The rest of the fractions remained unchanged, with Al levels of bleached soils, similar to previous days.

In general, it is observed that once the procedure of incubation is accomplished, the Al levels in different fractions are slightly increased after commercial lime addition to the initial doses. However, the Al content decreases as the bleacher dose increases, due to pH change (5.88±0.01) in the highest doses, that would be generating an Al deactivation responsible for soil acidification. It is noteworthy that the Al is mostly distributed in the labile soils, therefore, Al has not a high impact in soil-solution.

Grits

Aluminium distribution in different fractions of soils amended with G is depicted in Fig.4.

After two days of soils bleached with G, no considerably changes occur in the fractions, as compared to the control soil. If the fractions of G-amended soils are compared with those amended with commercial lime, no decrease was observed for F2 and F3. Therefore, no initial dampening effect, as occurred with commercial lime, exists.

Then, after 4 days no significant difference between a control soil and a soil with G in the exchangeable, adsorbed, organic and carbonated fractions was observed. Only F5 exhibited a decrease of *ca.* 9000 mg kg^{-1} with respect to the control soil when a 1 ton of CaCO$_3$/ha dose was applied. However, as the dose increases, so does the Al amount. When the fractions of this residue are compared, only in F5 a lower average value was observed, approximately 1000 mg kg^{-1}, in the determined Al in amended soils with G, behaviour that is opposite to that observed in lime amendments in this fraction.

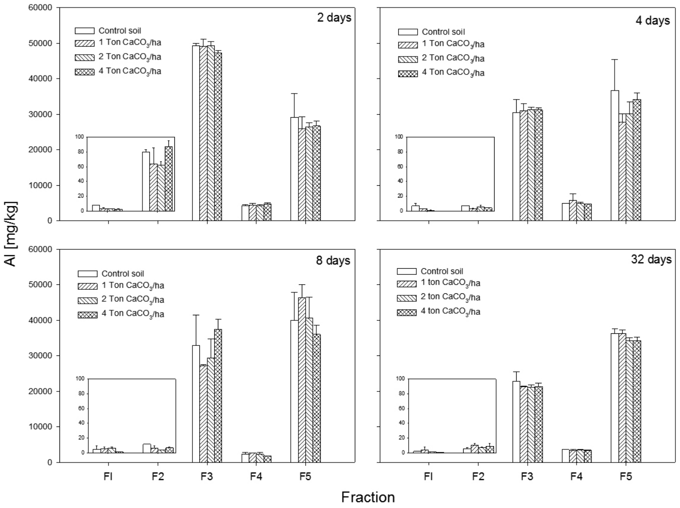

Figure 4 – Grits: Al chemical fractions based on days of incubation and dose

After 8 days of incubation of the G-amended soil, there are no important differences in F1, F2 and F4 as compared to the control soil, while in the organic and residual fractions a decrease and increase, respectively, took place. The G dose increases in F3 increases the Al content, however in F5 the behavior is just the opposite. If Al fractions in lime amended soils are compared, no great variations are obtained, because Al levels in soils with G do not markedly exceed those found in the control soil.

Then, once the incubation with G is accomplished, the Al levels in the five fractions do not exceed that of the control soil, hence the pH increase brought about by G is compensated by no addition of Al. From an environmental viewpoint, this is an important issue to be considered, since no Al addition in its toxic forms to the different chemical fractions takes place, taking into account that in a previous work (data not showed) high levels of Al was found in these residues. If a comparison of these fractions with the corresponding lime amended soil is made, it is demonstrated that soils with G exhibit a lower Al content, ascribed to organic components.

Dregs+Grits

Aluminum content in different fractions of three applied doses is shown in Fig. 5.

After two days of incubation, the control soil exhibited high levels of Al in the adsorbed and organic fractions, where the residual mixture decreases the Al that is present in these fractions due to its initial bleaching effect, similar to what happens when lime is applied. The rest of the fractions exhibit lower levels of Al than the control soils, with a trend to decrease its Al content in the different fractions, being more pronounced in F2 and F3. After 4 days of incubation, the Al in different fractions is equilibrated in the control soil. No considerable increase was obtained when the residual mixture dose is increased. In comparison to that with lime, a similar Al distribution in its five fractions is observed.

After 8 days, the F1, F2, F4 and F5 soil fractions of G in three doses resemble the content of Al extracted in the control soil, with no significant variations. Just a change of Al distribution in the organic fraction was found, with an increase of Al present in this fraction due to D+G addition. However, when the precision of Al content is considered, associated to the control soil, the Al levels are similar to those found in the soil with cellulose residues (D+G).

Finally, after 32 days of incubation, the Al chemical fractions in D+G-amended soils showed similar content in comparison as compared to the control soil, with no considerable addition of Al to each fraction. Consequently, the bleaching effect due to D+G is favorably considered advantageous since there is no important addition of Al to the labile fractions of the soils, with a minimum increase of Al, occurs. In this regard, sequential extractions (European Community Bureau of Reference, BCR) applied to green liquor waste have shown that the potentially bioavailable Al fractions are very low with values of 6.6 mg kg-1 (Makela et al., 2012). Likewise, for the fractions associated to species such as sulfides (Filgueiras et al., 2002), Cu and Al exhibited the highest values with 53.5 and 330 mg kg^{-1}, respectively. Heavy metal extractability studies using artificial gastric fluids have been performed in order to set the human health risk, showing a high degree of extractability of species such as Zn (1290 mg kg^{-1}), Ba (770 mg kg^{-1}) and Al (730 mg kg^{-1}).

Finally, in this study, independent of the added dose of bleaching mixture, a trend exists pointing at a higher Al content in the residual fraction at the end of the incubation as compared with the other fractions.

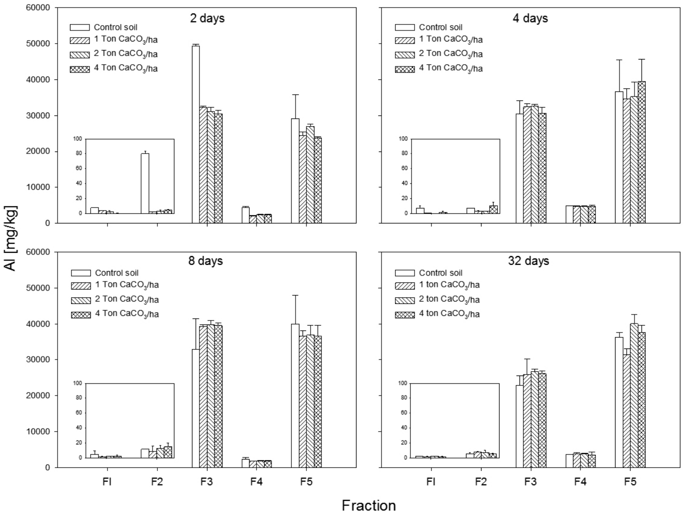

Figura 5 – *Dregs+Grits*: Al chemical fractions based on days of incubation and dose.

CONCLUSIONS

The addition of residues such as G and D+G in the studied proportion, would be a valid option to use in bleaching processes, since the experimental pH increases, enhancing thus the bleaching effect, being the D+G mixture better than commercial lime or G.

Aluminum incorporation in soil owing to cellulose residues is minimal and, at the same time, is compensated by pH increase as a result of the utilized bleachers, distributed in the less available fractions, *e.g.* residual, organic and carbonated; while in more available fractions, the adsorbed fraction is more important than the exchangeable one.

Finally, it was established that there is no significant Al distribution changes in the studied chemical fractions from Santa Barbara amended soil, using either commercial lime or cellulose residues.

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Full Length Research Paper

Effect of paper mill lime sludge as an acid soil amendment

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The possibility of using paper mill lime sludge as a soil amendment in an acid soil was investigated. Sludge used contained 58.4% calcium carbonates plus a small amount of heavy metals. A pot experiment was conducted with an acid soil and *Sorghum vulgaris variety speed seed* as test plant. Treatments with three replicates consisted of 0, 0.5 and 1, 2 and 4% paper mill lime sludge (L_0, $L_{0.5}$, L_1, L_2 and L_4, respectively). Shoot were harvested after 60 days and dry matter yield was determined after drying of the harvested shoots at 70°C for 48h. Subsamples of dry shoots were ground and then dry-ashed in a furnace at 550°C and then extracted with 2N HCl. The concentrations of P, K, Fe, Mn and Zn were measured in the extracts. Results showed that paper mill sludge significantly increased pH, which was proportional to the application rate of paper mill sludge. The application of 2% sludge (based on soil dry mass) remarkably increased shoot dry matter and P, K, Fe, Mn, K and P uptake.

Key words: Acid soil, paper mill lime sludge, soil amendment.

INTRODUCTION

About 30% of the world's arable soils are acidic (VonUexkull and Mutert, 1995) characterized by an excess of H^+, Al^{3+} and Mn^{2+} and lack (deficiencies or unavailabilities) of certain mineral elements, particularly calcium (Ca), magnesium (Mg) and phosphorus (P). Acid soils are deleterious to plant growth (Foy, 1992). The most common management practice to ameliorate acid soils is the surface application of lime and other calcareous materials (Bolan et al., 2003). The main aim of soil liming is to neutralize acidic inputs and recovering the buffering capacity to the soil (Ulrich, 1983).

Applications of industrial wastes as fertilizer and soil amendment have become popular in agriculture. Paper mill sludge is produced as a by-product of paper production that disposal of this material presents a problem for the mill (Battaglia et al., 2007; Calace et al., 2005; Mahmood and Elliot, 2006). Disposal by land filling, the most common disposal method, is costly and faces increasingly stringent environmental regulations (Feldkinchner et al., 2003). Lime sludge is the solid waste produced as part of the process that turns wood chips into pulp for paper. The major component of lime mud is calcium carbonate ($CaCO_3$) and it is estimated that about 0.47 m^3 of lime mud is generated to produce 1 ton of pulp (Wirojanagud et al., 2004).

Land application is one of the several limited methods available to manage solid waste (Schoof and Houkal, 2005) and is more economically and ecologically sound than landfill practice (Zule et al., 2007). For land application of sludges produced from pulp mills, Simpson et al. (1982) reported that combined Kraft paper mill secondary sludge-fly ash applied at a rate of 108 metric dry ton ha^{-1} significantly increased the yield of fescue and corn. The high alkalinity of lime mud has been utilized to precipitate heavy metals in tanning wastewater (Wirojanagud et al., 2004), remove phosphorus from piggery effluent (Weaver and Ritchie, 1987), stabilize sewage sludge (Fang and Wong, 1999) and immobilize heavy metals (Little et al., 1991; Fang and Wong, 1999). Mcbride and Spiers (2001) demonstrated that lime mud has heavy metal concentrations comparable to or lower than those of agricultural lime. Battaglia et al. (2007) reported the addition of paper mill sludge to a soil contaminated by lead and zinc induces a decrease in the mobile forms of both metals. Calacea et al. (2005) by leaching experiments showed that the addition of a paper

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mill sludge, consisting mainly of carbonates, silicates and organic matter to a heavy-metal polluted soil produces a decrease of available metal forms. Gaskin and Morris (2004) indicated that lime mud has potential to be used as an agricultural liming material because of its capability to neutralize soil acidity (increase soil pH) and add calcium and magnesium to the soil. Although high moisture content of lime mud creates more shipping and handling difficulties than typical dry agricultural liming materials (Mahmoudkhani et al., 2004), this obstacle can be overcome as sludge dewatering technology improves (Chen et al., 2002; Yin et al., 2004). The objectives of the present study were then to evaluate the value of the waste as an agricultural lime material. However, it should be noted that results from this controlled laboratory experiment can be different to actual field trials since actual field practice. Also, actual field conditions are under influence from consistently changing weather condition which is dramatically different than this laboratory experiment.

MATERIALS AND METHODS

The paper mill sludge was obtained from Pars and Chocka factories, Khoozestan and Guilan province, Iran. Total concentrations of some elements in the paper mill sludge were determined in the extract after digestion of samples with HNO_3 and HCl (Hossner, 1996) for elemental analysis. The amounts in the digests were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES, LEEMAN LABs, Inc.). The sludge pH and EC (Rhoads, 1996) were determined in a 1:2.5 paper mill sludge/ water suspension using a Metrohm 320 pH meter and Metrohm 644 conductometer, respectively.

A pot experiment was conducted in the greenhouse with a soil collected from the fields around Lahijan, Iran. Some physical and chemical properties of the soils are shown in (Table 1). Soils were air-dried and crushed to pass a 6 mm sieve. Treatments with three replicates consisted of 0, 0.5 and 1, 2 and 4% paper mill lime sludge (L_0, $L_{0.5}$, L_1, L_2 and L_4, respectively). *Sorghum vulgaris variety speed seed* was used as the test plant. Six seeds were sown in each pot. Seedlings were thinned to 3 when they were about 10 cm high. During the growth period, pots were irrigated with distilled water as needed. All pots received 50 mgN/kg as ammonium nitrate 1 week after germination. Shoot were harvested after 60 days and dry matter yield was determined after drying of the harvested shoots at 70°C for 48 h. Sub samples of dry shoots were ground and then dry-ashed in a furnace at 550°C and then extracted with 2N HCl. The concentrations of Fe, Mn and Zn were measured in the extracts by atomic absorption spectrophotometry, K by flame photometry and P by spectrophotometry. Soil samples from each pot were analyzed for AB-DTPA extractable Fe, Mn, Zn, K and P. Data were analyzed by standard ANOVA procedures using MSTATC and SAS software and significant differences was determined based on $P < 0.05$ level for the least significant difference Test.

RESULTS AND DISCUSSION

The chemical composition of the paper mill sludge showed that this compound contained about 58.4% calcium carbonates equivalent and a pH of about 13.2 (pH of 1:2.5 dry paper mill sludge/water suspension) and small amounts of Zn, Cu, Cr, Cd and Pb respectively 4.12, 2.35, 7.54, 3.25 and 28.6 $mg.kg^{-1}$.

Soil pH and EC

(Table 2) shows the effect of added paper mill sludge on soil pH. Paper mill sludge significantly increased pH, which was proportional to the application rate of paper mill sludge. Increase in pH was 0.76 units for $L_{0.5}$, 1.09 units for L_1, 1.76 units for L_2 and 2.68 units for L_4 compared to the control (L_0). Increase in soil pH indicates the usefulness of paper mill sludge as a liming agent for amelioration of acid soils. Similar results was obtained by He et al. (2009) for the use of paper mill lime mud as a liming agent and its effect on soil pH and ryegrass growth. It is indicated that the added lime mud increased soil pH to a range of from 6.5 to 10.2 and L_2 and L_3 brought initial soil pH to 7.6 - 8.3 higher than the recommended level of 6.0 – 7.0 for ryegrass (Hall, 1992). In an 84-d incubation study, boiler ash and lime by-products of paper industry applied to an acid (pH = 5.2) Marvyn loamy sand (fine-loamy, siliceous, thermic, Typic Kanhapludults) at equivalent rates based on CCE resulted in mean pH values significantly higher than values achieved with agricultural lime **(**Muse and Mitchel, 1995). Paper mill lime sludge increased EC, significantly in L_2 and L_4 treatments compared with control treatments. It should be regarded that the amount of soil electrical conductivity in treatments creates any problem for plant growth.

Dry matter yield

Dry matter yield increased significantly ($P \leq 0.05$) in 1% and 2% paper mill sludge treatments (L_1 and L_2) compared to the control (Figures 1 and 2). Yield was 1.37 and 1.9 times higher than control (L_0). Many studies have shown that the liming improved the growth of many crops cultivated on acid soils such as red clover (Steiner and Alderman, 2003), wheat and barley (Tang et al., 2003), peanut (Chang and Sung, 2004) and cotton (Pearson et al., 1973). Moustakas et al. (1999) reported significant yield increases of flue-cured tobacco cultivars in an acid soil, after the addition of 4 t ha^{-1} (MgO + CaO) which resulted in a pH increase from 4.8 to 6.1. A 4year field study in Alberta (Macyk, 1996) recommended an agronomically sound decomposed pulp mill sludge application rate of 40 – 80 dry ton ha^{-1} for brome grass. Rengel (1996) reported that retardation of root growth in acid soils was mainly due to aluminium toxicity. Therefore, increase in yield can be due to the reclamation of soil acidity and decrease in aluminum toxicity. Thus, increase of soil pH as the result of utilization paper mill sludge and subsequent increase in some nutrients availability may be reason for increase in yield. Increase

Table 1. Some properties of the used soil.

pH	5.8
EC (dS/m)	0.95
Total N (%)	0.06
P (mg/kg)	11.5
K (mg/kg)	113.0
Organic matter (%)	1.2
Texture	Sandy loam

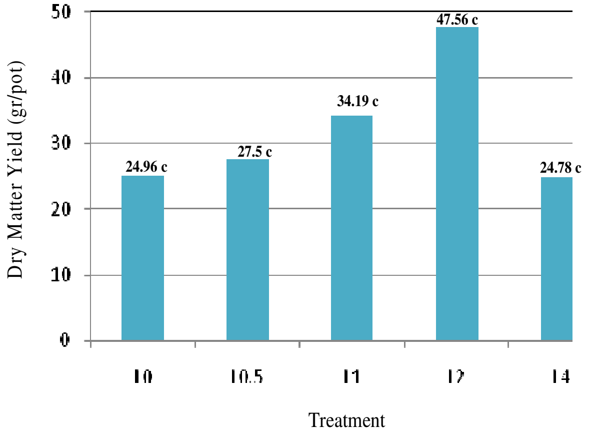

Figure 1. The effect of paper mill sludge on dry matter yield.

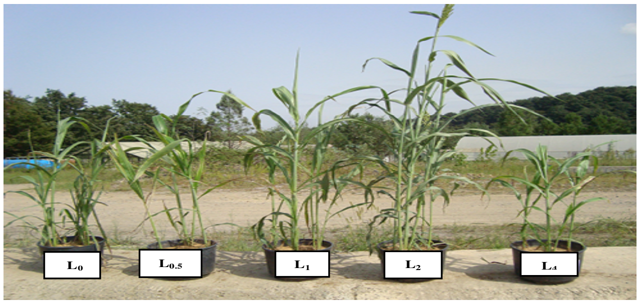

Figure 2. Sorghum growth in treated soil by paper mill sludge.

in plant yield as the result of utilizing calcareous by-products of other industries such as converter slag has also been reported in other studies (Ogutoinbo et al., 1996; Abou seeda et al., 2002; Prado et al., 2003; Barbosa Filho et al., 2004).

Phosphorus

The effect of treatments on P uptake is observed in (Table 3). Paper mill sludge increased P uptake by $L_{0.5}$ and L_1 treatments, but not significant. Utilizing 2% paper mill sludge remarkably ($P \leq 0.05$) increased P uptake that is due to the higher dry matter yield of this treatment compared with control, $L_{0.5}$ and L_1 treatments. Of course, the effect of treatments on leaf P concentration was not significant (Table 4). This can be due to soil P concentration, because the use of paper mill sludge did not affect soil phosphorus, significantly (Table 2). Phosphorus is an essential plant nutrient, it is indispensable for phospholipids, ATP and nucleic acids synthesis and therefore a deficiency can limit plant growth (Schachtman et al., 1998).

High pH values associated with high quantities of Ca probably facilitate precipitation of P as calcium phosphates, thus, limiting the availability of P to the plant. In contrast a similar increase in pH due to lime application, as happened in the present study, may cause some solubilization of P from Fe–P and Al–P complexes, thus, increasing P availability as was suggested by McCants and Woltz (1967). It seems that soil P concentration has not changed as the results of an interaction between precipitation and solubilization of P by liming.

Potassium

Based on (Table 3), paper mill sludge increased K uptake remarkably ($P \leq 0.05$) in L_1 and L_2 treatments that is due to the higher dry matter yield compared with control. Taking consideration into (Table 4), while the largest K uptake is related to L_2 treatment, but the lowest leaf K consideration is also related to this treatment. Karaivazoglou et al. (2007) reported that liming reduced leaf K concentration ($P \leq 0.05$) on average from 18.7 to 16.4 g kg^{-1} d.m. (12% reduction). The lower K content of leaves in limed treatments could be explained by the competition between K and Ca in their uptake by plants (Flower, 1999).

Therefore, liming may intensify K deficiency if low or no K fertilizer is applied. Mohammadi Torkashvand and Sedaghathoor (2007) reported that the use of a calcareous by-product of steel industry as a liming agent reduced K content in an acid soil. They stated that this decrease in soil K might be due to the potassium fixation. Al and Fe hydroxides polymers decline in clays interlayer or insoluble compounds, as K alominosilicates are formed consequently increasing K fixation (Malakouti and Afkhami, 1999).

Iron

Application of paper mill sludge significantly ($P \leq 0.05$) increased Fe uptake in L_2 treatment that is due to the higher yield compared with control (Table 3). (Table 4) shows that leaf Fe concentration has reduced in 1, 2 and 4% treatments of paper mill sludge, but this decrease is significant in 4% treatment. Decreasing leaf Fe Paper mill sludge increased Mn uptake in $L_{0.5}$, L_1 and L_2 concent-

Table 2. The effect of Paper mill sludge on some soil characteristics.

Treatment	pH	EC (dS/m)	P	K	Fe	Mn	Zn
			mg/kg				
Control	5.56 e	0.85 c	9.9 a	106.3 a	113.1 a	12.1 a	1.43 a
$L_{0.5}$	6.32 d	0.91 c	9.3 a	106.5 a	116.0 b	11.4 a	1.76 a
L_1	6.65 c	1.05 c	10.3 a	85.4 ab	104.6 a	11.7 a	1.66 a
L_2	7.32 b	1.28 b	10.3 a	73.6 b	92.4 ab	11.4 a	1.83 a
L_4	8.24 a	1.35ab	10.9 a	66.4 b	76.6 b	10.8 a	1.86 a

LSD (least significant difference) shows the significant difference (ρ = 0.05) among the different treatments.
Values followed by the same letters in each column are not significantly different at the 0.05 level (least significant difference).

Table 3. The effect of paper mill sludge on some nutrients uptake by plant.

Treatment	P	K	Fe	Mn	Zn
	mg/pot				
Control	60.86 b	285.2 c	3.56 bc	5.15 d	1.05 b
$L_{0.5}$	90.96 b	336.9 bc	4.02 b	7.64 bc	1.06 b
L_1	80.83 b	423.1 ab	4.16 b	9.00 ab	1.46 b
L_2	147.9 a	449.4 a	5.9 a	10.54 a	2.38 a
L_4	67.4 b	284.1 c	2.6 c	6.40 cd	1.00 b

Table 4. The effect of paper mill sludge on some nutrients concentration of leaf.

Treatment	Fe	Mn	Zn	K	P
	(mg/kg)			(%)	
Control	a 141.6	b 207.3	ab 42.4	a 1.14	b 0.24
$L_{0.5}$	a 145.6	a 279.0	b 38.6	a 1.22	a 0.33
L_1	ab 122.3	a 265.0	ab 42.7	a 1.24	b 0.23
L_2	ab 123.6	b 221.0	a 49.7	b 0.94	ab 0.31
L_4	b 105.3	a 259.0	b 40.0	a 1.15	ab 0.27

ration might be due to the soil Fe concentration. Extractable Fe decreased proportional to the application rate of paper mill sludge. Extractable Fe concentration depends on initial pH of soil. Increase in soil pH to the range of 7.4 - 8.5 decreased Fe level. It was found that Fe was precipitated as $Fe(OH)_3$ due to the increased pH (Norvell and Lindsay, 1982). Similar results were found by Mohammadi Torkashvand and sedaghathoor (2007) with the use of calcareous converter slag in acid soils.

Manganese and zinc

Paper mill sludge increased Mn uptake in L0.5, L1 and L2 treatments than in the control, significantly ($P \leq 0.05$) that is due to the higher yield of sludge treatments. Zn uptake only in L_2 treatments is significant as compared with control. Paper mill sludge had not a considerable effect on leaf Mn and Zn concentration and also soil available with Mn and Zn.

Conclusions

Treatments of acid soils with increasing rates from 0.25 to 16% of paper mill sludge increased soil pH. Application of paper mill sludge to pots increased the dry matter yield and P, K and micronutrients uptake for sorghum with the rate 2% being more effective. Results indicate a promising potential for paper mill sludge to be used as an inexpensive source of available lime for correction of soil acidity. This, however, needs further studies in the field and with various crops to determine the correct rates and to study the residual and environmental impact of application of this material to the soil.

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The complexity of wood ash fertilization disentangled: Effects on soil pH, nutrient status, plant growth and cadmium accumulation

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ABSTRACT

Wood ash is a by-product from energy production that can be recycled to forests to regain nutrients and prevent acidification. However, low concentrations of nitrogen (N) in wood ash may reduce its potential positive effect on plant growth. In addition, wood ash can have a high content of toxic heavy metals such as Cd, thus there are concerns that it may increase Cd accumulation in plants.

We grew *Deschampsia flexuosa* (Wavy hair-grass) in pots in acidic nutrient poor forest soil fertilized with different concentrations of wood ash (corresponding to field application of 0, 1.1, 3.3, 11 and 33 t ha^{-1}). Additionally, to disentangle the pH and nutrient effects of wood ash application, we included treatments with either CaO, to simulate pH effects of wood ash, or potassium (K) + phosphorus (P) fertilizer to mimic the nutrient effects. After 4.5 months of growth, we measured soil pH, plant biomass, Cd accumulation in shoots and N concentration in the various compartments of the system.

Wood ash addition stimulated plant growth, whereas CaO and K + P addition resulted in more moderate increases in biomass. Despite the low concentration of N in the wood ash, plant uptake of N increased in wood ash amendments, probably because wood ash stimulated mineralization of soil organic N. Plant Cd content significantly increased at the highest dose of wood ash.

Our results suggest that addition of wood ash significantly stimulates plant growth due to the combined effect of increased pH, elevated nutrient levels and increased N mineralization. Furthermore, despite the rather high Cd content in used wood ash (16.3 mg kg^{-1}), wood ash amendments up to 11 t ha^{-1} did not result in significantly increased plant uptake of Cd.

1. Introduction

Combustion of tree biomass for energy production has gained interest, as many countries wish to reduce their use and dependency of fossil fuels (Perkiomaki and Fritze, 2005). As a by-product, the incineration produces wood ash that consists of inorganic residues from the wood; thus most plant nutrients, notably phosphorus (P) and potassium (K) are preserved in the ash, whereas most nitrogen (N) is lost during incineration as NO_x compounds, and the remaining N is most likely strongly bound in organic residues and unavailable to organisms (Augusto et al., 2008; Demeyer et al., 2001). Further, wood ash is highly alkaline ($pH > 12$) due to its content of various metal oxides, mostly CaO, which is transformed to CaCO3 when the ash hardens. Wood ash may also contain considerable amounts of heavy metals, where the concentration of Cd (typically 1−20 mg kg^{-1}, but fly ashes can have higher concentrations) in this context is important (Bieser and Thomas, 2019; Maresca et al., 2017; Ring et al., 2006; Rosenberg et al., 2010).

In production forests with continuous harvest of tree biomass, soil acidification and nutrient depletion may present a serious problem for the long-term wood production (Huotari et al., 2015). Since wood ash is rich in both liming agents and plant nutrients it seems obvious to recycle it to the forest to mitigate these depletions (Arvidsson and Lundkvist,

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2003; Kjøller et al., 2017), and to improve the sustainability of the energy production by ensuring a circular nutrient flow. However, two major concerns may prevent wood ash recycling. Firstly, wood ash may be an insufficient fertilizer, since it contains little N. Secondly, it is unknown whether wood ash fertilization could lead to increased plant Cd accumulation and toxicity (Huotari et al., 2015). Therefore, the majority of wood ash is presently deposited as waste, which is costly and compromises the sustainability concept (Ingerslev et al., 2014).

Wood ash affects soil chemistry and biology in complex ways, due to primary effects, such as elevated pH and nutrient addition, and to derived effects such as changes in nutrient availability and interaction with biological processes (Bardgett, 2005). Plant growth is strongly affected by pH changes in the soil, mainly due to changes in availability of plant nutrients (Gough et al., 2000; Pärtel, 2002). Also, microorganisms and microbial processes are highly affected by soil pH (Rousk et al., 2009). Previous studies indicated that increased soil pH and nutrient concentration caused by wood ash application resulted in increased microbial mineralization of soil organic N into plant available N in the form of NH_4^+ and NO_3^- (Bang-Andreasen et al., 2017; Cruz-Paredes et al., 2017; Jäggi et al., 2004; Mortensen et al., 2020; Vestergård et al., 2018). This is particularly interesting since increased N mineralization might remedy the low concentration of N in wood ash.

The heavy metal content, especially of Cd, is a cause of concern in wood ash recycling (Ingerslev et al., 2014; McLaughlin and Singh, 1999). Cd is a non-essential element, and toxic to all organisms, which is actively taken up because it resembles the essential micro-nutrient zinc (Zn) (Clemens, 2006). Therefore, Cd may bioaccumulate in the food web and compromise ecosystem functioning and ultimately present a risk to human health (Godt et al., 2006; Järup and Åkesson, 2009). Plants in particular, could make up an important route of bioaccumulation as they take up Cd in the roots and translocate it to aboveground parts (Das et al., 1997; Kirkham, 2006). However, other research has shown that the bio-availability of Cd is generally low in soil (Johansen et al., 2019, 2018), and that it even decreases with increasing soil pH (Kindtler et al., 2019; Mortensen et al., 2018). Further, root symbionts, which are ubiquitous in natural ecosystems, reduce Cd accumulation in plants (Jiang et al., 2016; Rask et al., 2019).

The aim of this study was to disentangle the effect of wood ash application to soil, i.e. pH increase and nutrient addition, on plant growth, as well as to evaluate the potential problems with Cd accumulation in plants. We conducted a pot experiment with the perennial grass *Deschampsia flexuosa* (Wavy hair-grass) in a nutrient poor podzol soil. The pots were amended with different concentrations of either wood ash, CaO (to increase pH) or the mineral nutrients K + P to disentangle effects of pH and mineral nutrients. We used nutrient vector analyses to describe the effect of individual nutrients, which is often used to describe effects of complex fertilizers (Dumroese et al., 2018; Gale et al., 2017; Gale and Thomas, 2019; Omil et al., 2013). Furthermore, we evaluated the effects of wood ash application on Cd uptake in the plant shoots. We expected wood ash addition to increase pH, nutrient (mainly K and P) levels and N mineralization in the soil. We therefore hypothesised that wood ash fertilization would lead to increased plant growth. We expected the treatments with CaO and K + P to have a positive effect on plant growth, though not as pronounced as the wood ash treatment. Lastly, we hypothesised that Cd enrichment of the soil due to wood ash fertilization would lead to increased Cd concentration in plant tissue.

2. Materials and methods

2.1. Soil sampling

We collected soil in Gedhus Plantation (Karup, Denmark, 56°16′38.72″ N 9°05′5.78″ E) in August 2014. The plantation is a second generation *Picea abies* L. (Norway spruce) plantation established on old heathland. *Deschampsia flexuosa* is the dominating vascular plant in the understory, which is otherwise dominated by mosses. The site has very low bioturbation, as the only earthworm present is the epigeic earthworm *Dendrobaena octaedra*, and that in low abundances. The soil is a podzol formed on coarse well drained sand with silt and clay each below 5% of the mineral soil. The O-horizon is approximately 5 cm deep followed by a 10 cm A-horizon (for detailed description of soil and humus composition, see Hansen et al. (2018) and Maresca et al. (2018). The annual precipitation is 781 mm. We sampled material from the O-horizon (soil organic matter (SOM) content = 869 g kg^{-1}; carbon/nitrogen (C/N) = 29.9; cation exchange capacity (CEC) = 12.8 cmol kg^{-1}) and the underlying A-horizon (SOM = 184 g kg^{-1}; C/N = 37.0; CEC = 4.9 cmol kg^{-1}) in separate containers. We separately sieved portions of the sandy A-horizon (8 mm) and homogenized the organic O-horizon by hand.

2.2. Experimental design

For the experiment, we constructed artificial soil profiles in cylindrical plastic pots (h = 27 cm; D = 9 cm), with a removable bottom with six holes, which ensured that water could drain freely. The bottom was covered with water repellent cotton. Each pot was then filled with 1000 g (859 g DW) of material from the sandy A-horizon (approximately a 10 cm layer) and topped with 250 g (88.01 g DW) material from the O-horizon (approximately a 5 cm layer). The experiment consisted of 13 treatments, i.e. one unamended control, four wood ash levels, four liming (CaO) levels and four K + P fertilizer levels (the four levels of Wood ash, CaO and K + P were labelled low (L), low intermediate (LI), high intermediate (HI), high (H), see Table 2). Each treatment was replicated five times, i.e. we had in total 65 pots.

For the ash treatments, we used wood ash from Ebeltoft power plant (Ebeltoft, Denmark, 56°11′4.45″ N 10°41′10.03″ E). The wood ash was residues from incineration of Norway Spruce (*Picea abies* L.). We used fly ash, which is known to have a higher concentration of problematic elements compared to bottom ash. The ash was highly alkaline (pH = 12.7; EC = 2785 mS m^{-1}). The concentration of elements relevant for this study are listed in Table 1, and for a comprehensive chemical analysis of the ash, we refer to Maresca et al. (2017) sample FA-2b. The four ash levels (0.7, 2.2, 7.1 and 21 g wood ash pot^{-1}) were chosen to mimic field application of 1.1, 3.4, 11.2 and 33.7 t ha^{-1}, where 3.4 t ha^{-1} corresponds to a normal field dosage. For the liming treatments, we used CaO (Sigma-Aldrich, Germany). The four CaO treatments (0.04, 0.97, 2.5 and 4.6 g CaO pot^{-1}) served to mimic the increase in pH caused by wood ash without concomitant nutrient addition. We conducted a pilot experiment to determine the approximate amounts of CaO needed to reach the same pH as caused by the four wood ash levels. To provide nutrients without a pH increase, we used KCl (Sigma-Aldrich, Germany) and NaH_2PO_4 (Sigma-Aldrich, Germany), respectively. The amounts and ratio of K and P (2.3 + 1.3, 6.9 + 3.9, 23 + 13 and 68 + 39 mg K + P pot^{-1}) were calculated as equivalents to those of the wood ash (Table 2). Wood ash and CaO were applied on the top of the soil column. After amendment with wood ash and CaO, we watered the cylinders with 30 mL ddH_2O whereas K + P were added in a 30 mL solution with ddH_2O. Unamended control pots were watered with 30 mL ddH_2O. Finally, the water content of each system was adjusted to 45 % (W/DW) corresponding to 60 % of water-holding capacity.

We then transferred eight pre-germinated seedlings of *Deschampsia flexuosa* to each pot. The pots were placed in a growth chamber at 17.5 °C and exposed to a 16 h light cycle (355 μmol m^{-2} s^{-1} for 4 h, 860 μmol m^{-2} s^{-1} for 8 h and 355 μmol m^{-2} s^{-1} for 4 h) and then 8 h of darkness. The pots were watered every second day and weighed once a week to ensure a water content of 45 % (DW). After two months of growth, the pots were fertilized with 12.7 mg N as NH_4NO_3 pot^{-1} two times with a weekly interval to avoid severe N deficiency.

2.3. Sampling

After 4.5 months of growth, we destructively harvested the pots. We separated shoots from roots, rinsed the roots and dried shoots and roots

Table 1

Concentration of plant nutrients and potentially problematic elements in the used wood ash. The wood ash was obtained from Ebeltoft power plant, and is a fly ash with Norway spruce (*Picea abies* L.) as parent material. The metals Cu, Ni and Zn are both micronutrients for plants and considered problematic in large amounts. Data is adapted from Maresca et al. (2017).

Macro/meso nutrients (mg kg^{-1}):						Potentially problematic elements (mg kg^{-1}):						
N	P	K	Ca	Mg	S	Cd	Cr	Cu	Co	Ni	Pb	Zn
1670	21400	51200	263000	30000	8490	16.3	60.6	115	5.79	22.4	55.3	924

Table 2

Amendments applied in a greenhouse pot experiment aimed to disentangle effects of wood ash amendment on pH increase and nutrient levels. *Deschampsia flexuosa* was grown for 4.5 months in artificial soil profiles amended with wood ash at four levels, corresponding to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1}. CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients (K + P) were added at four levels to obtain nutrient addition without increases in pH.

Label	Added to pot	Field amendment equivalent
Control	Unamended	Unamended
Low ash (L ash)	0.7 g wood ash	1.1 t wood ash ha^{-1}
Low Intermediate ash (LI ash)	2.2 g wood ash	3.4 t wood ha^{-1}
High Intermediate ash (HI ash)	7.1 g wood ash	11.2 t wood ha^{-1}
High ash (H ash)	21 g wood ash	33.7 t wood ash ha^{-1}
Low CaO (L CaO)	0.04 g CaO	pH equivalent of 1.1 t wood ash ha^{-1}
Low Intermediate CaO (LI CaO)	0.97 g CaO	pH equivalent of 3.4 t wood ha^{-1}
High Intermediate CaO (HI CaO)	2.5 g CaO	pH equivalent of 11.2 t wood ha^{-1}
High CaO (H CaO)	4.6 g CaO	pH equivalent of 33.7 t wood ash ha^{-1}
Low K + P (L K + P)	2.3 mg K + 1.3 mg P	K and P equivalent of 1.1 t wood ash ha^{-1}
Low Intermediate K + P (LI K + P)	6.9 mg K + 3.9 mg P	K and P equivalent of 3.4 t wood ash ha^{-1}
High Intermediate K + P (HI K + P)	23 mg K + 13 mg P	K and P equivalent of 11.2 t wood ash ha^{-1}
High K + P (H K + P)	68 mg K + 39 mg P	K and P equivalent of 33.7 t wood ash ha^{-1}

at 70 °C for 24 h. Next, we removed remnants of wood ash from the pot surfaces and divided the soil in upper O-horizon (0–1 cm), lower O-horizon (1–5 cm) and A-horizon (5–10 cm). Soil pH was measured on soil slurries (soil to water ratio was 1:5) with a glass electrode in the 0–1, 1–5 cm and 5–15 cm layers (PHM240 pH/ION METER, Meter-Lab). To analyse for NO_3^-, NH_4^+ and H_2PO_4- content, 15 g of fresh soil (0–5 cm) was mixed with 75 mL water, shaken for one hour at 200 rpm and filtered overnight at 3 °C. NO_3^-, NH_4^+ and PO_4^- concentrations were measured colorimetrically on a flow injection analyser (FIAstar 5000, Foss A/S, Denmark). We dried and homogenized soil fractions for determination of K, Ca, Zn and Cd content. Aliquots of 2 g of the organic 0–5 cm topsoil were digested in 40 mL 32.5 % HNO_3 using the "plant material" program on a CEM MARS microwave (CEM, North Carolina, USA) and concentration of the elements were measured by Atomic Absorption spectrometry (Perkin Elmer PinAAcle 900 T). Cd concentration was measured with the graphite furnace technique, and Zn, Ca and K with the acetylene flame technique.

2.4. Plant analysis

We first determined dry weight of shoots and roots. For Cd, Zn, Ca and K analyses of shoots, samples of approximately 1 g were digested with 10 mL 16 % HNO_3 using the "plant material" program in a CEM MARS micro wave (CEM, North Carolina, USA). Samples were diluted with 10 mL ddH_2O and analysed for Cd content by Atomic Absorption spectrometry (Perkin Elmer PinAAcle 900 T) with the graphite furnace technique, and for Zn, Ca and K with Atomic Absorption spectrometry using the acetylene flame technique. Furthermore, 25 mg shoot material was digested with 7.5 mL HCl and total N and P contents were measured colorimetrically on a flow injection analyser (FIAstar 5000, Foss A/S, Denmark).

2.5. Data analyses

In Figs. 1–4, we use box plots to present the data. The box (Interquartile range, IQR) represents the third to first quartile with the median marked as a line. The whiskers mark the data range, and possible outliers are marked with a circle. For all measured parameters (Tables 3 and 4 and Figs. 1–4), we analysed the data with a one-way ANOVA with the measured parameters as dependent variable and the 13 treatments (categorical) as independent variable. In case of significant effects ($p < 0.05$) in the dataset, we used a Tukey's Honest Standard Deviation (HSD) test to separate and categorize means ($p < 0.05$). In Fig. 5, we constructed nutrient vector diagrams for the measured nutrients N, P, K, Zn and Ca. The diagrams were constructed by plotting the relative concentration, relative content and relative biomass for each nutrient in each treatment as compared to the control treatments, as in Haase and Rose (1995). One-way ANOVA and Tukey's HSD test were performed in SAS Enterprise Guide 6.1, while figures and nutrient vector diagrams were made in SigmaPlot 13.0.

3. Results

3.1. Effects on pH and element concentrations in soil

Amendments with wood ash and CaO resulted in a significant pH increase in both the uppermost 0–1 cm and in the lower 1–5 cm of the organic soil (Fig. 1). However, we observed no significant pH increases in the 5–15 cm mineral soil layer. The CaO treatment did not result in a pH increase at plant harvest as strong as expected from our initial experiments. Apparently, the alkaline component in CaO interacted with the soil in a different manner than the alkaline components in the wood ash during the 4.5 month experiment. The fertilizer treatment with K + P had no significant effect on pH (Fig. 1). It is not surprising that the strongly alkaline substances increase soil pH, however it is noteworthy that the effect is limited to the very top layers of the soil, which was also observed by Hansen et al. (2017).

The soil element concentrations (after removal of visible ash residues) increased significantly in those treatments where the particular element was added as part of the application i.e. soil Cd, Zn, Ca, P and K increased in the wood ash treatments, whereas only soil Ca increased in the CaO treatments, and only soil K and P increased in the K + P treatments (Table 3).

3.2. Plant biomass and element composition

Aboveground biomass of *Deschampsia flexuosa* increased significantly in all three treatment types, most markedly in wood ash treatments, where it increased with up to 270 % the biomass of the control treatment (Fig. 2). The CaO and K + P amendments resulted in moderate increases of respectively 110 % and 130 % in shoot biomass (Fig. 2). Plant concentration of K, P and Zn did not increase with wood ash application (Table 4). The CaO treatment reduced plant P concentration,

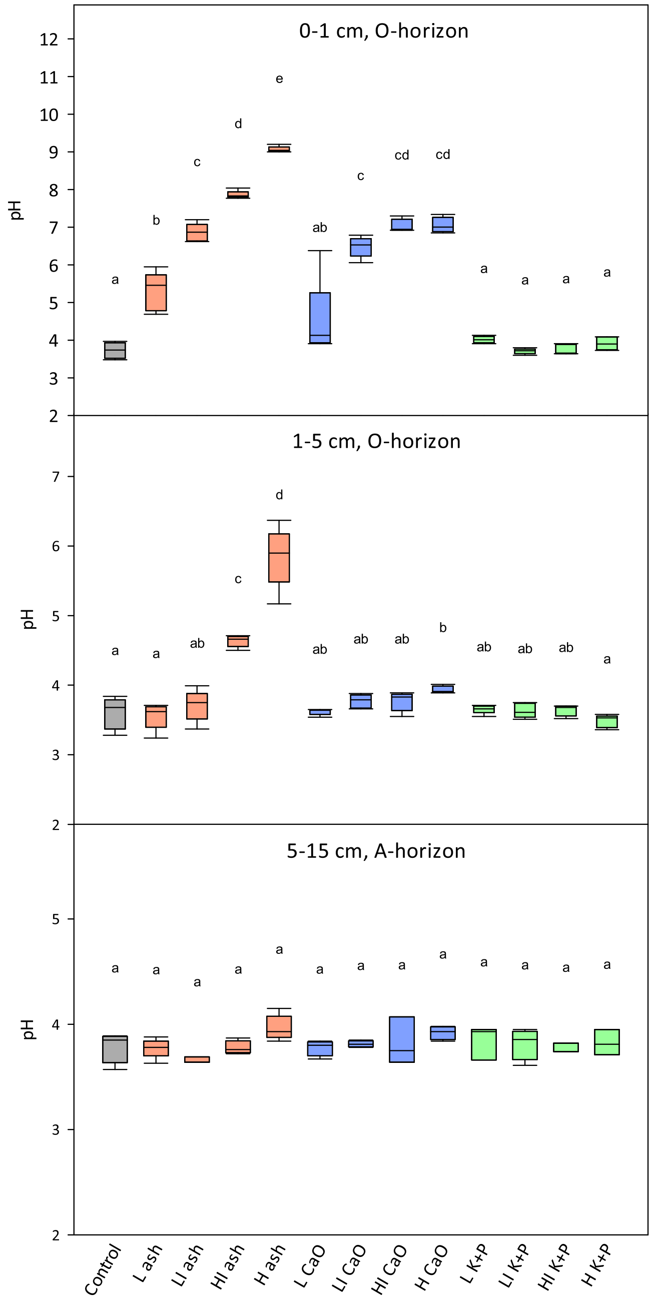

Fig. 1. Box plots (see section 2.6) of pH in the upper 0-1 cm O-horizon (top), the 1-5 cm O-horizon (middle) and the 5-15 cm A-horizon (bottom) from a greenhouse pot experiment, where *Deschampsia flexuosa* was grown for 4.5 months in artificial soil profiles amended with wood ash, corresponding to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1} (low (L), low intermediate (LI), high intermediate (HI), high (H)). CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients were added at four levels to obtain nutrient addition without increase in pH, Wood ash (orange), CaO (blue) and K + P (green), unamended control (grey). We found significant pH changes in the 0-1 cm and 1-5 cm layers ($p < 0.001$; one-way ANOVA), but not in the 5-15 cm layer. Treatment means are separated by letters ($p < 0.05$, Tukey HSD test) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

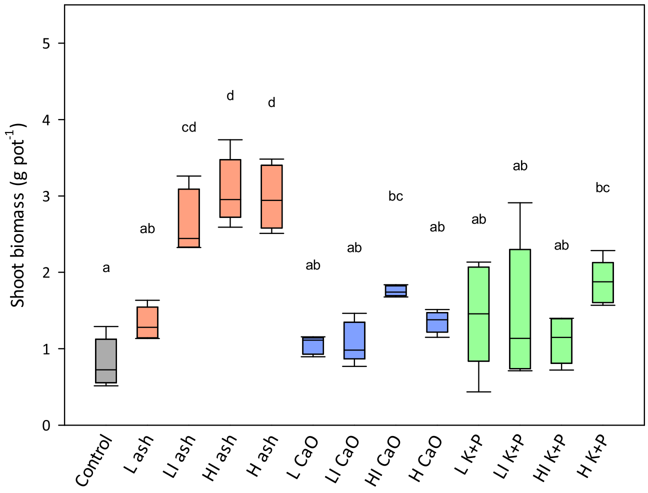

Fig. 2. Box plots (see section 2.6) of shoot biomass as affected by the four levels of wood ash (orange), CaO (blue) and K + P (green) as compared to the control (grey). Wood ash amendments corresponded to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1} (low (L), low intermediate (LI), high intermediate (HI), high (H)). CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients were added at four levels to obtain nutrient addition without increase in pH. Treatments differed significantly ($p < 0.001$, one-way ANOVA). Treatment means are separated by letters ($p < 0.05$, Tukey HSD test). For further details see Table 2 and Fig. 1 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

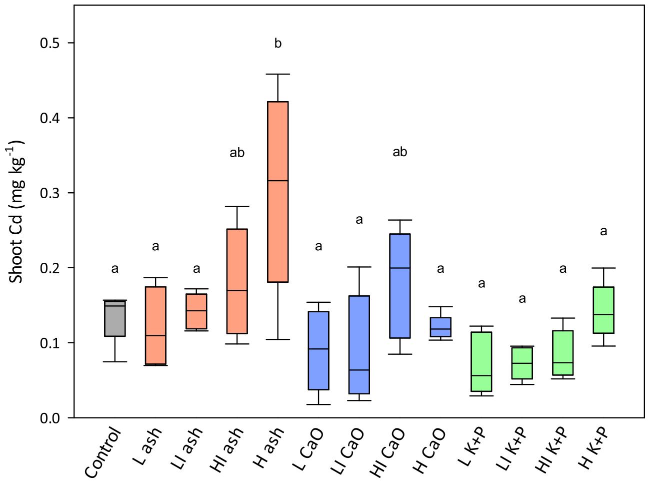

Fig. 3. Box plots (see section 2.6) of shoot Cd concentration as affected by the four levels of wood ash (orange), CaO (blue) and K + P (green) as compared to the control (grey). Wood ash amendments corresponded to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1} (low (L), low intermediate (LI), high intermediate (HI), high (H)). CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients were added at four levels to obtain nutrient addition without increase in pH. Treatments differed significantly ($p < 0.001$, one-way ANOVA). Treatment means are separated by letters ($p < 0.05$, Tukey HSD test). For further details see Table 2 and Fig. 1 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

whereas the K + P treatment affected plant uptake of P positively (Table 4). Plant Cd concentration increased with wood ash amendment, but the concentration was only significantly higher than the control in the highest (H) wood ash treatment (Fig. 3). The plant Ca concentration did not vary significantly between treatments, although the levels appeared elevated in wood ash and CaO treatments.

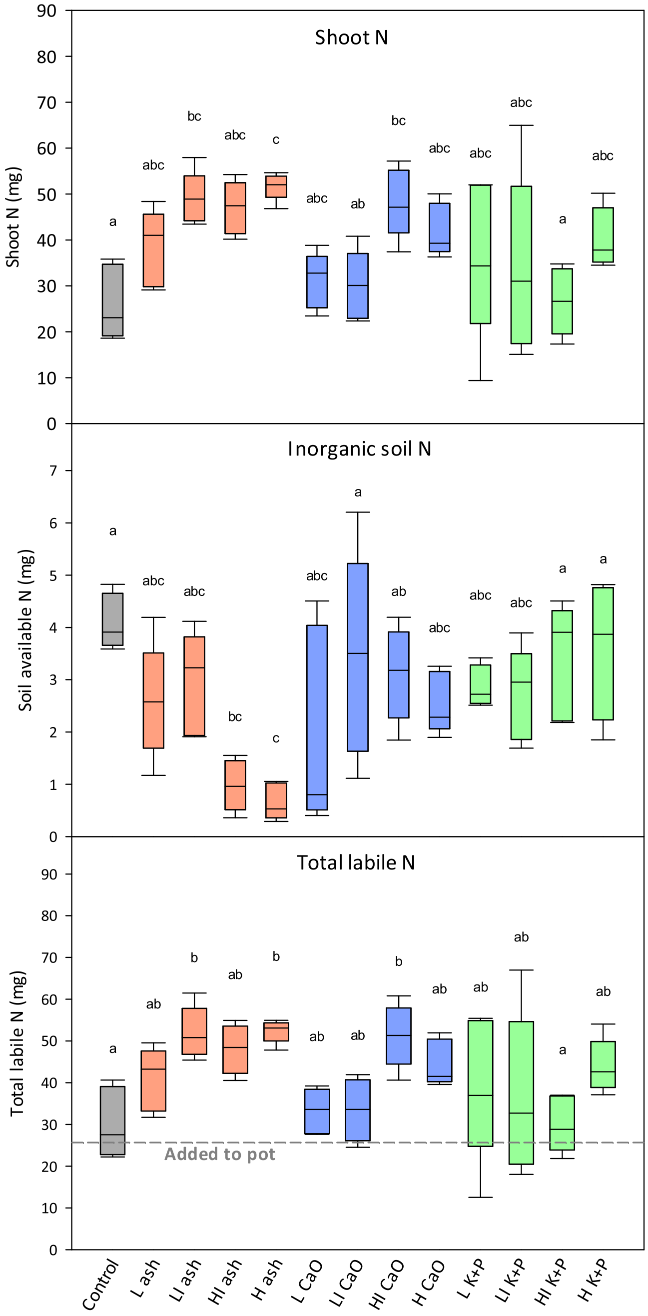

Fig. 4. Box plots (see section 2.6) of total shoot N (top), inorganic soil N ($NH_4^+ + NO_3^-$) (middle) and total labile N of the pots (shoot N + inorganic soil N) (bottom). The graphs show the effect of the four levels of wood ash (orange), CaO (blue) and K + P (green) as compared to the control (grey). Wood ash amendments corresponded to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1} (low (L), low intermediate (LI), high intermediate (HI), high (H)). CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients were added at four levels to obtain nutrient addition without increase in pH. The amount of added N fertilizer is marked as a dotted line on the bottom graph. Treatments differed significantly ($p < 0.001$, one-way ANOVA). Treatment means are separated by letters ($p < 0.05$, Tukey HSD test). For further details see Table 2 and Fig. 1 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

3.3. Nitrogen content in soil and plant

Plant uptake of N increased in the wood ash and CaO treatments, though only significantly in the LI and H ash treatments, and in the HI CaO treatment (Fig. 4 top). The inorganic soil N, which mostly consisted of NH_4^+ and only little NO_3^- (Table 3), decreased with increasing wood ash amendment, while CaO and K + P amendment had no significant effect on soil inorganic N (Fig. 4 middle). Total labile N in the system (shoot N + soil inorganic N) increased with ash and CaO treatments (Fig. 4 bottom). We found a significant positive linear correlation ($p < 0.001$; $r^2 = 0.58$) between labile N of the pots and shoot biomass, which suggests that mineralized N is very important to for plant growth in this system.

3.4. Nutrient vector analyses

We constructed nutrient vector analysis diagrams to evaluate the foliar nutritional status in the treatments compared to the control treatment (Fig. 5). Nutrient vector analysis diagrams are plots of relative nutrient concentration, relative nutrient content and relative biomass, for each nutrient (N, P, K, Zn, and Ca) in each treatment compared to the control treatment. The analyses revealed that in all treatments, increased biomass relative to the control coincided with increased N content and N concentration, signifying N limitation (Haase and Rose, 1995). The foliar concentration of K and P increased markedly in the K + P treatments, with moderate increases in biomass, which suggests some degree of K and P limitation (Haase and Rose, 1995). In wood ash treatments, K and P concentrations did not increase with increasing biomass, indicating K and P sufficiency. In CaO treatments, K and P concentrations appeared to decline with increasing biomass, indicating that K and P availability was also sufficient in CaO treatments. Foliar concentrations of Ca increased with biomass increase in wood ash and CaO treatments, and thus appeared limiting for plant growth in these treatments. However, the Ca concentrations decreased with biomass increase in the K + P treatments. Zn availability appeared to be sufficient in all treatments.

4. Discussion

4.1. Experimental design and limitations

Wood ash is a complex compound that contains several components, which may affect various soil parameters, and hence plant growth, in several ways. In our experimental design, we attempted to disentangle two basic characteristics of wood ash addition; its pH increasing effect and its increase of the two macro-nutrients K and P. We did this using separate amendments with CaO - to increase pH, and amendments with the two macro nutrients K and P. These treatments have some inherent challenges and limitations compared to wood ash treatments, and there are aspects of wood ash treatments that the CaO and K + P treatments do not encompass. Thus, the CaO treatments affected not only soil pH, but also the concentration and plant-availability of Ca. K and P were amended as salts and therefore Na and Cl were also included in these treatments. Finally, wood ash contains a number of micro-nutrients, such as Mg, B, S, Zn and Cu, the contents of which were only manipulated in the wood ash treatments.

4.2. pH and nutrient status of the soil

The aim of wood ash application in forestry is to counteract acidification and nutrient depletion of the soil in order to maintain productivity (Augusto et al., 2008; Rosenberg et al., 2010; Stupak et al., 2007). Our results suggest that wood ash application does prevent nutrient depletion as we recorded increased levels of K, P, Ca and Zn in the top soil (Table 3); in accordance with previous studies (Arvidsson and Lundkvist, 2003; Ohno and Erich, 1990). Moreover, wood ash increased

Table 3

Heavy metals and plant nutrients in 0-5 cm organic top soil in a greenhouse pot experiment, where *Deschampsia flexuosa* was grown for 4.5 months in artificial soil profiles amended with wood ash at four levels, corresponding to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1} (low (L), low intermediate (LI), high intermediate (HI), high (H)). CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients were added at four levels to obtain nutrient addition without increase in pH. Values are means ±1 SE (n = 5). All parameters showed significant treatment effects ($p < 0.001$; one-way ANOVA). Values with different letters differ significantly ($p < 0.05$; Tukey HSD) between treatments.

		Control	**L**	**LI**	**HI**	**H**
Cd (mg kg^{-1})						
	Wood ash	0.286 (±0.005) ^{ab}	–	0.344 (±0.023)^{b}	–	0.818 (±0.036) ^{c}
	CaO		–	0.258 (±0.003) ^{a}	–	0.276 (±0.014) ^{a}
	K + P		–	0.289 (±0.006) ^{ab}	–	0.242 (±0.003) ^{a}
Zn (mg kg^{-1})						
	Wood ash	24.2 (±0.4) ^{a}	–	27.7 (±1.5) ^{a}	–	57.7 (±3.7) ^{b}
	CaO		–	22.5 (±0.9) ^{a}	–	23.7 (±1.6) ^{a}
	K + P		–	23.5 (±0.7) ^{a}	–	22.1 (±0.7) ^{a}
Ca (mg kg^{-1})						
	Wood ash	1181 (±37) ^{a}	–	2459 (±115) ^{b}	–	5850 (±274) ^{d}
	CaO		–	1978 (±152) ^{b}	–	4017 (±234) ^{c}
	K + P		–	1253 (±30) ^{a}	–	1153 (±42) ^{a}
K (mg kg^{-1})						
	Wood ash	271 (±10) ^{ab}	–	353 (±29) ^{bc}	–	2651 (±248) ^{d}
	CaO		–	237 (±17) ^{a}	–	233 (±19) ^{a}
	K + P		–	489 (±83) ^{c}	–	2971 (±217) ^{d}
PO_4^{3-} (mg kg^{-1})						
	Wood ash	16.0 (±5.3) ^{ab}	28.0 (±2.2) ^{abc}	58.3 (±6.9) ^{cd}	134.4 (±9.9) ^{e}	48.9 (±12.7) ^{bcd}
	CaO		24.4 (±12.6) ^{ab}	10.3 (±5.9) ^{a}	6.1 (±1.8) ^{a}	7.6 (±3.17) ^{a}
	K + P		15.9 (±1.9) ^{ab}	28.9 (±3.0) ^{abc}	86.2 (±11.7) ^{de}	406.9 (±27.6) ^{f}
NH_4^+ (mg kg^{-1})						
	Wood ash	44.2 (±2.6) ^{c}	28.4 (±5.5) ^{abc}	32.8 (±5.0) ^{abc}	10.3 (±2.5) ^{ab}	5.9 (±1.5) ^{a}
	CaO		19.1 (±9.6) ^{abc}	36.2 (±10.2) ^{bc}	32.7 (±4.8) ^{abc}	24.0 (±2.4) ^{abc}
	K + P		30.7 (±1.9) ^{abc}	28.5 (±4.5) ^{abc}	37.8 (±5.4) ^{c}	40.5 (±6.6) ^{c}
NO_3^- (mg kg^{-1})						
	Wood ash	2.59 (±0.17) ^{abc}	1.12 (±0.22) ^{ab}	0.81 (±0.21) ^{ab}	0.88 (±0.31) ^{ab}	1.59 (±1.04) ^{ab}
	CaO		3.45 (±0.94) ^{bc}	3.00 (±0.31) ^{ab}	2.69 (±0.37) ^{abc}	5.02 (±0.82) ^{c}
	K + P		2.10 (±0.58) ^{ab}	2.69 (±0.96) ^{abc}	0.94 (±0.27) ^{ab}	0.22 (±0.06) ^{a}

Table 4

Plant parameters of *Deschampsia flexuosa* from a greenhouse experiment, where it was grown for 4.5 months in artificial soil profiles amended with wood ash at four levels, corresponding to field amendment with 1.1, 3.4, 11.2 and 33.7 t wood ash ha^{-1} (low (L), low intermediate (LI), high intermediate (HI), high (H)). CaO was applied at four levels to mimic the pH increase caused by the wood ash, without concomitant addition of mineral nutrients, whereas the mineral nutrients were added at four levels to obtain nutrient addition without increase in pH. Values are means ±1 SE (n = 5). All parameters except shoot Ca showed significant treatment effects ($p < 0.001$; one-way ANOVA). Values with different letters differ significantly ($p < 0.05$; Tukey HSD) between treatments.

		Control	L	LI	HI	H
Root biomass (g)						
	Wood ash	0.32 (±0.11) ^{a}	0.55 (±0.07) ^{a}	0.87 (±0.19) ^{ab}	1.31 (±0.07) ^{b}	0.79 (±0.23) ^{ab}
	CaO		0.43 (±0.05) ^{a}	0.69 (±0.14) ^{ab}	0.63 (±0.03) ^{a}	0.47 (±0.05) ^{a}
	K + P		0.37 (±0.12) ^{a}	0.41 (±0.14) ^{a}	0.33 (±0.06) ^{a}	0.54 (±0.06) ^{a}
Shoot K (g kg^{-1})						
	Wood ash	15.4 (±1.4) ^{ab}	16.9 (±0.8) ^{ab}	15.3 (±1.0) ^{ab}	18.2 (±1.7) ^{ab}	22.3 (±1.1) ^{ab}
	CaO		9.9 (±1.7) ^{ab}	8.6 (±1.4) ^{a}	10.4 (±0.8) ^{ab}	11.5 (±0.6) ^{ab}
	K + P		17.3 (±1.3) ^{ab}	20.4 (±2.0) ^{ab}	23.0 (±0.9) ^{ab}	33.0 (±1.3) ^{b}
Shoot P (g kg^{-1})						
	Wood ash	1.6 (±0.2) ^{def}	1.9 (±0.1) ^{ef}	1.3 (±0.1) ^{cde}	1.3 (±0.1) ^{bcd}	2.0 (±0.3) ^{fg}
	CaO		1.1 (±0.05) ^{bcd}	0.9 (±0.1) ^{abc}	0.7 (±0.03) ^{a}	0.9 (±0.04) ^{ab}
	K + P		2.8 (±0.1) ^{gh}	4.0 (±0.2) ^{h}	6.9 (±0.6) ^{i}	18.7 (±0.9) ^{j}
Shoot Ca (mg kg^{-1})						
	Wood ash	490 (±28)	616 (±58)	707 (±59)	858 (±89)	939 (±89)
	CaO		421 (±66)	442 (±97)	767 (±97)	832 (±77)
	K + P		362 (±48)	339 (±16)	380 (±35)	438 (±37)
Shoot Zn (mg kg^{-1})						
	Wood ash	29.5 (±3.1) ^{ab}	30.0 (±2.7) ^{ab}	25.4 (±2.8) ^{ab}	27.6 (±3.8) ^{ab}	36.3 (±0.9) ^{b}
	CaO		23.5 (±4.5) ^{ab}	20.2 (±3.8) ^{a}	32.5 (±3.2) ^{ab}	28.6 (±4.4) ^{ab}
	K + P		21.5 (±2.0) ^{ab}	22.3 (±0.14) ^{ab}	25.1 (±1.8) ^{ab}	29.4 (±2.8) ^{ab}

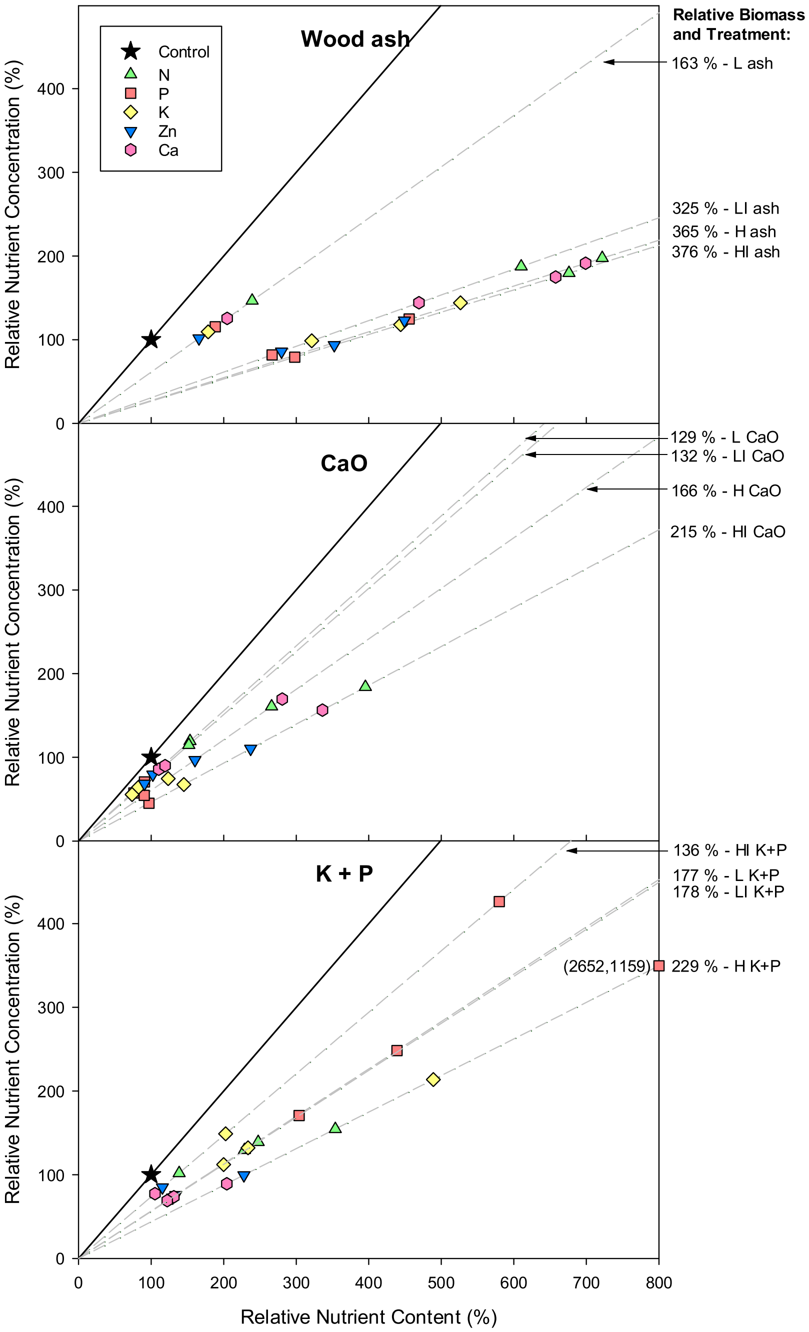

Fig. 5. Nutrient vector diagrams of the measured elements N, P, K, Zn and Ca in the four treatments L, LI, HI and H of each treatment type - Wood ash (top), CaO (middle) and K + P (bottom).The plot is a depiction of the relative concentration and relative content of each nutrient in each treatment compared to the Control treatment. The diagonal axis is the relative biomass of the treatment compared to the Control treatment (solid line is 100 % relative biomass). Each point represent a vector from the Control reference point.

pH in the 0−1 cm top soil layer from 3.7 to 9.0, and from 3.6 to 5.8 in the 1−5 cm organic layer, though not in the lower 5−15 cm bottom layer (Fig. 1). Apparently, the pH effects are limited to the uppermost layers, even in long-term experiments (Hansen et al., 2018), though this effect is probably limited to soils where there is no appreciable bioturbation or cryoturbation of soils. Jokinen et al. (2006) and Weber et al. (1985) similarly reported on mitigating effects on acidification and increases in the level of important plant soil nutrients.

4.3. Nitrogen mineralization and uptake

Wood ash contains little N (Table 1), as most of it is lost during the incineration (Ingerslev et al., 2014), but the wood ash may stimulate microbial processes that lead to mineralization of N from soil organic matter. The test plant *Deschampsia flexuosa* is known to take up small organic N compounds (Näsholm et al., 1998; Persson et al., 2003; Weigelt et al., 2005), and if the treatments increased the availability of these compounds, it may have contributed to the N consumption by the plants. We did not measure the organic N compounds in the soil, but such compounds taken up by the plant are included in the plant N measurements. We observed that total labile N increased with up to 25 mg N pot^{-1} (Fig. 4 bottom) after wood ash and CaO amendment. This suggests that mineralization of organic N was stimulated by increases in soil pH. Mortensen et al. (2019) demonstrated that wood ash stimulates decomposition of recalcitrant organic matter, which can lead to increases in N mineralization (Jäggi et al., 2004; Mortensen et al., 2020; Vestergård et al., 2018).

We found that wood ash fertilization actually decreased the soil concentration of inorganic and plant available N (Fig. 4 middle), probably due to efficient plant uptake. Yet, we observed a large increase in labile N in the system. This observation was only possible because our experimental pot system allowed assessment of all compartments. Thus this detailed insight into gross N flow from the soil to plants provides a valuable supplement to field experiments, where the flow of N is not easily assessed.

We found no indications that wood ash fertilization will lead to increased leaching of inorganic N, despite the increased mineralization. Likewise, ash application did not affect inorganic N leaching at field scale (Hansen et al., 2018). The effects of wood ash were limited to the uppermost layers shown by the steep pH profile (Fig. 1), which is also reported from an experiment designed to study this (Hansen et al., 2017). In our experiment, mineralized N was quickly taken up by plants, and the amount that could potentially be leached actually decreased with wood ash amendment.

4.4. Plant growth

We observed increases in growth of *Deschampsia flexuosa* in all three treatment types compared to the control, but wood ash treatments yielded by far the largest increases in biomass (up to 270 %) (Fig. 2). It is not surprising that wood ash is the best fertilizer, since each of the two other treatments only partially contribute the presumed plant growth promoting factors of wood ash, i.e. K + P and pH increase, respectively. This is underlined by the conclusions from nutrient vector analyses diagrams (Fig. 5), where growth of the CaO and K + P treated plants seem to be limited by the availability of Ca and N and the macronutrients K and P, respectively. In addition, the treatments with wood ash may have benefitted from nutrients that was not assessed in this experiment (e.g. Mg, S, Cu, B). This stresses the complementary effects caused by the chemically complex wood ash.

In field studies, similar effects have been recorded; application of 8 and 16 t ash ha^{-1} increased wood production of scots pine 13 and 17 times, respectively (Moilanen et al., 2002). Arvidsson and Lundkvist (2003)found that a smaller dose, 3 t wood ash ha^{-1}, had limited effect on Norway spruce growth over 5 years but that the coverage of *D. flexuosa* was slightly increased.

K and P addition will alleviate depletion of these nutrients, whereas the effect of increased pH is more complex. Generally, a pH increase will stimulate plant growth in acidic soil as the pH optimum for most plants is around 6.5–7, because nutrients like P and K in particular are more available at neutral pH (Raven et al., 2005) and because the microbial activity will facilitate nutrient mineralisation (e.g. inorganic N) (Mortensen et al., 2020; Vestergård et al., 2018).

The wood-ash-induced increases in plant biomass was achieved without addition of N fertilizer, which have been a concern with the use of wood ash as fertilizer, since N is commonly a limiting factor for plant growth. The limited effect of K + P fertilization on plant biomass (Table 4, Fig. 2) underlines that the high content of these macro nutrients in wood ash cannot account for enhanced biomass production alone. The additional effect on soil pH and other plant nutrients, makes wood ash a more complex and better fertilizer, as these factors have both a direct effect on plant growth and an effect on microbial processes such as N mineralization (Bang-Andreasen et al., 2017; Cruz-Paredes et al., 2017; Mortensen et al., 2020; Vestergård et al., 2018).

In our pot experiment, N mineralization was the sole supply of N for the plants, and it appears to be a limiting factor, as seen in the nutrient vector diagrams (Fig. 5). The site where we collected the soil for the experiment has a very large pool of organic matter (O-horizon SOM = 869 g kg^{-1}, C/N = 29.9; A-horizon SOM = 184 g kg^{-1}; C/N = 37.0), and the stimulation of N mineralization may continue for a long time, thus sustaining plant growth. In addition, this site receives N from atmospheric deposition, which is the case in many parts of the world. However, the supply of N must be taken into consideration when choosing sites for wood ash recycling, as it may otherwise have limited effects (Huotari et al., 2015; Stupak et al., 2007)

Application rates above 11.2 t ash ha^{-1} (HI ash) did not increase the biomass of *D. flexuosa* further, which may suggest that plant growth was no longer limited by the nutrients available in wood ash. The saturation pattern could however also be due to a reduced availability of N since plant N concentration decreased with larger ash amendments (see below). Nitrogen concentrations in the plant shoots decreased from 1.4 to 1.1 % (DW/DW, Fig. 4B and Fig. 2) when ash dose increased from 3 to 11.2 t ash ha^{-1}, which could be the reason for a smaller plant growth response with the largest ash amendments.

4.5. Cd accumulation

Another concern about the usage of wood ash as fertilizer is the Cd content. We saw that wood ash amendment did increase Cd concentration in leaves of *Deschampsia flexuosa*, but that only very high ash concentrations caused this response, despite the high Cd content (13.9 mg kg^{-1}) in the ash we used (Maresca et al., 2017). At the highest wood ash amendment (H ash), corresponding to field amendment of 33.7 t wood ash ha^{-1}, plant concentration of Cd significantly increased compared to the unamended control (from 0.14 mg kg^{-1} in the control treatment to 0.30 mg kg^{-1} in the H ash treatment; Fig. 3). However, in practice wood ash amendments above 10 t ha^{-1} are not relevant to consider. This amount would be too much with regard to mass balance and would compromise guidelines that define soils with more than 0.5 mg kg^{-1} soil as polluted soils (Ingerslev et al., 2014). Though Cd content in *Deschampsia flexuosa* increases at the highest ash application level, the concentrations are still well below EU recommended limits for leafy vegetables of 0.2 mg kg^{-1} fresh weight (EU, 2006). Thus, about the same as the highest value we measured (Fig. 3), but we measured in dry weight which is less than 10 % of fresh weight. Other studies have similarly concluded that application of wood ash in forest ecosystems is not a concern with regard to the bio-availability of Cd for soil microorganisms (Cruz-Paredes et al., 2017; Mortensen et al., 2018), Cd accumulation in the humus layer (Perkiomaki and Fritze, 2005) or with respect to Cd accumulation in berries and mushrooms (Moilanen et al., 2006).

5. Conclusion

We studied wood ash recycling to acidic forest soil as a strategy to achieve efficient nutrient recirculation within biomass-based energy production, secure long term biomass production and prevent acidification. Based on a greenhouse pot experiment with *Deschampsia flexuosa*, we conclude that wood ash fertilization increases pH and nutrient levels in the top soil. This, in combination with increased N mineralization from organic soil N, resulted in large increases in plant biomass. Cd concentration in shoots increased at the highest wood ash addition, which is unwanted. However, this level of wood ash application was unrealistically high based on current legislation (10 times higher), and the shoot Cd concentration is still within EU recommendations for foodstuff.

CRediT authorship contribution statement

Jesper Liengaard Johansen: Writing - review & editing, Data curation, Writing - original draft, Conceptualization, Methodology, Visualization, Investigation. **Maiken Lundstad Nielsen:** Writing - review & editing, Data curation, Writing - original draft, Visualization, Investigation. **Mette Vestergård:** Writing - review & editing, Data curation, Writing - original draft, Conceptualization, Methodology, Supervision. **Louise Hindborg Mortensen:** Writing - review & editing. **Carla Cruz-Paredes:** Writing - review & editing. **Regin Rønn:** Writing - review & editing, Data curation, Writing - original draft, Conceptualization, Methodology, Supervision. **Rasmus Kjøller:** Writing - review & editing. **Mads Hovmand:** Writing - review & editing, Supervision. **Søren Christensen:** Writing - review & editing, Data curation, Writing - original draft, Conceptualization, Methodology. **Flemming Ekelund:** Writing - review & editing, Data curation, Writing - original draft, Conceptualization, Methodology, Supervision.

Declaration of Competing Interest

The authors report no declarations of interest.

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