

# NUTRIENT LEACHING POTENTIAL FOLLOWING APPLICATION OF PAPERMILL LIME-SLUDGE TO AN ACIDIC CLAY SOIL<sup>(1)</sup>

S. C. VETTORAZZO<sup>(2)</sup>, F. C. S. AMARAL<sup>(3)</sup> & J. C. CHITOLINA<sup>(4)</sup>

## SUMMARY

**This experiment was carried out under greenhouse conditions with soil pots during 210 days, to evaluate the effect of calcitic papermill lime-sludge application (at the rates 0, 773, 1.547, and 2.320 mg kg<sup>-1</sup> or respective equivalents to control, 2, 4, and 6 t ha<sup>-1</sup>), on chemical composition of soil leachate and its effects on eucalypt growth and yield. Highest soil leachate pH, SO<sub>4</sub>, and Na concentrations occurred in the 4 and 6 t ha<sup>-1</sup> treatments. Soil leachate nitrate concentrations decreased with increasing lime-sludge rate. Soil leachate phosphate remained low (below the detection limit) in all treatments until 120 days, while the concentration increased in the lime-sludge treatments at 210 days (last sampling) in about 600 mg L<sup>-1</sup>. Lime-sludge decreased leachate Mg concentration, but had no significant effect among rates. Soil leachate Ca, K, B, Cu, Fe, and Zn did not change significantly for any lime-sludge application rates. The maximum NO<sub>3</sub>, Ca, Mg, K, and Na concentrations in the soil leachate occurred at 60 days after lime-sludge application (leaching equivalent to 1 pore volume), but for pH and SO<sub>4</sub>, the maximum occurred at 210 days (leaching equivalent to 4 pore volumes). Lime-sludge application decreased the concentration of exchangeable Al in the soil. Plant diameter growth and dry matter yield were increased with increasing lime-sludge rate. Beneficial effects on mineral nutrition (P, K, Ca, B, and Zn) of eucalypts were also obtained by the application of 4 and 6 t ha<sup>-1</sup> of lime-sludge.**

**Index terms: eucalypt, industrial residue, soil fertility, mineral nutrition, sodium, recycling.**

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<sup>(2)</sup> Biologist, Praça Santos Dumont 22/302, CEP 22470-060 Rio de Janeiro (RJ).

<sup>(3)</sup> Researcher, Embrapa Solos, Rua Jardim Botânico 1024, CEP 22460-000 Rio de Janeiro (RJ). E-mail: fernando@cnps.embrapa.br

<sup>(4)</sup> Professor, Departamento de Ciências Exatas, Escola Superior de Agricultura "Luiz de Queiroz" – ESALQ/USP, and Curso de Farmácia e Bioquímica, UNOESTE. Caixa Postal 09, CEP 13418-900 Piracicaba (SP).

**RESUMO:** *POTENCIAL DE LIXIVIAÇÃO DE NUTRIENTES EM UM SOLO ARGILOSO ÁCIDO APÓS A APLICAÇÃO DE LAMA DE CAL PROVENIENTE DE INDÚSTRIA DE PAPEL*

*Em casa de vegetação, realizou-se um experimento em vasos durante 210 dias, para avaliar os efeitos da aplicação no solo de um resíduo calcítico proveniente da indústria de papel, a lama de cal, nas doses 0, 773, 1.547 e 2.320 mg kg<sup>-1</sup>, equivalentes ao controle, 2, 4 e 6 t ha<sup>-1</sup>, respectivamente, sobre a composição química do lixiviado do solo e seus efeitos no crescimento e na produção de mudas de eucalipto. Os maiores valores de pH e das concentrações de SO<sub>4</sub> e Na no lixiviado do solo ocorreram nos tratamentos com 4 e 6 t ha<sup>-1</sup>. As concentrações de NO<sub>3</sub> no lixiviado do solo diminuíram com o aumento da dose de lama de cal aplicada. As concentrações de PO<sub>4</sub> no lixiviado do solo permaneceram baixas (abaixo do limite mínimo de detecção) em todos os tratamentos até 120 dias, enquanto, aos 210 dias (última amostragem), essas concentrações aumentaram nos tratamentos com lama de cal, sendo da ordem de 600 mg L<sup>-1</sup>. A concentração de Mg no lixiviado diminuiu com a aplicação de lama de cal, mas não houve efeito significativo entre as doses. As concentrações de Ca, K, B, Cu, Fe e Zn no lixiviado não foram significativamente influenciadas pelas doses de lama de cal aplicadas no solo. As concentrações máximas de NO<sub>3</sub>, Ca, Mg, K e Na no lixiviado do solo ocorreram após 60 dias da aplicação da lama de cal (lixiviação equivalente a uma vez o volume total de poros), mas, para pH e SO<sub>4</sub>, os valores máximos ocorreram aos 210 dias da aplicação (lixiviação equivalente a quatro vezes o volume total de poros). A aplicação de lama de cal diminuiu a concentração de Al trocável no solo. O crescimento em diâmetro das plantas e a produção de matéria seca aumentaram com o aumento da dose de lama de cal. Efeitos benéficos na nutrição mineral (P, K, Ca, B e Zn) do eucalipto foram obtidos com a aplicação de 4 e 6 t ha<sup>-1</sup> de lama de cal.*

*Termos de indexação: eucalipto, resíduo industrial, fertilidade do solo, nutrição mineral, sódio, reciclagem.*

## INTRODUCTION

Numerous studies conducted during the past three decades have demonstrated the potential benefits to forest and agricultural soils from the application of by-products, such as wood ash, lime by-products, sludge and other organic materials which are produced by the pulp and paper industry. These benefits include increased plant growth and yield, increased soil fertility, and improved soil moisture retention (Dolar et al., 1972; Simson et al., 1981; Naylor & Schmidt, 1986; Bockheim et al., 1988; Stape & Balloni, 1988; Bellamy et al., 1995). Adverse effects from land application of papermill by-products have been associated with high soluble salt levels, especially sodium (Na), and concern for groundwater contamination caused by potential leaching of nitrates and heavy metals (Harkin, 1982; Bockheim et al., 1988; Bellamy et al., 1995; Williams et al., 1996).

Various manufacturing lime by-products can be used to neutralize soil acidity. One of these, lime-sludge, results from a process designed to recover high cost chemicals from the digestion liquor used in the kraft paper process (Simson et al., 1981; Muse & Mitchell, 1995). Calcium oxide reacts with spent (used) liquor, yielding mainly CaCO<sub>3</sub>, NaOH, and Na<sub>2</sub>S. These materials are filtered and washed to recover NaOH and Na<sub>2</sub>S. The CaCO<sub>3</sub> can be

converted back to CaO in a lime-kiln. This step requires large amounts of fuel or gas, and has a high investment, since some pulpmill recovery systems accumulate a portion of lime-sludge due to the low capacity of the kiln burning lime-sludge to recover lime. Little information is available on the use of lime-sludge and the other lime by-products (dregs, grits) in Brazilian soils. At present, most of these lime by-products are under utilized as soil liming agents, but many of these could benefit forest production, by supplying essential plant nutrients low in forest soils.

The development of this study was motivated by the increasing interest in land application of lime-sludge from a paper pulp mill to acid soils of southeastern Brazil. Our objective was to determine the effects of papermill lime-sludge application on chemical composition of soil leachate and their effects on eucalypt growth and yield.

## MATERIALS AND METHODS

### Soil and lime-sludge

Soil samples were collected in a commercial eucalypt area in Mogi-Guaçu (SP), in January 1998, at two depths, 0-20 cm and 20-40 cm. The soil samples used for this study were identified and

classified previously as "Latossolo Vermelho-Amarelo distrófico" (LVAd). The papermill lime-sludge sample used was obtained from the Champion Co. located at Mogi-Guaçu (SP).

### Greenhouse study

Sixteen polyethylene plastic pots (30 cm in height by 24 cm in diameter), were filled with 15 kg of soil [7.5 kg of the subsurface layer (20-40 cm) placed at the bottom of the pot overlain by 7.5 kg of the surface layer (0-20 cm)]. The experimental design consisted of four lime-sludge rates (0, 773, 1.547, and 2.320 mg kg<sup>-1</sup>, or equivalent to control, 2, 4, and 6 t ha<sup>-1</sup>, respectively) and four soil leachate sampling times (2, 60, 120 and 210 days after lime-sludge application, or equivalent to 0.3, 1.0, 2.0, and 4.0 pore volumes of drainage, respectively). There were four replicates per treatment. Lime-sludge was applied on the surface and mixed in the first 3 cm of soil. All pots were wetted with distilled water several times a week to maintain soil moisture near to 60-70% of field capacity, except at leachate sampling time, when the soil was water-saturated to allow the collection of 250 ml of leachate solution. Leachate samples were placed in plastic bottles, and stored at 4°C. Leachate analysis were completed within 1 week after collection.

After the first 60 days, one young hybrid plant of *Eucalyptus grandis* x *E. urophylla* (about 90 days old) was planted in the center of each pot. The plants were harvested about 1 cm above the soil surface after 150 days, and measured for diameter growth (2 cm above the surface of the soil). Plant samples were dried for 48 h at 65°C in a convection oven, weighed for dry matter yield, and ground in a Wiley mill to pass a 1 mm screen, in preparation for elemental analysis (Malavolta et al., 1989).

Soil samples were collected at the end of the experiment of each treatment (surface and subsurface layers) to indicate changes in soil chemical characteristics and to determine if any unexpected element resulted from lime-sludge application.

### Analysis of soil, lime-sludge and plants

Particle-size distribution of the soil samples was determined by the pipette method (EMBRAPA, 1997). Soil chemical characteristics were determined by methods outlined in Raij et al. (1987): pH in CaCl<sub>2</sub> 0.01 mol L<sup>-1</sup>; organic matter by the colorimetric method; available P, and exchangeable Ca, Mg, and K were extracted by the cation-anion-exchange resin method, following P determined by the colorimetric (molybdenum blue) method, Ca and Mg determined by atomic absorption spectrophotometry (AAS), and K by flame emission spectrometry (FES); exchangeable Al was extracted with a 1 mol L<sup>-1</sup> KCl extract and determined by titrimetric method; exchangeable Na was extracted with a 0.1 mol L<sup>-1</sup> KCl extract and determined by FES; B was extracted

with hot-water and determined by the colorimetric method of azomethine-H; Cu, Fe, Mn, and Z were extracted by DTPA-TEA extracts and determined by AAS, and SO<sub>4</sub>-S was extracted with a 0.5 mol L<sup>-1</sup> NH<sub>4</sub>OAc extract in 0.25 mol L<sup>-1</sup> HOAc extract and determined by the turbidimetric method (Vitti, 1989).

The lime-sludge pH was measured in CaCl<sub>2</sub> 0.01 mol L<sup>-1</sup>, and organic matter by loss on ignition (Kiehl, 1985). Lime-sludge and plant subsamples were digested with nitric and perchloric acid and the concentrations of P, K, Ca, Mg, S, Na, B, Cu, Fe, Mn, and Zn were determined as above. Total N was determined by the micro-Kjeldahl method (Kiehl, 1985; Malavolta et al., 1989).

The leachate subsamples used for immediate pH measurements were also used for NO<sub>3</sub> and PO<sub>4</sub> analysis, determined by the micro-Kjeldahl and colorimetric methods, respectively, within 48 h after collection. Subsequently, Ca, Mg, K, Na, Cu, Fe, Zn, SO<sub>4</sub> and B concentrations were determined as above for soil analysis.

Sodium adsorption ratio (SAR) of the soil leachate was calculated by the formula proposed by the United States Salinity Laboratory Staff (1969).

### Statistical analysis

Data were submitted to analysis of variance and correlation analysis. The Tukey's test was used to compare mean values for each variable studied. Statistical Analysis System software was used to analyze the data (SAS INSTITUTE, 1990) and conclusions were assessed at a significance level of P < 0.05.

## RESULTS AND DISCUSSION

### Soil and lime-sludge characterization

Selected chemical characteristics, and particle-size distribution of soil are presented in table 1. It is an acidic clay soil, with medium organic matter amount, low nutrient concentrations (P, Ca, Mg and K), and a high aluminum concentration (Raij et al., 1987).

Total concentrations of various major and trace elements in the papermill lime-sludge for several cations and anions are presented in table 2. Lime-sludge had alkaline pH (9.7); low total organic matter (44 mg kg<sup>-1</sup>); high Ca, Na, S, Fe, and Mn concentrations (321, 39, 7, 2.6 g kg<sup>-1</sup>, and 415 mg kg<sup>-1</sup>, respectively); average Zn concentration (62 mg kg<sup>-1</sup>); low Mg concentration (2.5 g kg<sup>-1</sup>), and very low concentrations of other metals and other constituents (1.22 g kg<sup>-1</sup> P, 1.33 g kg<sup>-1</sup> K, and 3 mg kg<sup>-1</sup> Cu); with the exception of S and Cu, concentrations were within ranges previously reported (Simson et al., 1981; Stappe & Balloni, 1988; Benedetti, 1994; Muse & Mitchell, 1995). Individual lime-sludge particles are very fine

**Table 1. Chemical characteristics and particle-size distribution of the soil used in this study**

Soil depth	pH (CaCl <sub>2</sub> )	Organic matter	P resin	Exchangeable cations					Particle-size distribution		
				Al	Ca	Mg	K	Na	Sand	Silt	Clay
cm		g dm <sup>-3</sup>	mg dm <sup>-3</sup>	mmolc dm <sup>-3</sup>					g kg <sup>-1</sup>		
0-20	3.7	47	4	17	2	1	0.6	0.2	479	89	432
20-40	3.8	32	2	13	1	1	0.6	0.1	474	99	427

(< 0.3 mm  $\cong$  97%), and this material is classified as industrial calcitic lime (Bergamin et al., 1994). The calcium carbonate equivalency of this lime-sludge was about 81%. Taking into account the liming value of lime-sludge and the quantities produced by the pulp and paper industry (an average of 3,000 t per year was produced by each Brazilian mill), this material can be considered as under utilized as a soil liming amendment, due to the low number of land application programs in the southeast United States (Muse & Mitchell, 1995) and Brazil.

#### Leachate composition

The pH values in the soil leachate increased significantly with increasing lime-sludge rate and days after application (Table 3). The leachate pH in the 2 t ha<sup>-1</sup> treatment increased from 3.4 to 4.2 after 210 days of lime-sludge application; in the 4 t ha<sup>-1</sup> treatment increased from 3.5 to 4.8; and in the 6 t ha<sup>-1</sup> treatment increased from 3.5 to 5.2. Leachate pH values were positively correlated with leachate PO<sub>4</sub> concentration ( $r = 0.709$ ,  $P < 0.01$ ), leachate SO<sub>4</sub> concentration ( $r = 0.915$ ,  $P < 0.01$ ), and leachate Na concentration ( $r = 0.925$ ,  $P < 0.01$ ) and negatively correlated with leachate NO<sub>3</sub> concentration ( $r = -0.511$ ,  $P < 0.05$ ) and leachate Mg concentration ( $r = -0.591$ ,  $P < 0.05$ ). These increases in the leachate pH values were due to the presence of carbonates, oxides, hydroxides, and other alkaline compounds (40 g kg<sup>-1</sup> of Na, Table 2) in the lime-sludge chemical composition (Simson et al., 1981; Muse & Mitchell, 1995). At the end of the experiment (210 days), differences in leachate pH values between control and lime-sludge treatments were still significant, but no difference was observed between 4 t ha<sup>-1</sup> treatment and 6 t ha<sup>-1</sup> treatment.

Nitrate is usually the major inorganic form of N, as well as the dominant anion in the water percolated through most of the soil (White, 1997). Leachate NO<sub>3</sub> concentration in the control ranged from 62 to 171 mg L<sup>-1</sup>, while in the lime-sludge treatments ranged from 39 to 199 mg L<sup>-1</sup> (Table 3). Concentrations of NO<sub>3</sub> in the soil leachate decreased with increasing lime-sludge rate (ranging from 125 to 88 mg L<sup>-1</sup>, respectively, for control and 6 t ha<sup>-1</sup>) and with days after application. The maximum NO<sub>3</sub>

concentrations in the soil leachate occurred during the first 60 days after lime-sludge application (leaching equivalent to 1 pore volume), prior to eucalypt planting, and did not differ among application rates. Lowest concentrations of NO<sub>3</sub> occurred during the last sampling (leaching equivalent to 4 pore volumes), and except for the control, all lime-sludge treatments did not exceed drinking-water standards for human consumption of 45 mg L<sup>-1</sup> of NO<sub>3</sub> (i.e., 10 mg L<sup>-1</sup> of NO<sub>3</sub> expressed as N), established by the United States Environmental Protection Agency (USEPA, 1977). Probably, plant uptake was sufficient to decrease the leachate NO<sub>3</sub> concentration in the lime-sludge treatments. Nitrate concentration gradually declined as the readily available organic N was consumed and NO<sub>3</sub> was removed by leaching and by plant uptake of NO<sub>3</sub>, indirectly by plant uptake of NH<sub>4</sub> at the expense of nitrification, or by a combination of both mechanisms (Novais et al., 1990; White, 1997). In contrast to phosphate and the cationic plant nutrients, which are mainly involved in physical-chemical processes, the mobility of N in the soil depends largely on biological processes (Mengel & Kirkby, 1982).

According to Lindsay (1979), the predominant solution phosphate species at the pH range of 3.5 to 7.0 is H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Orthophosphate concentration in the soil leachate remained near detection limits (0.03 mg PO<sub>4</sub> L<sup>-1</sup>) during the first 120 days following lime-sludge application. The last sampling showed PO<sub>4</sub> concentrations ranging from below the detection limits in the control to about 600 mg L<sup>-1</sup> in the lime-sludge treatments. Soil pH, clay, sesquioxide content and exchangeable aluminum all influence P availability. In comparison with adsorbed PO<sub>4</sub>, the amount of PO<sub>4</sub> present in soil solution at any given time is very low, due to the low solubility of P compounds in the soil, and to the high P-adsorption capacity of soil particles, a process called phosphate 'fixation' (Raij, 1991). In this study, the increase of phosphate in the last leachate can be attributed to leachate pH rise rather than to lime-sludge additions by treatments. However, the phosphate in the solution is actively absorbed by plants and readily reacts with Al, Fe, and Mn in acidic soils, which minimizes the potential for P mobility.



**Table 2. Chemical characteristics, C/N ratio, and application rate of the lime-sludge**

Lime-sludge	Concentration or application rate											pH (CaCl <sub>2</sub> )	C/N ratio
	N	P	S	Ca	Mg	K	Na	Fe	Cu	Mn	Zn		
Conc.	0.70	1.22	7.10	320.9	2.50	1.33	38.9	2.62	3.00	415	62.0	9.7	36
t ha <sup>-1</sup>	0.67	1.17	6.78	306.5	2.38	1.27	37.2	2.49	2.87	396	59.2		

**Table 3. Effect of lime-sludge rates and sampling times on soil leachate composition**

Lime-sludge rate	Sampling time			
	2 days	60 days	120 days	210 days
	<b>pH</b>			
Control	3.30 bB	3.15 cB	3.70 cA	3.75 bA
2 t ha <sup>-1</sup>	3.43 abC	3.43 bcC	3.93 cB	4.15 bA
4 t ha <sup>-1</sup>	3.50 aC	3.68 abC	4.23 bB	4.75 aA
6 t ha <sup>-1</sup>	3.50 aD	3.95 aC	4.68 aB	5.15 aA
	<b>NO<sub>3</sub>, mg L<sup>-1</sup></b>			
Control	31.5 abA	34.1 aA	27.1 abA	20.1 aA
2 t ha <sup>-1</sup>	33.3 aA	35.0 aA	14.0 cB	9.7 aB
4 t ha <sup>-1</sup>	28.0 abA	32.8 aA	34.1 aA	8.8 aB
6 t ha <sup>-1</sup>	21.0 bB	31.9 aA	16.6 bcBC	10.1 aC
	<b>SO<sub>4</sub>, mg L<sup>-1</sup></b>			
Control	0.38 aA	0.13 aA	0.75 bA	0.26 bA
2 t ha <sup>-1</sup>	0.26 aB	0.03 aB	1.13 bAB	2.05 bA
4 t ha <sup>-1</sup>	1.88 aB	1.38 aB	6.75 abB	17.13 bA
6 t ha <sup>-1</sup>	1.50 aB	2.75 aB	7.03 aB	27.63 aA
	<b>Ca, mg L<sup>-1</sup></b>			
Control	4.0	6.8	1.2	1.8
2 t ha <sup>-1</sup>	3.8	3.3	0.8	0.8
4 t ha <sup>-1</sup>	2.5	3.5	1.0	1.0
6 t ha <sup>-1</sup>	2.8	3.5	1.0	0.8
	<b>K, mg L<sup>-1</sup></b>			
Control	1.48	2.25	1.20	1.08
2 t ha <sup>-1</sup>	1.48	1.60	0.28	0.30
4 t ha <sup>-1</sup>	0.98	1.30	0.20	0.30
6 t ha <sup>-1</sup>	0.98	0.95	0.10	0.20
	<b>Na, mg L<sup>-1</sup></b>			
Control	1.68	2.83	0.50	0.01
2 t ha <sup>-1</sup>	2.15	2.68	0.50	0.01
4 t ha <sup>-1</sup>	2.15	3.30	0.50	0.01
6 t ha <sup>-1</sup>	1.85	2.35	0.50	0.01
	<b>Mg, mg L<sup>-1</sup></b>			
Control	2.09 bA	1.44 bB	0.11 bC	0.30 bC
2 t ha <sup>-1</sup>	14.94 abA	14.88 bA	4.36 bB	2.45 bB
4 t ha <sup>-1</sup>	24.44 aAB	35.75 aA	27.88 aAB	16.75 aB
6 t ha <sup>-1</sup>	21.75 aB	37.75 aA	33.13 aA	25.25 aAB
	<b>SAR</b>			
Control	0.32 bA	0.17 bB	0.03 bC	0.07 bC
2 t ha <sup>-1</sup>	2.40 abA	2.45 bA	1.43 bAB	0.87 bB
4 t ha <sup>-1</sup>	4.69 aB	6.78 aAB	9.43 aA	5.31 abB
6 t ha <sup>-1</sup>	4.00 abB	6.88 aB	11.95 aA	12.38 aA

Different small letters within rows and capital letters within a columns, indicate means that are significantly different by Tukey test at the 5% probability level. Absence of letter in rows or columns indicates there was no significant difference by F test.

Leachate  $\text{SO}_4$  concentrations remained low for the first 60 days after lime-sludge application, ranging from below the detection limits ( $0.03 \text{ mg L}^{-1}$ ) to  $16.5 \text{ mg L}^{-1}$ , and there were no significant differences in concentrations among any of the treatments (Table 3). After this time,  $\text{SO}_4$  concentrations in the lime-sludge treatments began to increase and continued to increase to maximum concentrations at 210 days, while concentrations in the control remained relatively constant. According to Parfitt (1978), losses of sulfate by leaching are more significant in soils that are low in hydrous oxides of iron and aluminum, particularly in A horizons. Sulfate is adsorbed by soils less strongly than phosphate. The order of adsorption for different anions is phosphate > molybdate > sulfate > chloride > nitrate.

Calcium, Mg, and K in the soil leachate behaved similarly (Table 3). Highest concentrations of Ca, Mg, and K occurred during the first 60 days after lime-sludge application (leaching equivalent to 1 pore volume), before eucalypt planting. Calcium and K concentrations did not change significantly for any lime-sludge application rate (Ca varied from below the detection limits to  $8.0 \text{ mg L}^{-1}$ ; and K from below the detection limits to  $5.1 \text{ mg L}^{-1}$ ), while Mg was reduced significantly in the lime-sludge treatments in comparison with control (Mg varied from 0.10 to  $2.80 \text{ mg L}^{-1}$ ). Calcium, Mg, and K are held mainly as exchangeable cations, the supply of which buffers the soil solution against depletion (White, 1997). Potassium leaching rates are relatively high in kaolinitic soils, because this clay mineral does not adsorb K selectively. Magnesium is only weakly adsorbed by kaolinitic clay mineral and, for this reason, it is particularly susceptible to leaching. Calcium is also not strongly adsorbed by inorganic colloids, and it is often the dominant cation in the water percolated through most of the soil (Tisdale et al., 1985). Low levels of Ca in the soil leachate can be associated with the low solubility of calcium carbonates present in the lime-sludge, by the soil retention of this cation, and by eucalypt removal.

Sodium concentrations in the soil leachate increased significantly with increasing lime-sludge application rates (Table 3). Changes in the concentrations of Na were similar in the control and in the  $2 \text{ t ha}^{-1}$  treatment, while other patterns were evident in the treatments with 4 and  $6 \text{ t ha}^{-1}$ . Lowest concentrations of Na occurred at 210 days, except for the  $6 \text{ t ha}^{-1}$  treatment. This suggests that most soluble Na had been removed with leaching equivalent to 4 pore volumes. Sodium is only weakly adsorbed by clay minerals and, for this reason, it is particularly susceptible to leaching. In well-drained soils, if higher concentrations of Na occur, this cation is leached more rapidly, while if lower concentrations occur, its rate of leaching is diminished (Lindsay, 1979).

The calculated SAR for the  $2 \text{ t ha}^{-1}$  lime-sludge treatment was below the limit of 5.0 (UNITED

STATES SALINITY LABORATORY STAFF, 1969) during the experiment, indicating that sufficient exchangeable Ca and Mg were present to offset negative effects due to exchangeable Na. On the other hand, the SAR of the leachate increases from below the limit to 5.0 at 2 days to 9.4 and 12.4, respectively, to  $4 \text{ t ha}^{-1}$  treatment at 120 days and  $6 \text{ t ha}^{-1}$  at 210 days, indicating that adverse changes in the soil structure can occur. However, increases of Na amounts had no effect on soil permeability (visual observation of soil drainage) and root growth.

Boron concentrations were not affected by lime-sludge application, but decreased significantly during the experimental time. Concentrations of Cu, Fe, Mn, and Zn in the soil leachate were very low or not detectable ( $\leq 0.001 \text{ mg L}^{-1}$ ) in all the treatments. The absence of micronutrients in the soil leachates was not particularly surprising. According to Sposito et al. (1982), the concentration of free micronutrients in the soil solution is normally very low, many times below the detection limits. Because of precipitation and strong retention by mineral and organic surfaces, micronutrient losses by leaching are very low, except for B, and Fe and Mn in some gleyed soils (White, 1997).

Nitrate was the major anion in the soil leachate of all treatments during the first 120 days, but in the last sampling in the lime-sludge treatments,  $\text{PO}_4$  had become the dominant anion. Generally in acid soils, phosphate in the soil solution is a negligible component of the anion sum, because it forms insoluble precipitates with Fe and Al. Furthermore, phosphate is required by plants in high amounts, which reduces markedly the potential for P leaching. In the control, Ca was the dominant cation in the soil leachate, while in the lime-sludge treatments, Na was the dominant cation.

### Changes in the soil chemical characteristics

Because the lime-sludge was surface-applied with incorporation only at the first 3 cm of soil, rate did not significantly affect soil pH ( $\text{CaCl}_2$ ) at depths of 5-15 and 15-30 cm (Table 4). On the other hand, the leachate pH values in the lime-sludge treatments were still increasing, notably in the 4 and  $6 \text{ t ha}^{-1}$  treatments, at the end of the experiment (Table 3). This demonstrates the role of soil buffering capacity in controlling leachate pH and soil pH.

Exchangeable Al concentration in the soil was significantly reduced by the application of  $6 \text{ t ha}^{-1}$  (Table 4), resulting in precipitation of Al into relatively unavailable compounds. According to White (1997), most buffering in the pH ( $\text{H}_2\text{O}$ ) 4 to 5.5 range is due to exchangeable  $\text{Al}^{3+}$ , and lime-sludge additions react readily with Al. The pH ( $\text{CaCl}_2$ ) value is generally 0.6 to 0.8 units lower than pH ( $\text{H}_2\text{O}$ ) at the same soil/liquid ratio.

Lime-sludge increased the concentration of  $\text{SO}_4\text{-S}$  in the soil from the 5-15 cm depth from  $17.3 \text{ mg dm}^{-3}$

**Table 4. Effect of lime-sludge rates on the soil chemical characteristics at two depths**

Soil chemical characteristic	Lime-sludge rate			
	Control	2 t ha <sup>-1</sup>	4 t ha <sup>-1</sup>	6 t ha <sup>-1</sup>
<b>Surface layer, 5-15 cm</b>				
pH (CaCl <sub>2</sub> )	3.70	3.75	3.80	4.05
Organic matter (g dm <sup>-3</sup> )	39.5	34.3	33.0	34.5
P resin (mg dm <sup>-3</sup> )	4.0	4.0	3.3	3.8
SO <sub>4</sub> -S (mg dm <sup>-3</sup> )	17.3 c	23.3 b	28.3 a	30.5 a
Al (mmol <sub>c</sub> dm <sup>-3</sup> )	18.5 a	17.5 a	16.8 a	12.5 b
Ca (mmol <sub>c</sub> dm <sup>-3</sup> )	1.25	1.00	3.75	10.25
K (mmol <sub>c</sub> dm <sup>-3</sup> )	0.25	0.20	0.25	0.40
Na (mmol <sub>c</sub> dm <sup>-3</sup> )	0.23 b	0.52 b	1.04 a	1.51 a
B (mg dm <sup>-3</sup> )	0.31	0.31	0.32	0.27
Cu (mg dm <sup>-3</sup> )	0.90	0.75	0.78	0.90
Fe (mg dm <sup>-3</sup> )	296	292	254	232
Mn (mg dm <sup>-3</sup> )	1.45	0.93	0.98	1.10
Zn (mg dm <sup>-3</sup> )	0.83	0.83	0.60	0.73
<b>Subsurface layer, 15-30 cm</b>				
pH (CaCl <sub>2</sub> )	3.80	3.85	3.83	3.83
Organic matter (g dm <sup>-3</sup> )	27.0	27.0	25.5	26.8
P resin (mg dm <sup>-3</sup> )	3.3 a	2.8 a	3.0 a	2.0 b
SO <sub>4</sub> -S (mg dm <sup>-3</sup> )	25.0 b	30.5 b	30.8 b	41.3 a
Al (mmol <sub>c</sub> dm <sup>-3</sup> )	16.3 a	16.5 a	15.5 ab	14.0 b
Ca (mmol <sub>c</sub> dm <sup>-3</sup> )	1.00	1.00	1.75	1.50
K (mmol <sub>c</sub> dm <sup>-3</sup> )	0.30	0.15	0.20	0.20
Na (mmol <sub>c</sub> dm <sup>-3</sup> )	0.21 c	0.45 c	1.32 b	1.80 a
B (mg dm <sup>-3</sup> )	0.26	0.26	0.27	0.23
Cu (mg dm <sup>-3</sup> )	0.70	0.60	0.70	0.70
Fe (mg dm <sup>-3</sup> )	137	109	116	89
Mn (mg dm <sup>-3</sup> )	0.80	0.68	1.10	0.75
Zn (mg dm <sup>-3</sup> )	0.50	0.40	0.43	0.55

Different letters within rows indicate means that are significantly different by the Tukey test at 5%. Absence of letter in rows indicates no significant difference by the F test.

in the control to 30.5 mg dm<sup>-3</sup> at 6 t ha<sup>-1</sup>, and from the 15-30 cm depth from 25 mg dm<sup>-3</sup> in the control to 41.3 mg dm<sup>-3</sup> at 6 t ha<sup>-1</sup> (Table 4), due to the possible presence of Na<sub>2</sub>S in this by-product (Simson et al., 1981).

Available phosphorus, exchangeable Ca, Mg, and K, and trace metals did not change significantly for any lime-sludge application rate (Table 4). The variabilities of the Ca and K concentrations in the lime-sludge treatments were high and no consistent trends were apparent, except for Ca in the 5-15 cm depth which was increased eight-fold by the application of 6 t ha<sup>-1</sup>. This retention of Ca in the surface layer was due to an increase of cation exchange capacity arising out of an increase in pH; negative charge on surfaces of variable charge minerals is increased by an increase in pH (Uehara & Gillman, 1981).

Soil Na concentrations in the surface (5-15 cm) and in the subsurface layer (15-30 cm) were increased six-fold and eight-fold, respectively, by the application of 6 t ha<sup>-1</sup> of lime-sludge at 210 days (Table 4). According to Tisdale et al. (1985), Na is not of immediate concern unless it occurs in excess of 10 to 20% of soil cation exchange capacity. High Ca in papermill lime by-products will replace Na on soil exchange sites, thus allowing Na to be leached from the soil and preventing Na accumulation in soils of humid regions.

Some studies have shown that application of lime-sludge to forested sites tended to increase soil pH value and Ca concentration and decrease exchangeable Al concentration (Stape & Balloni, 1988; Benedetti, 1994), but Na concentration has not been investigated. Utilization as a forest soil amendment would be a beneficial alternative to disposal.

### Eucalypt response

Plant diameter growth and dry matter yield increased significantly with increasing lime-sludge rate (Table 5). Plots amended with 2 or 6 t ha<sup>-1</sup> of lime-sludge resulted in 43 to 65% more yield than control, respectively. These results are consistent with the data of Stape & Balloni (1988), Benedetti (1994), and others presented by Guerrini & Villas-Bôas (1996). Plant yield was positively correlated with leachate pH ( $r = 0.758$ ,  $P < 0.01$ ), leachate P concentration ( $r = 0.876$ ,  $P < 0.01$ ), leachate SO<sub>4</sub> concentration ( $r = 0.758$ ,  $P < 0.01$ ), and leachate Na concentration ( $r = 0.651$ ,  $P < 0.01$ ).

Beneficial effects on eucalypt mineral nutrition were obtained with the application of lime-sludge (Table 5). It was observed that amounts of P, K, Ca, Na, B, and Zn in the eucalypt dry matter increased with increasing lime-sludge application rate. The amounts of Cu and Mn in the eucalypt plants decreased in all the lime-sludge treatments related to the control. Addition of lime-sludge did not change Mg uptake. However, induced Mg deficiency on field crops due to the use of papermill lime-sludge should be a problem if soil exchangeable Mg is in an inadequate range (Simson et al., 1981; Guerrini & Villas-Bôas, 1996).

Lime-sludge contained relatively high concentrations of Na (39 mg kg<sup>-1</sup>, Table 2), but the eucalypt plants did not exhibit typical salt toxicity symptoms (stunted growth, necrosis of leaf tips) with the high lime-sludge rate (6 t ha<sup>-1</sup>). There is evidence

that exchangeable Na can partially substitute exchangeable K, when K in soil is low (Tisdale et al., 1985).

A subject of considerable concern when using papermill lime-sludge is the fate of potentially toxic Na and trace metal concentrations. Other concerns include the potential for metals leaching through the soil and polluting groundwater. However, our results indicate these concerns are unfounded. The fact that yields significantly increased with lime-sludge applications indicates that these papermill lime by-products can be effective at increasing soil solution pH, reducing Al toxicity, and providing supplemental quantities of plant nutrients. The results of this study also suggest that lime-sludge which have Na concentration of about 40 mg kg<sup>-1</sup> or less can possibly be applied ( $\leq 6$  t ha<sup>-1</sup>) to soils without immediate detrimental effects on eucalypt growth and yield. Because Na can become toxic to plant growth, a detailed evaluation of their availability in lime-sludge amended soils must be part of further studies of this type.

### CONCLUSIONS

1. Soils amended with lime-sludge showed increases in soil leachate pH, PO<sub>4</sub>, SO<sub>4</sub>, and Na concentrations and decreases in NO<sub>3</sub> and Mg concentrations, 210 days after application. Calcium, K, B, Cu, Fe, and Zn leachate did not change significantly for any lime-sludge application rate.

**Table 5. Effect of lime-sludge rate on eucalypt diameter growth, dry matter yield and nutrient uptake**

Plant parameters	Lime-sludge rate			
	Control	2 t ha <sup>-1</sup>	4 t ha <sup>-1</sup>	6 t ha <sup>-1</sup>
Diameter (mm)	7.1 c	8.5 b	9.2 ab	10.0 a
DM yield (g/pot)	21.2 b	30.3 a	32.0 a	35.0 a
N (mg/pot)	315 ab	284 b	356 a	331 ab
P (mg/pot)	19 c	24 b	32 a	34 a
K (mg/pot)	74 c	71 c	116 b	146 a
Ca (mg/pot)	173 b	481 a	559 a	557 a
Mg (mg/pot)	45	45	47	46
S (mg/pot)	28 b	28 b	33 a	31 ab
Na (mg/pot)	9 c	82 b	92 ab	101 a
B (µg/pot)	724 b	833 b	1050 a	1097 a
Cu (µg/pot)	168 a	140 b	76 d	109 c
Fe (µg/pot)	1.522 c	2.776 a	2.098 b	1.711 c
Mn (µg/pot)	3.320 a	1.816 b	1.898 b	1.890 b
Zn (µg/pot)	605 b	678 b	927 a	852 a

Different letters within rows indicate means that are significantly different by the Tukey test at 5%. Absence of letters in rows indicates no significant difference by the F test.



2. Highest NO<sub>3</sub>, Ca, Mg, K, and Na concentrations in the soil leachate occurred at 60 days after lime-sludge application (leaching equivalent to 1 pore volume), but for pH and SO<sub>4</sub>, the maximum occurred on last sampling (leaching equivalent to 4 pore volumes).

3. Lime-sludge application decreased exchangeable Al in the soil, and increased exchangeable Na and SO<sub>4</sub>-S concentrations in the soil.

4. At a high rate (6 t ha<sup>-1</sup>), lime-sludge increased eucalypt yield 65%, markedly decreased the uptake of Cu and Mn, and increased the uptake of P, K, Ca, B, and Zn. There was no evidence of Na phytotoxicity in eucalypts as a result of lime-sludge additions.

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