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EFECTO DEL CALCIO EN LA DELIGNIFICACIÓN DE MADERA PARA PULPA KRAFT DE *Eucalyptus dunnii*, *Eucalyptus globulus Y Eucalyptus grandis*.

CALCIUM EFFECT ON THE KRAFT PULP DELIGNIFICATION OF *Eucalyptus dunnii*, *Eucalyptus globulus* AND *Eucalyptus grandis*.

Autor: Ing. Agr. Ismael Fariña.

Director de Tesis/Supervisor: MSc. Kimmo Ruohoniemi

Advisors: Lic. Eng. Ulla Jansson/MSc.Chem. Eng. María Noel Cabrera

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Ismael Fariña
Tesis de Maestría en Ingeniería de Celulosa y Papel
Facultad de Ingeniería
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RESUMEN

Estudios previos indican que en *Populus tremula* y *Betula pendula* el proceso de cocción puede ser afectado por el contenido de calcio. Se sugiere que los iones de calcio disminuyen la tasa de deslignificación en la cocción Kraft debido a la formación de interacciones calcio-lignina, las cuales llevan a la disminución de la solubilidad de la lignina durante el proceso. En *Eucalyptus globulus*, la formación de diferentes enlaces entre el calcio y sustancias liberadas por esta especie durante el proceso de deslignificación Kraft es expuesto como la explicación para la ausencia o reducción del efecto calcio. El género *Eucalyptus* en Uruguay es considerado un gran consumidor de nutrientes del suelo debido a su alta tasa de crecimiento, aunque existen apreciables variaciones en el contenido de nutrientes entre diferentes especies de *Eucalyptus* y dentro de la misma especie. Este trabajo estudia el efecto del calcio en la deslignificación Kraft en cinco *Eucalyptus dunnii*, cuatro *Eucalyptus globulus* y tres *Eucalyptus grandis* de diferentes edades, tipos de suelos y áreas geográficas del Uruguay, y determina el contenido de calcio y fósforo en madera, pulpa y licor negro. Los resultados sugieren que hay una influencia perjudicial del calcio en la performance del proceso Kraft en el género *Eucalyptus* desde que contenidos de calcio en madera más altos dan rendimientos más bajos a número de Kappa constante, y números de Kappa más altos y grados de blanco más bajos en condiciones de cocción constantes. Fueron encontradas importantes diferencias en el contenido de calcio en madera entre las especies, *E. dunnii* presentó valores más altos y rango más amplio que *E. globulus* y *E. grandis*, por lo tanto el efecto perjudicial del calcio en el proceso Kraft es observado más claramente en las muestras de *E. dunnii*. Por otra parte tres muestras de *Eucalyptus* fueron elegidas para realizar una extracción ácida previa al proceso Kraft, en orden de comparar el comportamiento en la cocción con y sin extracción de metales, estos resultados indicaron que no parece ser este procedimiento una manera adecuada para remover el calcio de la madera de *Eucalyptus*, al menos para las muestras utilizadas en este trabajo y especialmente en los casos con alto contenido de calcio en madera.

ABSTRACT

Previous studies indicate that in *Populus tremula* and *Betula pendula* the cooking process could be affected by calcium content. It is suggested that calcium ions decrease Kraft delignification rate by formation of calcium-lignin interaction, which lead to decrease solubility of lignin during the process. In *Eucalyptus globulus*, formation of different bindings between calcium and substances released from this species during Kraft cooking delignification is exposed as explanation for the absence or reduction of the calcium effect. The *Eucalyptus* genus in Uruguay is considered a heavy consumer of soil nutrients due to its high growing rate, even though appreciable variations in nutrient content exists between different *Eucalyptus* species and within the same species. This work studies the calcium effect on Kraft delignification in five *Eucalyptus dunnii*, four *Eucalyptus globulus* and three *Eucalyptus grandis* of different age, soil type and geographical Uruguayan areas, and determines the content of calcium and phosphorus in wood, pulp and black liquor. Results suggest that there is a detrimental influence of calcium on the performance of the Kraft process in the *Eucalyptus* genus since higher wood calcium content gives lower yield at constant Kappa number, and higher Kappa number and lower ISO brightness at constant cooking conditions. Important differences among species were found in wood calcium content, *E. dunnii* presented higher values and a wider range than *E. globulus* and *E. grandis*, so the calcium detrimental effect in Kraft process is clearer observed in *E. dunnii* samples. Moreover three *Eucalyptus* samples were chosen to perform an acid leaching previous Kraft process, in order to compare the cooking behavior with and without metals extraction, these results indicate that not appear to be this procedure a suitable way to remove calcium from *Eucalyptus* wood, at least for samples used in this work and especially in cases with high wood calcium content.

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LITERATURE REVIEW

The objective of this work is to study the effect of calcium on the Kraft delignification of *Eucalyptus grandis*, *Eucalyptus globulus* and *Eucalyptus dunnii* and determine the content of calcium and phosphorus in the wood, in the resulting pulp and black liquor. For this reason the literature review addresses the item nutrients content in *Eucalyptus sp*. (with emphasis on commercial logs as they are the ones that will enter to mill) and amount of nutrients in forest soils, mentioning only laterally aspects related to the dynamics of nutrients in soils and other agronomic factors.

1. NUTRIENT CONTENT IN EUCALYPTUS IN URUGUAY AND THE REGION AND ITS DETERMINING FACTORS

1.1. GENERAL CONSIDERATIONS

Vegetal biomass is formed almost 95% of its dry weight of carbon, oxygen and hydrogen, who are found in nature in the form of carbon dioxide and water. Since these elements exist in abundance, are not usually included in nutrient cycle's studies. There are a number of essential elements called macronutrients (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur), who are those that can further limit the growth of forests (and in which will focus in this work). Finally there are the micronutrients (manganese, iron, chlorine, copper, zinc, boron, molybdenum) that are also essential, but because they are needed in very small quantities only in special conditions may limit the growth of trees (Binkley, 1993).

The Eucalyptus genus because of its high growth rate is presented as great soil nutrients demanding (Camara *et al*., 2000).
Survival and growth of this tree genus in soils with poor nutrient content is due to the mechanisms that these trees have developed through the strong selection pressure to which they have been subjected (Beadle cited by Grove *et al.*, 1996). Improve the absorption, utilization efficiency and nutrients retention within the tree is essential for biomass growth in low fertility soils. One of the most important mechanisms to improve nutrients absorption is the symbiotic association between eucalypts fine roots and ectomycorrhizal fungi (especially for nitrogen and phosphorus) (Grove *et al*., 1996) (Pallardy, 2008).

Relatively mobile nutrients soil absorption (e.g. NO_3-, SO_4^{-2}, Ca^{+2}, Mg^{+2}) who can move towards the roots by mass flow is limited by the characteristic roots absorptive capacity, while less mobile nutrients (e.g. $H_2PO_4^-$, NH^{+4}, Zn^{+2}, Cu^{+2}) which react with minerals and soil organic matter are limited in their absorption by diffusion to the root surface (Nye and Tinker cited by Grove *et al*., 1996).

The nutrients absorption by eucalyptus trees is essential to their development and reproduction. Most metabolic reactions are not possible without mineral elements presence. Deficiency of important nutrients for tree metabolism determine according level its weakening (and therefore susceptibility increase to plagues and diseases), poor growth, not reaching sexual maturity or even death (Foelkel, 2005). Among many roles of plants nutrients are constituents of plants tissues, catalysts in various reactions, osmotic regulators, constituents of buffer systems, and regulators of membrane permeability (Pallardy, 2008).

The nutrient content in any forestry plantation in general and in Eucalyptus genus in particular depends on several factors, among which are: species, genotype, climatic conditions and plantation silvicultural management (Poggiani, 1985) (Foelkel, 2005) (Pallardy, 2008), as well as site quality (fertility, porosity, soil moisture, etc.), plantation age, nutrient distribution in the different biomass compartments and nutrient distribution along the stem (Varela, 2009).

1.2. SPECIES

Regarding the incidence of species, in a study conducted by Freddo *et al*. (1999) in several species of eucalyptus destined to pulp production in the region of Guaíba (Brazil), it was showed that *Eucalyptus grandis* had larger growth and smaller nutrient tenor than *Eucalyptus globulus* and *Eucalyptus dunnii*, so that the latter introduce greater amounts of non-process elements in the mill and thus larger industrial problems. The author states that in a pulp mill with a production of 1000 tons per day would enter into the wood, depending on the species, the following amounts of non process elements: 6.0 / 4.9 / 3.8 tons per day in *Eucalyptus dunnii, Eucalyptus globulus and Eucalyptus grandis* respectively. Foelkel (2005) agrees with the fact that for genetic reasons *Eucalyptus globulus* and *Eucalyptus dunnii* concentrates more minerals than *Eucalyptus grandis*.

Table 1 shows the nutrient wood content in different eucalyptus species in a management of non process elements study conducted by Salmenoja *et al*. (2009).

Table 1. Nutrient wood content (mg/kgds) in different *Eucalyptus* sp. Source: Salmenoja *et al*. (2009).

	Different *Eucalyptus* sp.					
Nutrient	A	B	C	D	E	F
Na	82	200	160	240	170	110
K	900	500	540	640	410	610
Ca	850	510	1900	1000	1000	2700
Fe	30	48	32	18	22	39
Mg	270	110	310	210	76	790
Mn	38	56	71	53	27	68
Cl	460	430	300	340	240	440
Si	15	8.7	7.9	8.2	5.5	4.7
P	88	270	45	51	34	87

In Table 1 can be seen the considerable nutrient content variations that exist between different eucalyptus species. The most remarkable variations in this study are found in calcium content (from 510 mg/kg up to 2700 mg/kg in dry wood) (Salmenoja *et al*., 2009).

1.3. PLANTATION AGE

As will be seen when discussing the nutrient distribution in the different biomass compartments, minerals are found in the tree in amounts that vary considerably depending on the part of the tree under study. Therefore, must take into account as is changing the relative importance of each compartment (and thus the nutrient content) in relation to the total tree biomass during its growth.

During the juvenile phase an important part of carbohydrates resulting from photosynthesis will be destined to biomass tree canopy formation. Once the tree canopy begin to compete with each other, will gradually change the flow favoring the production of stem biomass. This explains the fact that tree canopy accumulate on average about 25% of nutrients in adult plantations while in young plantations represent more than 50% (Freitas *et al*., 2004).

With older age the biomass proportion in the stem will be larger at the expense of the branches, leaves, bark and roots proportion. Between 2 and 3 years old, the stem wood represented between 50 and 55% of the total biomass, at 7 years between 70 and 75% and 9 years nearly 80% (Foelkel, 2005). Laclau *et al*. (2000) in a clonal eucalyptus plantations study while observing the same behavior differs in the ages at which changes in the proportions of each compartment are performed, finding stabilization already at 4 years of age. The wood proportion in total aboveground biomass increase from 35% in the first year to 80% in the fourth year, showing a simultaneous decrease in the proportion of leaf area and branches in the same period. Anyway, the author indicates that at the age of seven years has not yet reached the point at which the increase in biomass starts to decrease.

Although tree nutrition is important throughout development, the nutritional demands are larger from planting to canopy closure, because at this early stage of growth is predominantly the chlorophyll-producing tissues formation (Gómez, 2006) (Grove *et al*., 1996). Despite the decline in nutritional demand that some authors report from that point, the empirical evidence shows that nutritionally deficient sites in the early development stages, will remain so at later stages (Fisher and Binkley, cited by Gómez, 2006).

Bellote *et al*. (1980) conducted a study in Sao Paulo (Brazil) in *Eucalyptus grandis* on the evolution of the nitrogen, phosphorus, potassium, calcium, magnesium and sulfur content as function of age (1 to 7 years). Table 2 shows the nutrient content data for each year as a percentage of totals extracted at the end of 7 years.

Table 2. Percentage of nutrients at different ages in *E. grandis* plantation. Source: Bellote *et al*, 1980.

	Age (years) / % of the total extracted nutrient						
Nutrient	1	2	3	4	5	6	7
N	21.6	34.6	47.7	60.8	73.9	86.9	100
P	21.8	28.1	46.6	69.7	90	99.9	100
K	13.4	27.8	42.2	56.7	85.6	85.6	100
Ca	8.2	15.9	32.7	49.5	83.2	83.2	100
Mg	1.1	18.7	36.2	53.8	89	89	100
S	9.9	24.9	39.9	54.9	85	85	100

All nutrients showed a maximum accumulation at seven years old (increasing trend with increasing age) with the exception of phosphorus, which at six years had already accumulated 99.9% of the total extracted.
By the fourth year more than 50% of the total of all nutrients have been removed except calcium, with an accumulation at that age of 49.5%.

Brañas *et al*. (2000) studied different *Eucalyptus globulus* plantations from 6 to 18 years of age. The author notes that although differences in nutrient content between young and old plantations were small, it was observed a tendency to get larger nitrogen and smaller calcium and magnesium concentrations in young plants.

Poggiani (1985) from nutrient dynamics point of view in *Eucalyptus saligna* in São Paulo state (Brazil) recommended the implementation of longer rotations, thus allowing better tree and ecosystem nutrient utilization.
Fernandez (2002) agrees with this idea, stating that nutrient utilization efficiency increases with increasing rotation age (greater biomass produced per unit of nutrient). In the same direction Camara *et al*. (2000) and Pallardy (2008) consider that in a given period, the shorter time existing between rotations, the greater nutrients extraction from forest biomass.

Studying *Eucalyptus grandis* nutritional behavior in Entre Rios province (Argentina), Goya *et al*. (1997) also considers that harvest nutritional cost decreases when plantation age increase (especially for nitrogen and phosphorus that are found in high concentrations in leaves, which have a larger biomass proportion at an early age), however indicates that calcium behaves contrary to other nutrient, increasing accumulation with increasing age of the tree. This calcium behavior is verified by Woodwell cited by Grove *et al*. (1996).

1.4. NUTRIENT CONTENT AND DISTRIBUTION IN DIFFERENT BIOMASS COMPARTMENTS

The nutrient amount in forest biomass depends on several factors as already mentioned. The differences in nutrient distribution in biomass compartments respond to physiological function and mobility of each element within the tree. Also depends on the species, age or tree size and variations in the external nutrient supply (Grove *et al*., 1996). On the other hand, Foelkel (2005) mentions that nutrient distribution trend in different tree compartments do not present major variations between eucalyptus species.

In a study conducted by Schumacher *et al*. (2001) in Rio Grande do Sul (Brazil) it was determined nutrient content in different compartments of forest biomass in 4 years old *Eucalyptus globulus* sub species *maidenii*.
The tree stem represents 69% of total biomass, despite which contained only 29% of the nitrogen, 28% of the phosphorus, 40% of the potassium, 12.5% of the calcium and 34% of the magnesium. However leaves with 15% of the total biomass (larger canopy proportion than in other studies because are young trees in this instance) contained 60% of the nitrogen, 45% of the phosphorus, 33% of the potassium, 23% of the calcium and 29.5% of the magnesium. On the other hand, bark was the element that accumulated 55.3% of the total calcium, representing only about 9% of total biomass. Similar results were obtained by others authors cited by Schumacher *et al*. (2001).

Brañas *et al*. (2000) in their study on 6 to 18 years old *Eucalyptus globulus*, observed that from nutrient concentrations point of view the smaller records were found in wood (0.044% weight of nitrogen, 0.005% of phosphorus, 0.082% of calcium, 0.008% of magnesium and 0.132% of potassium), while in leaves were obtained the highest nitrogen (1.307%), phosphorus (0.023%) and potassium (0.555%) concentrations.
The highest calcium and magnesium concentrations were found in the bark (1.119% and 0.090% respectively). The author notes that other studies found similar results in this species (González Esparcia *et al.* and Cortez and Madeira), and in other eucalyptus species (Hopmans *et al*. and Judd *et al*.). On the other hand, Brañas mentions there are some studies where the highest magnesium levels are recorded in leaves.

Taking into account the amount of biomass for each compartment was observed that wood with 73% dry weight of the total biomass accumulated almost half of the phosphorus and potassium and between 20 to 30% of the nitrogen, calcium and magnesium. Meanwhile bark with 11% of the biomass contained 50% of the calcium and magnesium and 20% of the nitrogen, phosphorus and potassium. Moreover, leaves with 6% of the biomass contained half the nitrogen, 30% of the phosphorus and 20% of the calcium, magnesium and potassium. Brañas notes that these results are comparable to those found by him in literature.

In the Freitas *et al*. work (2004) in nine years old *Eucalyptus grandis* in Rio Grande do Sul (Brazil), the author also found the highest calcium amounts in bark, explaining the fact by the low mobility of this nutrient in phloem, resulting in their low redistribution in plant tissues.

Goya *et al*. (1997) in their study with *Eucalyptus grandis* in Entre Rios province (Argentina) noted that nutrient distribution in different tree compartments may be affected by soil texture. The results showed that there is a greater accumulation tendency for nitrogen and smaller for phosphorus in canopy in the clay soils. In sandy soils there were larger nitrogen, phosphorus, calcium and magnesium proportions in stem wood compared to other compartments.

Foelkel (2005) summarizes the data found in Brazilian and foreign literature about the amount and distribution of nutrients in Eucalyptus genus (among the analyzed species are *Eucalyptus globulus*, *Eucalyptus grandis*, *Eucalyptus dunnii* and *Eucalyptus maidenii*) with biomass production from 120 to 250 megagrams (equal to tons) per hectare. The data are presented in Table 3 and Table 4.

Table 3. Nutrient concentration ranges in% by weight in different *Eucalyptus* sp. compartments. Source: adapted from Foelkel (2005).

	N	P	K	Ca	Mg
Leaves	1.0- 2.8	0.1 - 0. 25	0.5 - 1.2	0.4 - 1.0	0.15 - 0.35
Bark	0.15 - 0.35	0.02 - 0.10	0.3 - 0.8	0.8 - 3.5	0.15 - 0.4
Wood	0.08 - 0.25	0.01 - 0.05	0.05 - 0.2	0.05 - 0.25	0.01 - 0.06
Branches	0.15 - 0.30	0.02 - 0.05	0.2 - 0.5	0.35 - 0.8	0.1 - 0.25

Table 4. Nutrient amount ranges (Kg.ha^{-1}) in different *Eucalyptus* sp. compartments. Source: adapted from Foelkel (2005).

	N	P	K	Ca	Mg
Leaves	80 - 200	5 - 10	30 - 100	25 - 45	10 - 20
Bark	20 - 40	5 - 12	30 - 120	150 - 400	25 - 45
Wood	100 - 250	10 - 40	150 - 400	60 - 250	30 - 80
Branches	10 - 30	2 - 8	25 - 75	30 - 65	10 - 20
Total aereal biomass	**210 - 520**	**22 - 70**	**235 - 695**	**265 - 760**	**75 - 165**

From these data, Foelkel (2005) provides the following nutrient extraction average order for *Eucalyptus* sp. Ca>N=K>Mg>P.

Table 5 shows data on nutrient amount and concentration per hectare in different compartments of *Eucalyptus* sp. aboveground biomass in several studies conducted in Uruguay.

Table 5. Nutrient amount and concentration per hectare in different compartments of *Eucalyptus* sp. aboveground biomass in several studies conducted in Uruguay. Source: adapted from Gonzalez (2008) and Hernandez *et al*. (2009).

***Eucalyptus globulus* (González, 2008)**											
Component	Biomass ($Mg\ ha^{-1}$)	N (%)	P (%)	K (%)	Ca (%)	Mg (%)	N ($Kg\ ha^{-1}$)	P ($Kg\ ha^{-1}$)	K ($Kg\ ha^{-1}$)	Ca ($Kg\ ha^{-1}$)	Mg ($Kg\ ha^{-1}$)
Commercial logs	106.7	0.04	0.005	0.033	0.13	0.02	43.8	5.4	34.6	138.3	25.8
Leaves	2.3	1.35	0.074	0.45	1.3	0.1	31.7	1.8	10.3	29.6	2.3
Thin branches	1.3	0.67	0.007	0.46	1.64	0.09	8.8	0.1	6.3	21	1.1
Medium branches	1.5	0.42	0.019	0.45	0.99	0.17	6.3	0.3	6.9	14.6	2.5
Thick branches	10	0.12	0.005	0.35	0.79	0.09	11.1	0.5	34.6	78.3	8.9
Bark	15.8	0.23	0.025	0.55	3	0.24	36.3	4	87.1	479.6	37.9
Total harvested	137.6						138	12	180	761	79

***Eucalyptus maidenii* (González, 2008)**											
Component	Biomass ($Mg\ ha^{-1}$)	N (%)	P (%)	K (%)	Ca (%)	Mg (%)	N ($Kg\ ha^{-1}$)	P ($Kg\ ha^{-1}$)	K ($Kg\ ha^{-1}$)	Ca ($Kg\ ha^{-1}$)	Mg ($Kg\ ha^{-1}$)
Commercial logs	199.2	0.04	0.008	0.033	0.16	0.03	90.8	12.9	65.2	321.7	49.2
Leaves	11.3	1.27	0.074	0.45	1.22	0.1	144.6	8.3	50.4	136.3	11.3
Thin branches	4.1	0.63	0.007	0.45	1.59	0.11	26.3	0.3	18.3	64.6	4.3
Medium branches	4.5	0.4	0.022	0.43	0.96	0.22	17.9	0.9	19.3	42.5	9.9
Thick branches	24.7	0.1	0.003	0.32	0.72	0.11	25	0.8	80.4	177.9	27.1
Bark	33.4	0.25	0.021	0.58	3.61	0.26	82.5	6.9	190.8	1196.3	86.3
Total harvested	277.2						387	30	425	1939	188

***Eucalyptus dunnii* (Hernández et al., 2009)**											
Component	Biomass ($Mg\ ha^{-1}$)	N (%)	P (%)	K (%)	Ca (%)	Mg (%)	N ($Kg\ ha^{-1}$)	P ($Kg\ ha^{-1}$)	K ($Kg\ ha^{-1}$)	Ca ($Kg\ ha^{-1}$)	Mg ($Kg\ ha^{-1}$)
Commercial logs	144	0.09	0.01	0.06	0.17	0.07	132	19	86	240	98
Non commercial logs	28	0.12	0.02	0.19	0.28	0.1	34	5	55	77	28
Leaves	13	1.42	0.1	0.74	1.45	0.22	184	13	96	188	29
Branches	22	0.35	0.03	0.47	0.95	0.11	76	7	101	206	24
Bark	29	0.24	0.04	0.47	2.73	0.22	70	11	134	783	62
Total harvested	236						496	55	472	1494	241

Figure 1 shows data on nutrient content per hectare in *Eucalyptus* sp. aboveground biomass in different studies conducted in Uruguay.

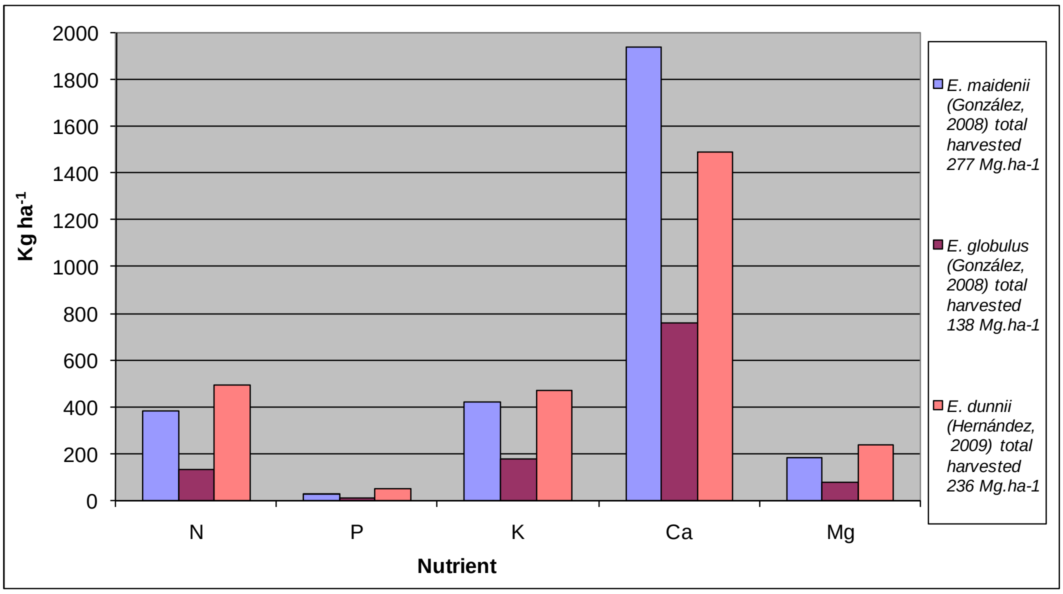


Figure 1. Nutrient content of *Eucalyptus* sp. aboveground biomass in different studies conducted in Uruguay. Source: adapted from Gonzalez (2008) and Hernandez *et al*. (2009).

As shown in Figure 1, in Uruguay, Gonzalez work (2008) in *Eucalyptus maidenii* and *Eucalyptus globulus* and Hernández *et al*. work (2009) in *Eucalyptus dunnii*, beyond the marked differences between species in harvested biomass (*Eucalyptus maidenii* 277 $Mg.ha^{-1}$, *Eucalyptus dunnii* 236 $Mg.ha^{-1}$ and *Eucalyptus globulus* 138 $Mg.ha^{-1}$) presented similar results to each other and those observed in the foreign literature regarding to the extraction order of different nutrients. Calcium was the nutrient most notoriously extracted by trees, followed by potassium and nitrogen (potassium more extracted in *Eucalyptus* maidenii and *Eucalyptus globulus* and nitrogen more extracted in *Eucalyptus dunnii*), then the magnesium and finally phosphorus. Besides Foelkel (2005) in his bibliographic summary, this order of extraction was observed by Freitas *et al*. (2004) for nine years old *Eucalyptus grandis* in Brazil (with nitrogen as second most extracted nutrient but very close to the potassium found third). In the same way Goya *et al*. (1997), also in *Eucalyptus grandis* in the Entre Rios province (Argentina) obtained the same nutrient extraction order, taking second in importance to nitrogen or potassium depending on soil type.

Beyond it is different species and soils Gonzalez (2008) and Hernandez *et al*. (2009) works showed some similar results between them and foreign works above mentioned, as calcium was the most variability nutrient within the tree, being found in very high concentrations in bark and significantly smaller in logs. On the other hand phosphorus showed larger concentrations in leaves and smaller but similar to each other compartments (Table 5).

Both Uruguayan works shows that commercial logs are the biomass part that has the smallest concentrations for all studied nutrients. With regard to total nutrient amount removed by surface, is observed that *Eucalyptus globulus* commercial logs which represented 77% of total aboveground biomass, contained 45% of the phosphorus, 33% of the magnesium, 32% of the nitrogen, 19% of the potassium and 18% of the calcium of the total harvested biomass (the total aboveground biomass nutrient content in kilograms per hectare were: 12 phosphorus, 79 magnesium, 138 nitrogen, 180 potassium and 761 calcium, (Table 5)). In *Eucalyptus maidenii*, commercial logs represented 72% of the biomass, containing 43% of the phosphorus, 26% of the magnesium, 24% of the nitrogen, 17% of the calcium and 15% of the potassium (the total aboveground biomass nutrient content in kilograms per hectare were: 30 phosphorus, 188 magnesium, 387 nitrogen, 1939 calcium and 425 potassium (Table 5)). For *Eucalyptus dunnii* the results showed that commercial logs with 61% of harvested biomass contained 35% of the phosphorus, 41% of the magnesium, 27% of the nitrogen, 16% of the calcium and 18% of the potassium (the total aboveground biomass nutrient content in kilograms per hectare were: 55 phosphorus, 241 magnesium, 496 nitrogen, 1494 calcium and 472 potassium (Table 5). It underlines the important stem magnesium content in Hernandez *et al*. work (2009) compared both with national studies as foreign literature. The differences in commercial logs harvested biomass percentages resides in morphological characteristics of each species and minimum diameters taken as commercial production in each work.

Within harvest residues, highlights calcium, magnesium and potassium content in bark and nitrogen and phosphorus in leaves.

In *Eucalyptus globulus*, *Eucalyptus maidenii* and *Eucalyptus dunnii*, bark represented in all cases 12% of total aboveground biomass, however in *Eucalyptus globulus* contained 63% of the calcium, 48% of the magnesium and 48% of the potassium of total harvested, in *Eucalyptus maidenii* 62% of the calcium, 47% of the magnesium and 45% of the potassium while in *Eucalyptus dunnii* somewhat smaller values were obtained, containing the bark 52% of the calcium, 26% of the magnesium and 28% of the potassium. In the leaves component, Gonzalez (2008) found that *Eucalyptus globulus* representing only 2% of the harvested biomass contained 23% of total nitrogen and 15% of total phosphorus. The same author observed for leaves component in *Eucalyptus maidenii* that representing 4% of total biomass, contained 38% of total nitrogen and 28% of phosphorus. Meanwhile Hernandez *et al*. (2009) in *Eucalyptus dunnii* obtained a leaves mass corresponding to 5% of the total aboveground biomass, containing 37% of total nitrogen and 24% for total phosphorus (Table 5).

For nutrient concentration in different compartments of biomass, data from national work (Table 5) are generally within the ranges presented by Foelkel (2005), except for wood compartment where nitrogen, phosphorus and potassium have smaller values in the uruguayan works. On the contrary calcium has generally larger concentrations in all compartments in the uruguayan studies.

Regarding nutrient amount per hectare (Figure 1 and Table 5), at the level of total aboveground biomass it is observed that *Eucalyptus dunnii* (Hernández *et al*., 2009) and *Eucalyptus maidenii* (Gonzalez, 2008) are within the ranges described by Foelkel (2005) (Table 4) for the nutrients nitrogen, phosphorus and potassium while *Eucalyptus globulus* (Gonzalez, 2008) with smaller production per hectare, does not reach the inferior limit range. For magnesium, *Eucalyptus dunnii* is well above the range, *Eucalyptus maidenii* is slightly above the upper limit and *Eucalyptus globulus* is within the lower range. In calcium, even *Eucalyptus globulus* is slightly above the range, while *Eucalyptus dunnii* and *Eucalyptus maidenii* reach double the upper limit value.

Analyzing the nutrient per hectare found by compartment it is observed that logs in uruguayans works have smaller potassium amount in all cases than the lower registers within the data presented by Foelkel (2005) and *Eucalyptus globulus* in Gonzalez (2008) in particular due to its lower productivity, also obtained minor records for nitrogen, phosphorus and magnesium in this compartment and in leaves too. On the other hand in uruguayan works in "branches" and "bark" compartments were obtained values per hectare for all nutrients (except phosphorus) usually above the range reported by Foelkel (2005) (Table 4 and Table 5).

1.5. NUTRIENT RETRANSLOCATION

Nutrient retranslocation from senescing or dead tissue (leaves, heartwood or bark) to growing tissues is one of the ways to increase utilization efficiency of limited nutrients by trees. Nutrient retranslocation from leaves mean the largest contribution to the biogeochemical cycle of nitrogen, phosphorus and potassium (mobile nutrients), followed in importance by retranslocation due to duraminization process and in lesser extent by redistribution from the outer bark (Grove *et al*., 1996).

Nutrient retranslocation proportion due leaf senescence depends on the initial concentration and mobility of nutrient in the phloem (Loneragan *et al.*, cited by Grove *et al*., 1996).

Nutrient distribution in wood varies according if region under study is sapwood or heartwood (Foelkel, 2005). In tree development are given internal nutrient translocation during heartwood formation which produces larger nutrient concentration in living components of plant in relation to heartwood. With increasing plantation age, the proportion of heartwood in total biomass increases and therefore improves the nutrient utilization efficiency (Laclau *et al*., 2000) (Grove *et al*., 1996) (Wise and Pitman, 1981).

In the heartwood formation process, occurs radial movement of sparingly mobile elements such as calcium to growing tissues. These changes show the importance of taking into account sapwood/heartwood proportions when measuring stem nutrient distribution (Silva *et al*. cited by Aparicio, 2001). Calcium can also be radially retranslocated from the outer bark towards growing tissues. On the other hand, due to its low phloem mobility calcium remains in senescing leaves (which becomes more important its retranslocation in the stem). Eucalyptus trees are particularly efficient in phosphorus retranslocation in wood during heartwood formation, finding for various species concentrations from five to thirty times higher in sapwood than in heartwood. Potassium generally follows the same behavior as phosphorus, while nitrogen has smaller concentration differences between sapwood and heartwood. Calcium retranslocation in duraminization process shows significant differences depending on species and site. Therefore in cases where the internal calcium redistribution is small, the tree requires continuous absorption from the soil of this nutrient (Turner and Lambert cited by Grove *et al*., 1996).

1.6. NUTRIENT CONTENT AND DISTRIBUTION ALONG STEM

Stem nutrient content is of great importance from the pulp industry viewpoint because of the all nutrients accumulated in biomass tree, only those present in debarked commercial logs will enter at the production process.

There are different views about the nutrient distribution along stem. Foelkel (2005) mentions that due to proximity to roots and canopy, the stem extremes have larger nutrient content than the middle, with differences that can reach the order of 30 to 40%. The author explains this by the large nutrient proportion in canopy (for being the area of greatest metabolic activity) and high parenchyma cells concentration that serves as a nutrient reservoir near roots.

Furthermore Bellote *et al*. (1980) in *Eucalyptus grandis* in Sao Paulo state (Brazil) noted that nutrient amount in stem trees between 6 and 7 year old did not follow the behavior in height mentioned by Foelkel (2005). For nitrogen, phosphorus, potassium, calcium and magnesium Bellote *et al*. found a significant increase in the nutrient amount extracted from the basal portion towards the middle and then maintenance of values or a slight decrease towards the apex.

In works done at national level are found different results depending on species, assessed nutrient and study site. The following figures show nutrient distribution along *Eucalyptus globulus* and *Eucalyptus grandis* stem in different studies conducted in Uruguay.

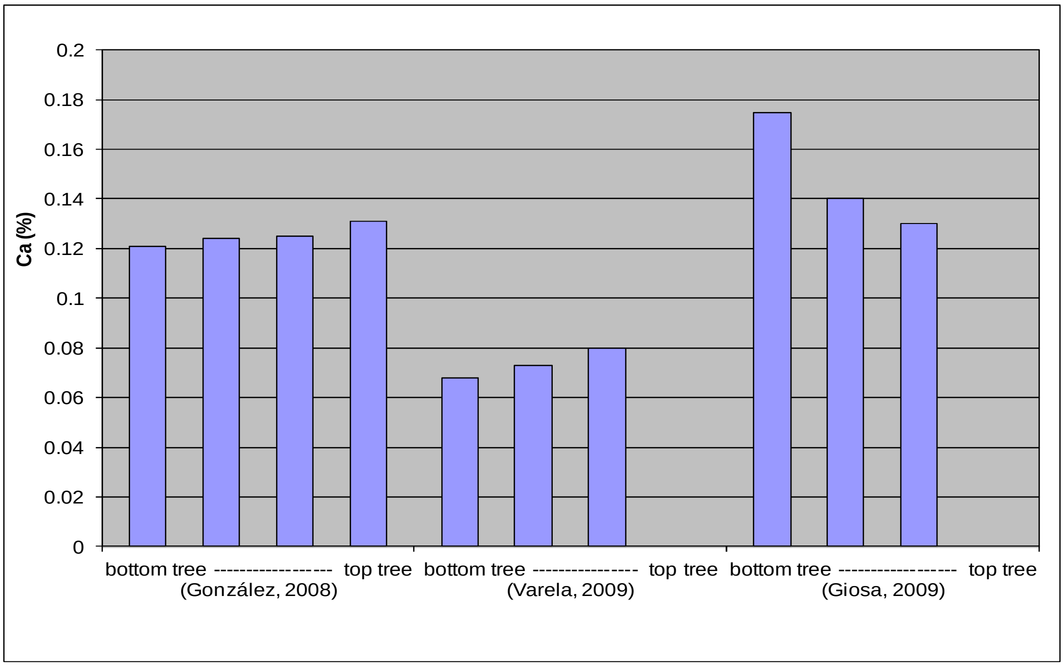


Figure 2. Calcium concentration along stem in three studies conducted in Uruguay in *Eucalyptus globulus* (Gonzalez, 2008 and Varela, 2009) and *Eucalyptus grandis* (Giosa, 2009). Source: adapted from Gonzalez (2008), Varela (2009) and Giosa (2009).

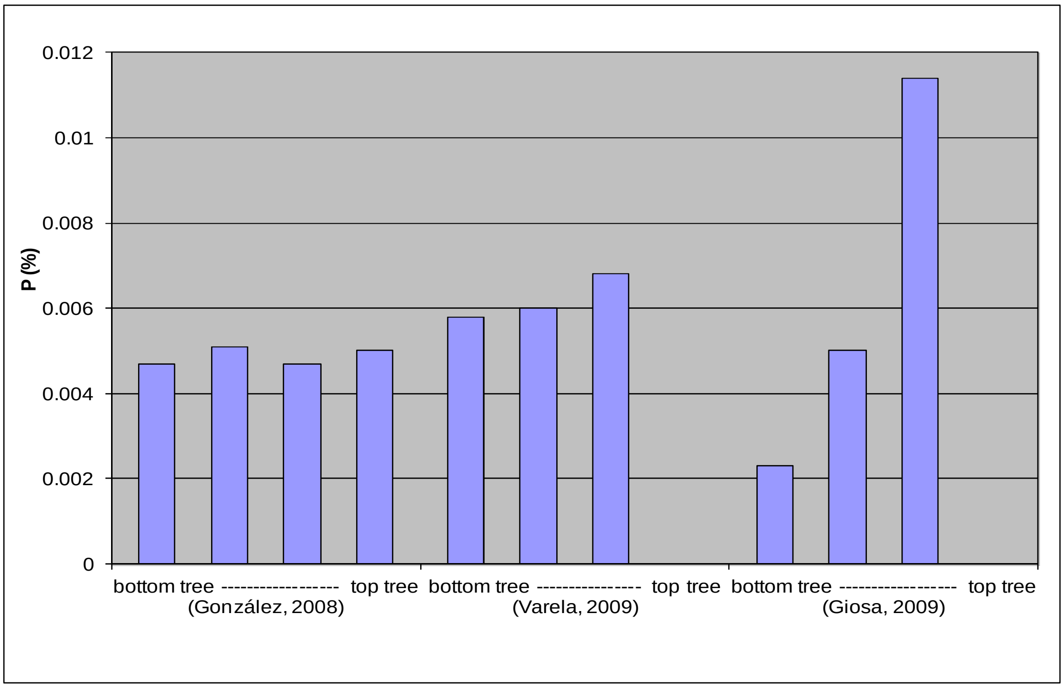


Figure 3. Phosphorus concentration along stem in three studies conducted in Uruguay in *Eucalyptus globulus* (Gonzalez, 2008 and Varela, 2009) and *Eucalyptus*

grandis **(Giosa, 2009). Source: adapted from Gonzalez (2008), Varela (2009) and Giosa (2009).**

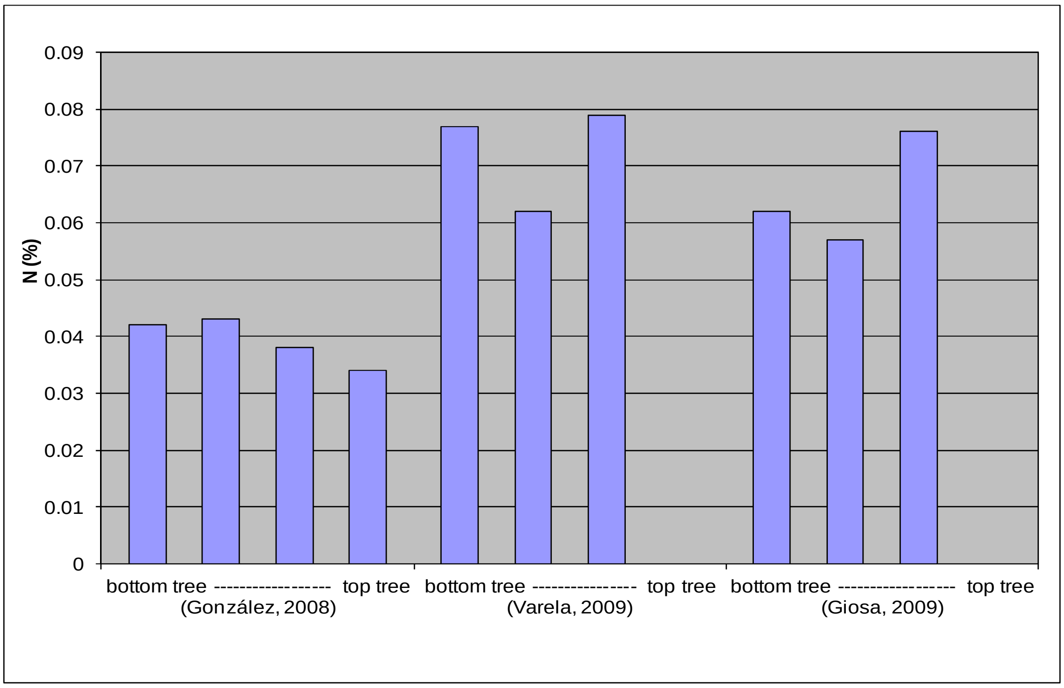


Figure 4. Nitrogen concentration along stem in three studies conducted in Uruguay in *Eucalyptus globulus*(Gonzalez, 2008 and Varela, 2009) and *Eucalyptus grandis* (Giosa, 2009). Source: adapted from Gonzalez (2008), Varela (2009) and Giosa (2009).

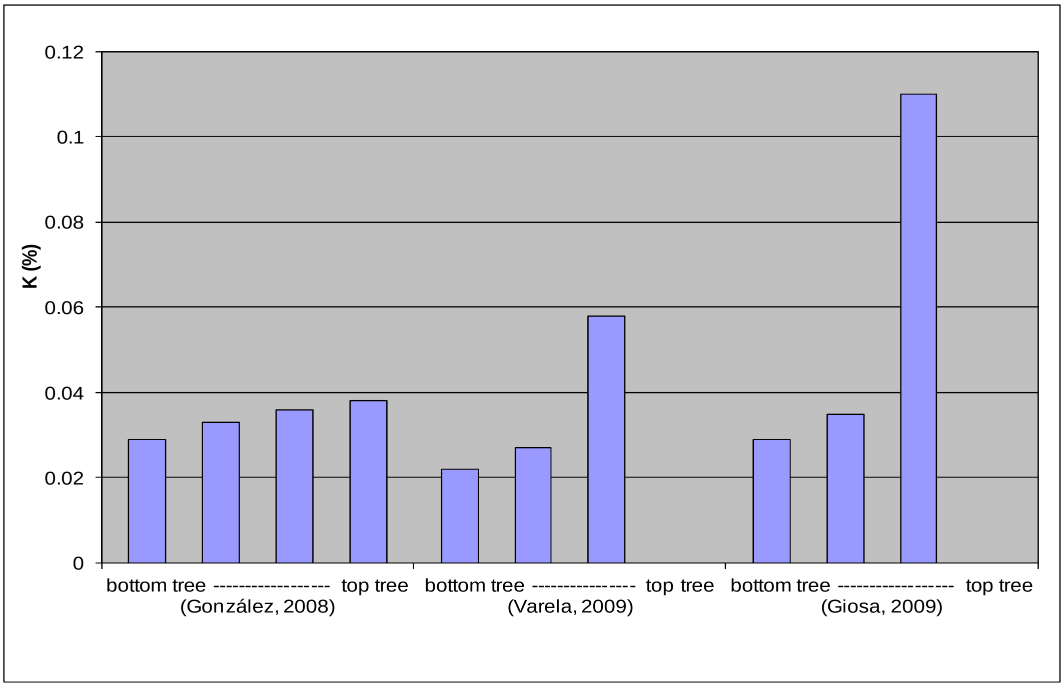


Figure 5. Potassium concentration along stem in three studies conducted in Uruguay in *Eucalyptus globulus* (Gonzalez, 2008 and Varela, 2009) and *Eucalyptus*

***grandis* (Giosa, 2009). Source: adapted from Gonzalez (2008), Varela (2009) and Giosa (2009).**

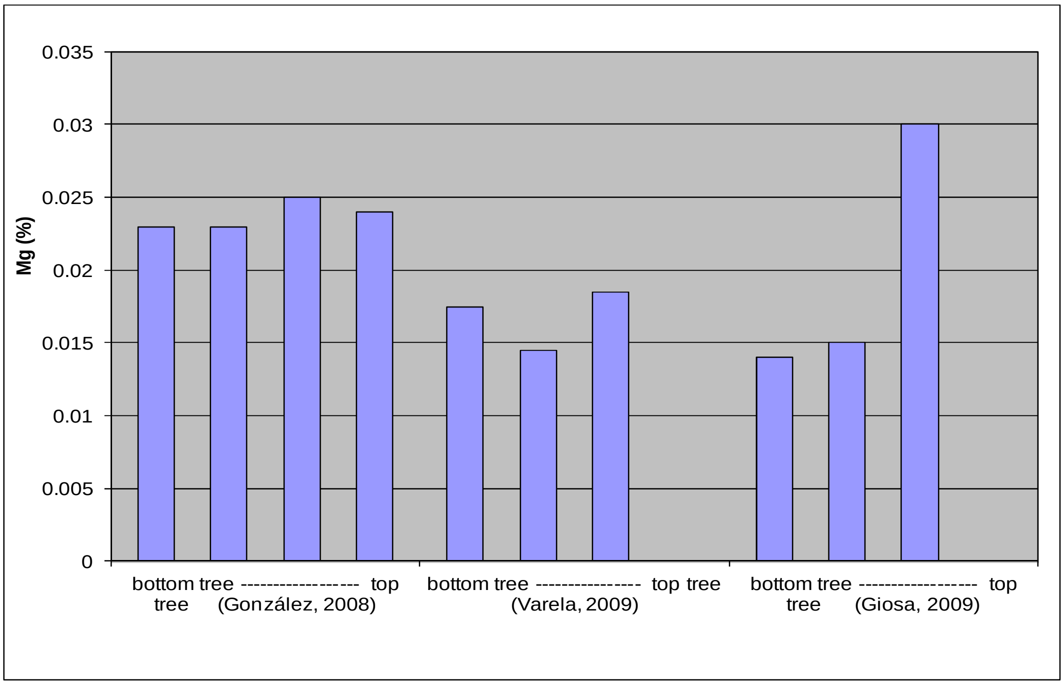


Figure 6. Magnesium concentration along stem in three studies conducted in Uruguay in *Eucalyptus globulus* (Gonzalez, 2008 and Varela, 2009) and *Eucalyptus grandis* (Giosa, 2009). Source: adapted from Gonzalez (2008), Varela (2009) and Giosa (2009).

Figures 2 to 6 shows that in 10 years old *Eucalyptus globulus* in Soriano department, Gonzales (2008) found a nutrient concentration distribution relatively homogeneous along stem, with the exceptions of a very small nitrogen decrease and slightly potassium increased towards the apex. The same author in 10 years old *Eucalyptus maidenii* in Río Negro department found an even distribution all over the stem for nitrogen, calcium and magnesium, whereas for phosphorus and potassium observed a slight increase towards the apex. Giosa (2009) in *Eucalyptus grandis* with nearly average 11 years old in Río Negro and Paysandu departments observed a well defined increasing trend towards the apex of nutrients nitrogen (this with a small decline in middle), potassium, phosphorus and magnesium, whereas calcium distribution along stem behaved inverse. Furthermore Varela (2009) for *Eucalyptus globulus* with average close to 10 years old evaluated in east of the country, found for nitrogen and magnesium a larger concentration in the base and apex with respect to the middle, for calcium and potassium an increased distribution from base to apex as well as to phosphorus (in the latter case with a milder increase).

Analyzing nutrient behavior in the different national studies we can see that for calcium, concentrations observed by Varela (2009) in *Eucalyptus globulus* were smaller than those found by Gonzalez (2008) in the same species and Giosa (2009) in *Eucalyptus grandis*. Varela (2009) mentions the lower availability of exchangeable calcium in the soil of their study in relation to other work, which can give an explanation to this fact. With regard to distribution dissimilar behavior are observed, Gonzalez obtained homogeneous data in height (with a slight increase towards the apex), Varela more marked increase towards the apical zone and Giosa in contrast a clear decrease in this direction. Being calcium a scarcely mobile nutrient within the tree is expected that trends observed were maintained over time for these trees.

In phosphorus even though Gonzalez (2008) did not observe a slight increase on concentration distribution in the stem length as Varela (2009) for *Eucalyptus globulus*, similar concentrations of the nutrient in these studies were found. Moreover, Varela (2009) agrees with distribution along the stem with those found by Giosa (2009) in *Eucalyptus grandis* but mentions that the latter species had smaller nutrient concentration in the base and middle stem and higher in the apical area.

In nitrogen as already mentioned, the distributions along the stem had more points in common between Varela (2009) and Giosa (2009) works than with Gonzalez (2008). Furthermore, regarding concentration levels are also similar between *Eucalyptus grandis* in Giosa (2009) and *Eucalyptus globulus* in Varela (2009), while the values are smaller in *Eucalyptus globulus* observed by Gonzalez (2008) in the littoral of the country. Varela (2009) explains this difference between the two *Eucalyptus globulus* works given that forestations on the east country area were implemented on natural field while probably the plantations in the littoral were made on land with a nitrogen extraction history due to agriculture.

In potassium the three national works observed an increasing concentration distribution trend in the stem from base to apex. Base and middle stem concentration was also similar to these studies, while for the apex Giosa (2009) in *Eucalyptus grandis* found larger potassium concentration than Varela (2009) and Gonzalez (2008) in *Eucalyptus globulus*.

For magnesium as mentioned above, the concentration distributions along the stem are not concordant. On the other hand, concentration levels observed by Giosa (2009) in *Eucalyptus grandis* and Varela (2009) in *Eucalyptus globulus* are similar in the base and middle but larger in the apex to the first. Varela (2009) meanwhile found smaller nutrient concentrations than Gonzalez (2008) along the whole stem for *Eucalyptus globulus*.

In figures of distribution along the stem of all nutrients in national level works, is observed that in Giosa (2009) clearly highlights the large mobile nutrients concentration (nitrogen, potassium, phosphorus and magnesium) in the apical area (near the canopy), fact that is not so clearly in the other works, except for potassium who also behaves in this way.
These differences along stem length indicate the need to take precautions in obtaining representative samples in next studies.

1.7. NUTRIENT CONTENT IN THE WHOLE STEM

Figure 7 shows nutrient concentration in commercial logs of *Eucalyptus* sp. in different studies conducted in Uruguay.

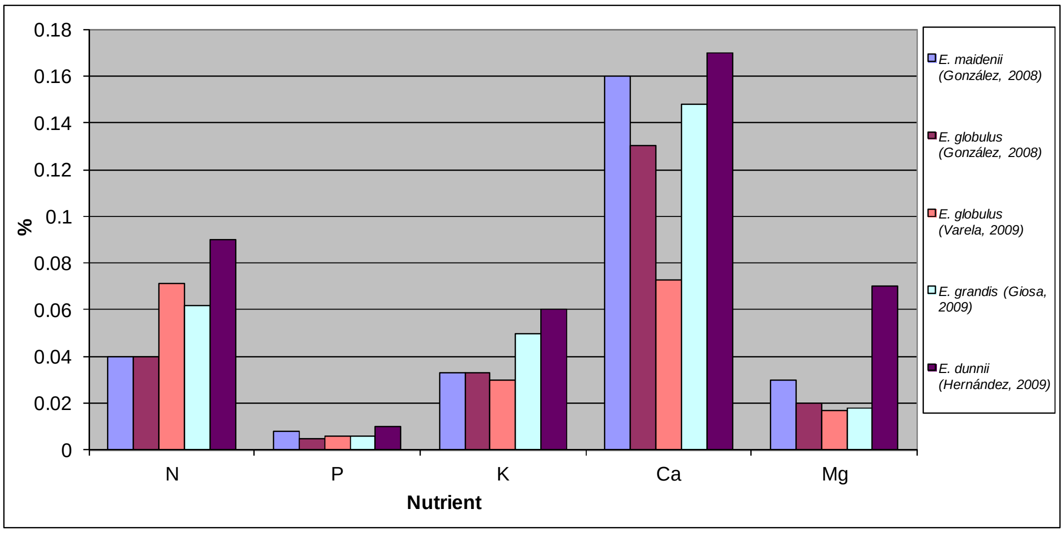


Figure 7. Nutrient concentration in commercial logs of *Eucalyptus* sp. in different studies conducted in Uruguay. Source: adapted from González (2008), Varela (2009), Giosa (2009) and Hernández (2009).

Considering the whole stem, the removed nutrient concentration in commercial logs in the works of Giosa (2009) in *Eucalyptus grandis*, Varela (2009) in *Eucalyptus globulus* and González (2008) in *Eucalyptus globulus* and *Eucalyptus maidenii* followed the order Ca>N>K>Mg>P. In Hernandez work (2009) in *Eucalyptus dunnii* highlights the high magnesium concentration compared to the other studies even having a magnitude greater than the potassium concentration (Ca>N>Mg>K>P).

As can be seen in Figure 7, in the nine years old *Eucalyptus dunnii* study in the Río Negro department was obtained the largest concentrations for all nutrients in commercial logs with respect to the other species. Gonzalez (2008) observed in *Eucalyptus maidenii* larger calcium, magnesium and phosphorus concentration than in *Eucalyptus globulus*, while values were the same to nitrogen and potassium in both species. Unlike those reported by Freddo *et al*. (1999) and Foelkel (2005) in that *Eucalyptus grandis* has smaller nutrient concentrations than *Eucalyptus globulus*, in national studies, the latter is the specie which shows in all cases the smallest nutrient concentrations, except nitrogen in the work of Varela (2009) whose concentration is only surpassed by *Eucalyptus dunnii*. This shows that beyond the difference of soils and species may be a significant variability in nutrient contents within the same species.

Comparing national works with data presented by Foelkel (2005) can be see that although in both cases is wood compartment that presents smallest concentrations for all nutrient, it is observed except for calcium and magnesium smaller nutrient concentration (even below the lower ranges presented by Foelkel) (Table 3 and Table 4) in the uruguayan works for this compartment.

In order to visualize the importance of nutrient removal in a plantation, besides the concentration of each nutrient, it is need to know the total produced biomass in a given area. This parameter is a function of species, planting density, and soil fertility among others (Hernández *et al*., 2009). Figure 8 and Figure 9 shows biomass production and nutrient content per hectare of commercial logs in different studies conducted in Uruguay in *Eucalyptus* sp.

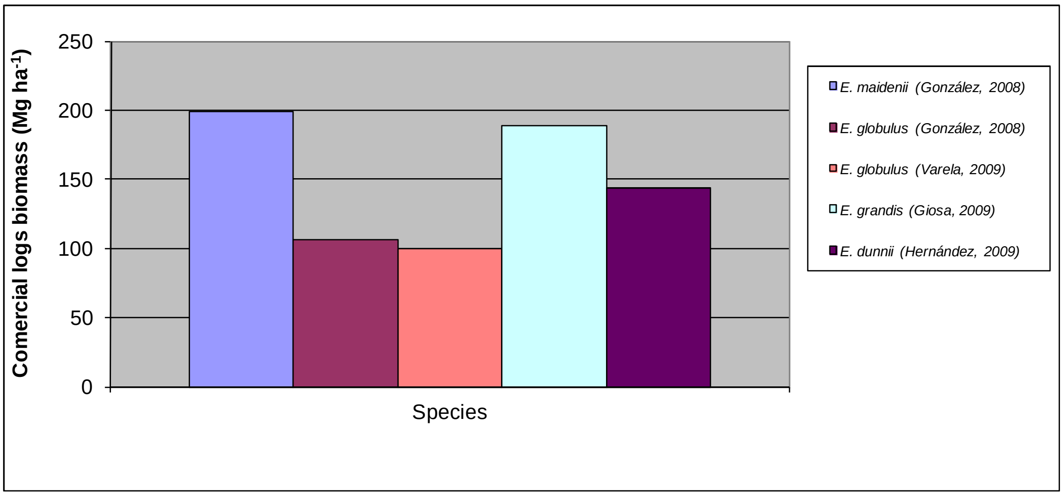


Figure 8. Biomass production per hectare of commercial logs in different studies conducted in Uruguay in *Eucalyptus* sp. Source: adapted from Gonzalez (2008), Varela (2009), Giosa (2009) and Hernandez *et al.* (2009).

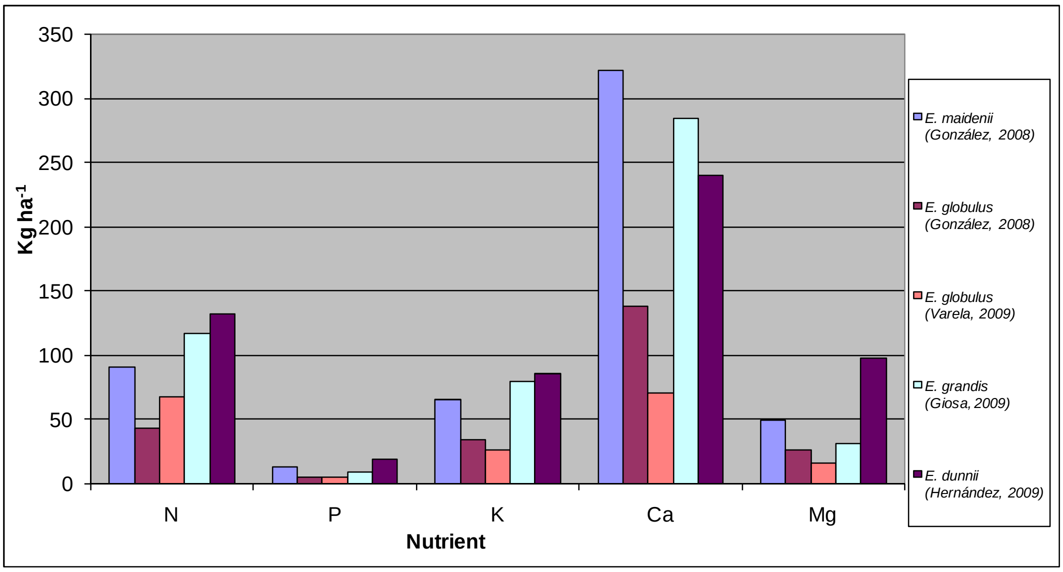


Figure 9. Nutrient content per hectare of commercial logs in different studies conducted in Uruguay in Eucalyptus sp. Source: adapted from Gonzalez (2008), Varela (2009), Giosa (2009) and Hernandez *et al.* (2009).

The nutrient extraction order per hectare predominant in different species is Ca>N>K>Mg>P with the exception of *Eucalyptus dunnii* where the order is reversed between magnesium and potassium (showing concordance with the nutrient concentration extraction order).

Regarding nutrient magnitude export per hectare and comparing the two *Eucalyptus globulus* studies in Uruguay, it is observed differences between them despite the biomass produced in both cases were similar.
Gonzalez obtained larger extraction values than Varela for potassium, magnesium and calcium (almost double in this case), smaller for nitrogen and similar level for phosphorus. *Eucalyptus globulus* is the species that obtained in all cases smallest nutrient removal as expected, because it has minor biomass production per hectare and minor concentration of all nutrients (with the exception of nitrogen in the Varela work as already mentioned).

Eucalyptus dunnii produced per hectare 28% less biomass than *Eucalyptus maidenii* (highest performance) despite which extracted more nitrogen, potassium, magnesium and phosphorus than the latter (and that all other species) due to its high nutrient concentration in wood.

Eucalyptus grandis with a somewhat lower biomass production per hectare than *Eucalyptus maidenii* removed more nitrogen and potassium per hectare than the latter.

1.8. NUTRIENT EFFICIENCY UTILIZATION

Nutrient efficiency utilization can vary considerably between different *Eucalyptus* species (Aparicio, 2001). But in addition to genotype, influences the soil nutrient availability (beyond the roots have selectivity in absorption of nutrients), when there is abundance of a particular element in the soil, the plant tends to abuse in their absorption, thus lowering its efficiency. A more productive plantation is more efficient in the nutrient use for the biomass formation, even that has a higher mineral extraction per unit area due to its larger production, it will have a smaller proportion of these per product unit. Generally can be say that wood is very efficient in the use of phosphorus, and leaves and bark are very inefficient in the use of nitrogen and calcium respectively (Foelkel, 2005).

There are several indexes to determine the nutrient efficiency utilization absorbed in the forest biomass formation. Among them is the biological utilization coefficient which measures kilograms of dry wood produced in commercial logs per kilogram of nutrients in the logs.

Since nutrients that have greater biological utilization coefficient are found in smaller concentrations in tree, it is logical that the prevailing order for this coefficient in the uruguayan works is P>Mg>K>N>Ca. Since the meaning of biological utilization coefficient can be seen as the inverse of the concentration, it seems unnecessary to delve deeper into appreciations that emerge from those already made when discussing the issue nutrient concentration in stem.

1.9. SITE QUALITY

The quality of a forest site is the capacity of a particular place for the development of tree species as function of soil, climatic and biotic conditions (Varela 2009). The site quality along with the potential of each tree species determines the biomass development. For each particular site is a sustainable optimum biomass over time which is function of nutrient availability, precipitation, soil water retention capacity and silvicultural management practices (Noble and Herbert, cited by Geldres *et al*., 2006). In development of forest cultivation, site characteristics related to the physical soil properties such as texture, density and the depth are very important (Pozo Peñalosa, 2005).

The results obtained by Campos Santana *et al*. (1999) and Campos Santana *et al*. (2000) in the study of biomass and nutrient content of *Eucalyptus* sp. in different sites of Brazil confirmed the close relationship between biomass production and nutrient content in trees, finding the largest nutrient amounts in stem at those more productive sites and with genetic material better adapted to these conditions. On the other hand was found that calcium and potassium were the most limiting nutrients regarding the productivity in the different sites in the following rotations, fact which agrees with Wise and Pitman (1981). For the case of calcium this situation could be mitigated if bark is left in place given their high content in this nutrient.

Nutrient and water absorption by the tree is influenced by the site climatic characteristics and the physical and chemical soil properties. In addition to the annual water regime, soil texture is what determines the water availability and therefore the nutrient transport during certain periods. For this reason, larger productivity is observed in clay soils that have higher water retention capacity and larger organic matter content in topsoil horizons, allowing greater nutrient retention and preventing its leaching. Furthermore the undulating topography cause increased surface and subsurface runoff, which subjects the trees to water stress (Campos Santana *et al*., 1999).

1.10. MICRONUTRIENTS

In addition to macronutrients existing in all plant compartments, are found elements in fewer amount but no less important, called micronutrients. Despite the importance of these elements, is not abundant the literature about the cycle of micronutrients in the genus *Eucalyptus*. Although micronutrient lack is harmful to trees, the excess can be toxic, so the plants must be very selective in absorbing of them. For example, elements such as boron, copper and zinc are needed in very small amounts in enzyme systems but are extremely toxic if present in large quantities. The more absorbed micronutrients by eucalyptus are manganese and iron which can be a problem in pulp bleaching sequences using ozone and/or hydrogen peroxide (Foelkel, 2005) (Pallardy, 2008). The following table shows micronutrient extraction ranges by surface in *Eucalyptus* sp. plantations.

Table 6. Micronutrient extraction ranges by surface in *Eucalyptus* sp. Source: Foelkel, 2005.

kg extracted.ha^{-1}	stem (wood+bark)	canopy (leaves+branches)
Fe	0.7 - 4	1 - 2.5
Cu	0.3 - 1	0.08 - 0.15
Mn	2 - 15	2 - 3.5
B	1 - 1.5	0.2 - 0.35
Mo	0.01 - 0.02	0.002 - 0.004
Zn	0.3 - 0.5	0.05 - 0.15

2. NUTRIENT CONTENT IN FOREST SOIL IN URUGUAY AND THE REGION

2.1. GENERAL CONSIDERATIONS

The soil plays a central role in the global cycle of nutrients within forest ecosystem. This is via the regulation of nutrient sources by means of mineralization of organic matter through microorganisms and acting as nutrient sink by immobilization in soil organic matter and microorganisms, developing the mineral weathering (alteration and dissolution), controlling the process of desorption and adsorption of nutrients in soil surfaces and precipitation of mineral phases (Maquere, 2011).

Soil parent material consists of mineral materials, organic material or a mixture of both. The mineral materials are different kinds of rock-forming minerals and are generally the predominant type of parent material. Ion release from the minerals is given by the weathering process of these, and is the initial source of calcium, magnesium, potassium and phosphorus in the soil. The organic matter meanwhile comes mostly from dead and decaying vegetables and is the main soil nitrogen source. The nutrient contribution from atmosphere is of long-term importance in forest ecosystems (Fisher and Binkley, 1999).

As already mentioned the nutrient reserves at be found in soil in organic matter, not weathered minerals, the exchange complex, poorly soluble compounds, or fixed to clays, the nutrients that can be available to plants in a given time will be a function of the rates of release and replacement of these reservoirs (Fernández, 2002). The nutritional condition of a site thus depends on the chemical and microbiological processes that determine these processes (Pozo Peñalosa, 2005). These include inorganic complex reactions in the soil between solid phases (minerals, mineral surfaces, organic matter), liquid (near surfaces and in the bulk soil solution) and a wide variety of soil microorganisms (Fisher and Binkley, 1999).

The soil natural fertility can be defined as the ability of it to supply nutrients in chemically available forms to plants. Anyway fertility and productivity cannot be taken as synonymous, since although the soil might contain nutrients in available form, the vegetables could not use them due to physical impairments and other factors as water availability (Durán and García Préchac, 2007).

Most attention in the soil nutrients study should focus on the A horizon, since it is in the Eucalyptus forested soil surface where there are the highest organic matter, nutrients and roots concentrations (Shea and Dell cited by Grove *et al*, 1996). Furthermore, beyond the study of nutrient concentration available in soil for trees, is important to consider the amount of them in rooting depth. Varela (2009) found that the highest potassium, calcium and magnesium concentration in trees did not correlate with the greater availability (concentration) of them in different soils but it did with profile depth. On the other hand, Giosa (2009) in relatively deep soils found highly significant correlations between potassium, calcium and magnesium content in tree stem and the amount of these nutrients in soil A+E horizons. Also, there are many complicated interactions among various mineral nutrients, therefore one element can modify absorption and utilization of others (Pallardy, 2008).

2.2. NUTRIENTS

Calcium is one of the most abundant minerals in the rocks under the form of Ca^{+2}, can also be found in organic matter and in negative charge soil surfaces (cationic exchange sites). It is absorbed by trees in the soluble form Ca^{+2} (Binkley, 1993) (Fisher and Binkley, 1999).

The phosphate anion (PO_4^{-3}) is the only chemical phosphorus form that abounds in forest ecosystems. In soil, the phosphorus can be found in not decomposed organic matter, adsorbed on the rocks surfaces or precipitated as salts in inorganic phosphate form. Phosphorus is "released" from organic matter by the action of phosphatase enzyme secreted by various microorganisms and plants. The dissolved phosphate is associated with one to three H^+ depending on soil pH, being in forest ecosystems $H_2PO_4^-$ the predominant form. It is absorbed by trees in the soluble phosphate form (Binkley, 1993) (Fisher and Binkley, 1999).

It is noteworthy that by increasing soil acidity decreases inorganic phosphorus availability (Lugo, cited by Pozo Peñalosa, 2005).

Nitrogen (unlike other nutrients) is not found in the rock, therefore the main sources in soils are organic matter, ammonium and nitrate ions dissolved in water and biological fixation of this element made by microorganisms. It is mostly absorbed by trees in the nitrate soluble form and exchangeable ammonium (Binkley, 1993) (Fisher and Binkley, 1999).

The mineral potassium is found in rocks (mainly potassium feldspar), in the exchange complex and is also presented in dissolved salts form. Another potassium source is the soil organic matter. It is absorbed by plants in soluble K^+ form (Binkley, 1993) (Fisher and Binkley, 1999).

The magnesium sources in soil are found in mineral magnesium, the exchange complex and the organic matter. It is absorbed by plants in soluble Mg^{+2}form (Binkley, 1993) (Fisher and Binkley, 1999).

The following figures show schematically nutrient cycles in soils.

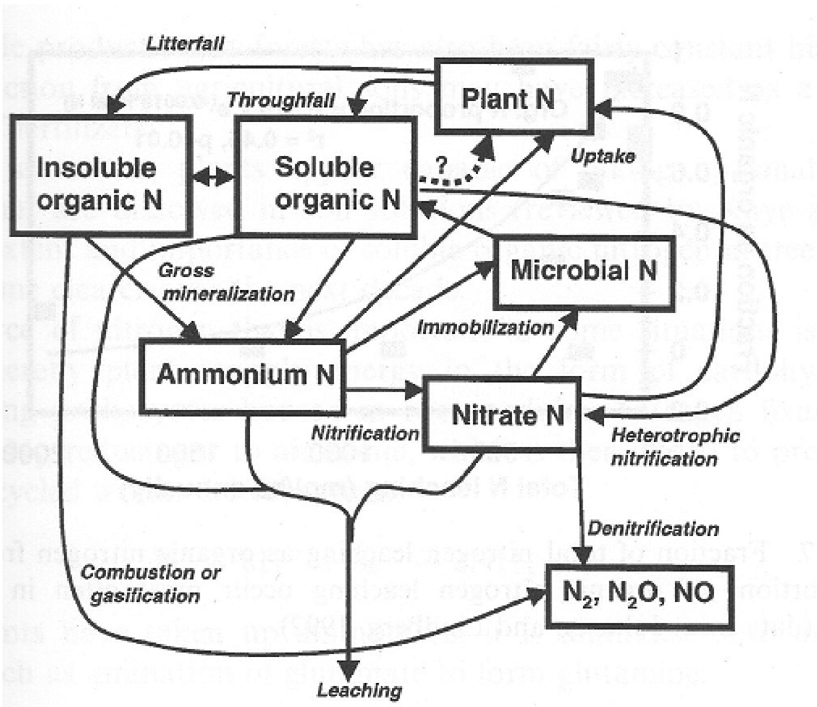


Figure 10. Basic features of soil nitrogen cycle (the dotted line with "?" notes the current lack of knowledge about the importance, if any, of direct uptake of organic nitrogen by trees). Source: Fisher and Binkley, 1999.

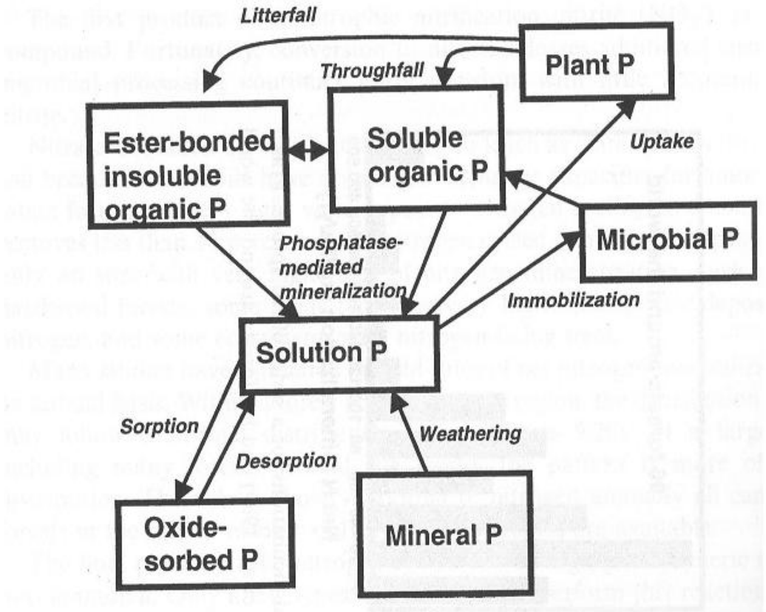


Figure 11. Soil phosphorus cycle. Source: Fisher and Binkley, 1999.

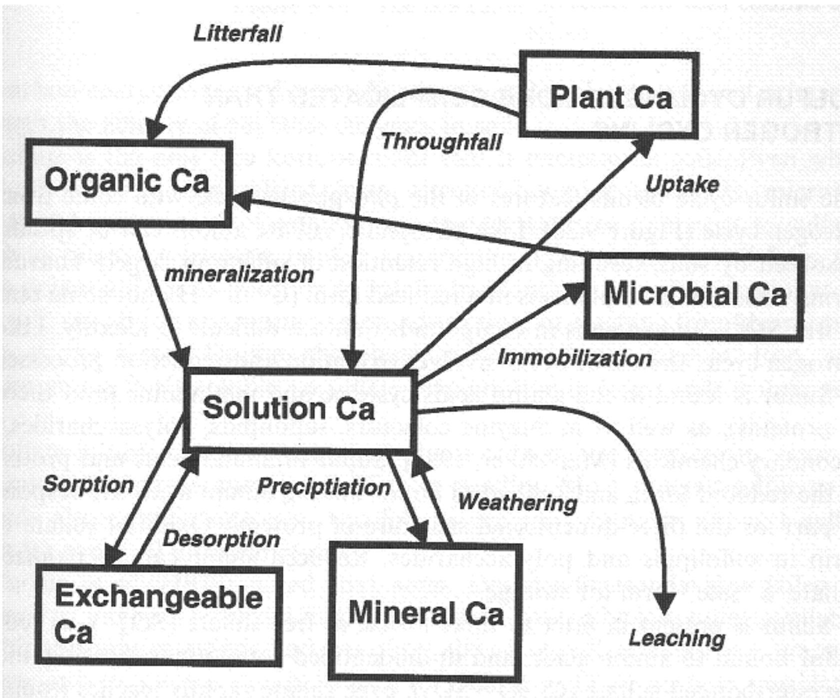


Figure 12. Soil calcium cycle. The cycles for other cations have a similar structure. Source: Fisher and Binkley, 1999.

2.3. NUTRIENT CONTENT IN FOREST SOIL IN URUGUAY AND THE REGION

The forest priority soils declared in Uruguay by the Forestry Law (Poder Legislativo, 1987) are those forest lands (forested or not) that by their conditions of soil, aptitude, weather, location and other characteristics are unsuitable for any other use or permanent and profitable purpose. Moreover should be classified as such by the Ministry of Livestock, Agriculture and Fisheries (MGAP) in according to their forestry aptness or public utility reasons. Have forestry aptness those soils that by its conditions allow for better growth of forests. In Uruguay, the total area of forestry priority soils "pure" plus those soils that require a prior endorsement to be considered as such ("conditional" priority) reach about 4,420,000 hectares. Roughly, these soils are distributed in our country in the following physiographic areas: midwest sedimentary region, northeast sedimentary region and the crystalline sierras, each of which presents a geological substrate, macro relief and soil associations particular of each (Califra and Durán 2010).

The following table shows the CONEAT groups (National Commission of Land Agro-economic Study) and their average productivity index that occur in priority forest soils. CONEAT groups are homogeneous areas of soil, defined by its production capacity in terms bovine meat, ovine meat and wool standing (but are also used for agricultural purposes) and are expressed by a relative index according to country average production capacity, to which are assigned the index 100).

Table 7. Average productivity index in CONEAT soil forestry priority groups. Source: Califra and Durán, 2010.

CONEAT group	Productivity average index
2	65
7	67
8	77
9	80
09 y S09	range from 26 to 74

The legislation establishes CONEAT soil forestry priority groups (Table 7) that have average productivity index smaller than 100 (agricultural and livestock aptitude low or at most average). The most common forestry priority soils are classified as Luvisoles, Acrisoles, Brunosoles and Argisoles (Califra y Durán 2010).

Soils assigned to forest production in Uruguay have low nutrient availability for being very acid soils, with low levels of bases, medium to light texture and low organic matter content.

Added to this, it has been shown in some cases an acidification process associated with the high bases extraction rate by eucalyptus trees, mainly calcium and magnesium (mitigated in part this process by the recycling of bases in the mulch decomposition). On the other hand, is not discarded the contribution made by soil tillage on soil acidification. The limited nutrient supply is in contrast to a relatively high demand from the trees.

This mismatch is minimized somewhat by the nutrient recycling during the biomass growth and decomposition of harvest residues at the end of turn (Hernández, 2010).

As a result of the significant limitations for use in agriculture and intensive livestock production in forestry priority soils, the first forest plantations are developed to a large extent on natural field. This brings some peculiarities in the soil nutrient behavior when forestation is made. For being fragile his organic matter, nitrogen mineralization will be in a short period when tillage is performed, running the risk of releasing nitrogen amounts that may not be used for trees in an excessive tillage. Beyond organic matter mineralization supply phosphorus in assimilable forms, the natural content of our soils are low, being larger phosphorus levels only in soils where there were previous fertilizations. Furthermore, most of forested soils have medium to high contents of both exchangeable as non exchangeable potassium. However, in those soils with smaller reserves of this nutrient and after several years of forestation, could be instances of potassium deficiency (Zamalvide and Ferrando, 2010).

Tables 8 to 13 shown chemical analysis data of some soils planted with *Eucalyptus* sp., representatives of the different forest physiographic areas of Uruguay: midwest sedimentary region (Littoral), northeast sedimentary region (Tacuarembó-Rivera) and the crystalline sierras (east zone of the country).

Usually phosphorus content does not appear in the soil profile analysis since it is not a property that is used for characterization (personal communication Agr. Eng. Ph.D. Amabelia del Pino, 2012).

Table 8. Chemical parameters of representative soils of the littoral zone (Río Negro and Paysandú departments) forested with *Eucalyptus grandis*. Source: Giosa, 2009. O.M. (organic material) --- E.A. (exchangeable acidity) --- cmolc.kg^{-1} (centimol carga.kg^{-1})= Meq/100 g soil. The bases data refer to exchangeable bases.

Field	Horizont Depth (cm)	pH (H_2O)	OM%	Ca ($cmol_c.kg^{-1}$)	Mg ($cmol_c.kg^{-1}$)	K ($cmol_c.kg^{-1}$)	Na ($cmol_c.kg^{-1}$)	E.A. ($cmol_c.kg^{-1}$)	CONEAT group
H251	A (0-48)	5.02	0.62	0.77	0.46	0.36	0.47	0.99	9.1
H252	A (0-48)	5.07	0.52	13.1	3.2	0.22	0.27	0.58	9.3
	E (48-80)	5.27	0.12	11.8	2.86	0.2	0.22	-	
	B (80-110)	5.4	0.12	9.8	2.34	0.31	0.28	0.27	
H269	A (0-28)	5.19	0.75	7.4	2.52	0.37	0.31	0.36	9.3
	B (28-95)	5.13	0.62	4.35	1.34	0.23	0.39	1.08	
MO22	A (0-16)	5.02	1.39	4.4	1.75	0.18	0.47	0.99	09.3
	B (16-75)	7.51	0.61	20.5	6.4	0.45	1.22	-	
MO18	A (0-43)	4.75	0.73	3.1	1.02	0.12	0.33	0.54	09.3
	B (43-96)	6.92	0.36	14.85	4.6	0.5	0.9	-	
MO13	A (0-51)	4.92	0.53	0.91	0.4	0.17	0.27	0.63	09.3
	B (51-92)	4.82	0.79	7.15	3.16	0.38	0.53	2.21	
MO67P	A (0-37)	4.55	0.68	2.7	0.93	0.22	0.38	0.81	09.3
	B (37-72)	4.94	0.88	12.25	2.79	0.42	0.29	0.77	
CO38a	A (0-32)	4.55	1.6	1.7	0.71	0.21	0.42	0.64	09.3
	E (32-45)	5.07	0.53	1.8	0.41	0.08	0.49	0.02	
	B (45-103)	6.62	0.53	12.45	2.8	0.45	0.9	-	

Table 8 shows that within the littoral zone, despite being soils belonging to a common physiographic region, there are variations between the characteristics of each.

Table 9. Chemical parameters of representative soils of the littoral zone (Río Negro department, 9.3 CONEAT soil) forested with *Eucalyptus dunnii*. Source: adapted from Hernández *et al*., 2009. O.M. (organic material) --- cmolc.kg^{-1} (centimol carga.kg^{-1})= Meq/100 g soil. The bases data refer to exchangeable bases.

Horizont	Depth (cm)	pH (H_2O)	OM%	Ca ($cmol_c.kg^{-1}$)	Mg ($cmol_c.kg^{-1}$)	K ($cmol_c.kg^{-1}$)	Na ($cmol_c.kg^{-1}$)
A	0-3	4.92	4.50	6.6	1.75	0.38	0.23
	3-6	4.58	2.50	4.3	1.45	0.18	0.19
	6-12	4.69	2.09	5.1	1.55	0.17	0.17
	12-20	4.74	2.33	8.9	2.1	0.3	0.18
B	20-40	5.09	2.05	11.7	2.6	0.3	0.19
	40-60	5.85	0.90	19.9	3.6	0.39	0.26
	60-80	6.71	0.33	24.7	3.9	0.4	0.28

Table 10. Chemical parameters of representative soils of the littoral zone (Río Negro department, 09.3 CONEAT soil) forested with *Eucalyptus maidenii*. Source: adapted from González, 2008. **O.M. (organic material) --- cmolc.kg^{-1} (centimol carga.kg^{-1})= Meq/100 g soil. The bases data refer to exchangeable bases.**

Horizont	Depth (cm)	pH (H_2O)	OM%	Ca ($cmol_c.kg^{-1}$)	Mg ($cmol_c.kg^{-1}$)	K ($cmol_c.kg^{-1}$)	Na ($cmol_c.kg^{-1}$)
A	0-31	5.4	0.79	2.4	0.7	0.25	0.23
E	31-45	4.9	0.33	1.7	0.74	0.28	0.3
Bt	45-80	5.1	0.97	8.1	3.7	0.42	0.35
BC	80-107	5.2	0.57	6.5	3.04	0.29	0.28
C	107+	5.2	0.45	7	3.33	0.3	0.29

Table 11. Chemical parameters of representative soils of the northeast sedimentary region (Rivera Unit), forested with *Eucalyptus grandis* (average of 4 sites). Source: adapted from Hernández, 2010. **O.M. (organic material) --- T.B. (total bases)= $Ca^{+2}+Mg^{+2}+K^{+}+Na^{+}$ --- C.E.C. (cationic exchangeable capacity to soil ph)= $Ca^{+2}+Mg^{+2}+K^{+}+Na^{+}+Al^{+3}+H^{+}$ --- BS% (bases saturation)=TB/CECx100 --- E.A. (exchangeable acidity) --- cmolc.kg^{-1} (centimol carga.kg^{-1})= Meq/100 g soil. The bases data refer to exchangeable bases.**

Horizont	Soils	pH (H_2O)	OM%	Ca ($cmol_c.kg^{-1}$)	Mg ($cmol_c.kg^{-1}$)	K ($cmol_c.kg^{-1}$)	Na ($cmol_c.kg^{-1}$)	T.B. ($cmol_c.kg^{-1}$)	E.A. ($cmol_c.kg^{-1}$)	C.E.C. ($cmol_c.kg^{-1}$)	B.S. (%)
A	7.32	4.4	1.90	0.59	0.3	0.15	0.3	1.34	1.29	2.62	51
B	7.32	4.5	1.47	1.4	0.87	0.19	0.36	2.82	3.21	6.04	48

Table 11 shows that Tacuarembó-Rivera zone has low content of bases. In this region of the country there is less variability between soils compared to the other zones (personal communication Agr. Eng. Ph.D. Amabelia del Pino, 2012).

Table 12. Chemical parameters of representative soils of the crystalline sierras region, forested with *Eucalyptus globulus* (average of 7 sites) Source: adapted from Hernández, 2010. **O.M. (organic material) --- T.B. (total bases)= $Ca^{+2}+Mg^{+2}+K^{+}+Na^{+}$ --- C.E.C. (cationic exchangeable capacity to soil ph)= $Ca^{+2}+Mg^{+2}+K^{+}+Na^{+}+Al^{+3}+H^{+}$ --- BS% (bases saturation)=TB/CECx100 --- E.A. (exchangeable acidity) --- cmolc.kg^{-1} (centimol carga.kg^{-1})= Meq/100 g soil. The bases data refer to exchangeable bases.**

Horizont	Soils	pH (H_2O)	OM%	Ca ($cmol_c.kg^{-1}$)	Mg ($cmol_c.kg^{-1}$)	K ($cmol_c.kg^{-1}$)	Na ($cmol_c.kg^{-1}$)	T.B. ($cmol_c.kg^{-1}$)	E.A. ($cmol_c.kg^{-1}$)	C.E.C. ($cmol_c.kg^{-1}$)	B.S. (%)
A	2.11 - 2.12	4.9	3.17	2.16	1.51	0.38	0.4	4.45	1.47	5.92	75
B	2.11 - 2.12	5.4	1.60	5.38	4.64	0.42	0.72	11.15	1.68	12.84	79

Although Table 12 provides representative soils data in the region of crystalline sierras, it should take into account that in this zone can be observed important variations between soils, since their characteristics depend on the type of rock on which were formed (personal communication Agr. Eng. Ph.D. Amabelia del Pino, 2012).

Table 13. Chemical parameters (average values) of the A horizons of representative soils of forest areas in Brazil and some forestry priority soils in Uruguay. Source: adapted from Zamalvide and Ferrando, 2010. **O.M. (organic material) --- T.B. (total bases)= Ca^{+2}+Mg^{+2}+K^{+}+Na^{+} --- C.E.C. (cationic exchangeable capacity to soil ph)= Ca^{+2}+Mg^{+2}+K^{+}+Na^{+}+Al^{+3}+H^{+} --- BS% (bases saturation)=TB/CECx100 --- cmolc.kg^{-1} (centimol carga.kg^{-1})= Meq/100 g soil. The bases data refer to exchangeable bases.**

Place	pH (H_2O)	OM%	P (ppm)	Ca ($cmol_c.kg^{-1}$)	Mg ($cmol_c.kg^{-1}$)	K ($cmol_c.kg^{-1}$)	C.E.C. ($cmol_c.kg^{-1}$)	B.S. (%)
Brasil representative soils	4,3?	1.6	2?	0.23	0.12	0.03	4.8	10
Luvisol, zone 2 (East)	5	3.8	3	4.5	2.1	0.45	11.1	55
Acrisol, zone 7 (Tacuarembó)	5.2	1.7	4	0.9	0.5	0.3	3	53
Argisol Cretácico, zone 9 (littoral)	5.5	2.5	6	3.6	1	0.3	7.7	65

In the different soil types presented in Tables 8 to 13, is observed regarding the distribution in the profile as is logical, a greater organic matter percentage in the A horizon (where are developed most of roots). On the other hand in the B horizons due to leaching process and greater clay content with retention capacity, are found larger amounts of exchangeable bases than in the A horizons.

Observing the different tables of chemical parameters in different forest regions of our country, can be noted in general terms, that the zone Tacuarembó-Rivera present noticeably smaller bases contents in soil compared to the east and littoral zone of the country. Predominant soils in the zone Tacuarembó-Rivera are Alisoles (ex- Luvisoles) and Acrisoles, belonging to the soil Desaturated Leachate order. This denomination comes from the mechanical (of clay) and chemical leaching processes from the upper horizons, resulting in a net loss of bases and a strong acidification of the profile, therefore these soils are considered the most acidic and impoverished of the country. This desaturation, not only affects the A horizon (which normally occurs in other soils) but also lower horizons, indicating that the cation release by decomposition of primary minerals is not enough to compensate the losses. These characteristics however are not an impediment to development of forest, instead the Soil and Water Division RENARE/MGAP includes the Rivera and Tacuarembó Units within the classification according to forest aptitude as a class I (land very apt for implantation of artificial forests). Chapicuy and Algorta Units belonging to the littoral forest area also are found in this category (Durán and García Préchac, 2007). Evaluation criteria in this kind of classification include the chemical properties but also, morphological, physical and associated characteristics such as slope, rockiness and stoniness (Durán, cited by Durán and García Préchac, 2007).

In Brazil (from where technological information is usually taken) plantations tend to occupy low fertility soils (Maquere, 2011) (Laclau *et al*., 2010) (Barros and Novais, Reis and Barros cited by Wadt, 2004) (Camara *et al*., 2000) as occurs in Uruguay. However, forestry priority soils in our country appear as noticeably more fertile. One of the reasons as already mentioned, is that our soils are developed on natural vegetation pastures (rare situation elsewhere), this usually associated with greater natural fertility. The levels of exchangeable bases are about 10 times larger and the base saturation of about 5 times larger in forest soils of our country compared to Brazil. These data indicate that in general terms, in uruguayan soils there are smaller number of limiting nutrients than in brazilian soils (Zamalvide and Ferrando, 2010).

Nutrient in soil versus limiting nutrients for forest growth:

In the study conducted by Zamalvide and Ferrando (2010) on commercial forest plantations of *Eucalyptus grandis* and *Eucalyptus globulus* in the main production areas of the country, with plants of about 18 months old,

foliar analysis were performed to measure nitrogen, phosphorus, potassium, calcium, magnesium, iron, manganese, copper, zinc and boron, concluding that there would be no clear limitations to growth of trees in practically none of studied sites, and even though there were no deficiencies in macronutrients, boron is detected as the element most likely to be limiting and magnesium as more limiting than potassium.
In the same direction Durán and García Préchac (2007) regarding the site quality requirements posed by Herbert, in relation to forest nutrition in plant development, suggest that this is generally not critical in Uruguay.

Meanwhile Bellote and Ferreira (1995) found that magnesium but mainly potassium measured in leaf tissue were the mineral nutrients that most limited the growth of specimens of *Eucalyptus grandis* 3 years old in 5 different sites in São Paulo state (Brazil). The author also explains that soil phosphorus content beyond the amount present in leaves influenced the growth of trees, probably because the availability of this nutrient allows an increase in potassium and magnesium absorption.

In Brazil the plantations often are established in low fertility soils, so they almost always require fertilizer applications to support the high biomass production (Maquere, 2011). This practice, although it can also be used in Uruguay, it is known that technological packages in our country need less nutrient amount than those used in Brazil soils.

3. FUNCTIONS AND FORMS OF CALCIUM AND PHOSPHORUS IN THE TREE

Each nutrient has different specific functions within tree and these affect their mobility (Fisher and Binkley, 1999). As already mentioned in the chapter on Eucalyptus nutrient content, calcium is a nutrient that has low mobility and phosphorus on the contrary is considered as a mobile nutrient within tree.

3.1. CALCIUM

Calcium plays an important regulatory role in many processes, among which are: phosphorylation of nuclear proteins; cell division; cell wall and membrane synthesis and function (which regulate nutrient flowthrough roots and both water and solute fluxes through leaf membranes); intra and intercellular signaling; protein synthesis; responses to environmental stimuli (low temperatures, gravity, insects and disease);stomatal regulation (control of water flux from foliage); and carbohydrate metabolism (McLaughlin and Wimmer, 1999). Calcium also appears to play a role in lignin synthesis processes (Eklund and Eliasson cited by McLaughlin and Wimmer, 1999).

Furthermore calcium is important in adding stability and structural integrity to biological tissues (from intercellular membranes to the cell walls of woody stems) (McLaughlin and Wimmer, 1999).
Calcium is used by the trees in the cell walls to bind organic molecules, remaining relatively immobile once incorporated into these molecules. Due to this characteristic presents limited retranslocation prior to leaf abscission (Binkley, 1993) (Fisher and Binkley, 1999).

Since calcium is so strongly involved in wood formation process and in crosslinking within wood structure, the reductions in wood calcium have the potential to affect structural properties (weakening of wood in relation to mechanical stress) as well as the rate and total quantity of wood formed. In addition, reduced lignin content in the cell walls could lead to a more fragile and brittle xylem (wood inhibition lignification is a potentially consequence of low calcium availability) (McLaughlin and Wimmer, 1999).

Moreover, calcium is essential in the plant defense against disease through maintenance of membrane integrity, signaling multiple pathways of defense through enzyme activation, release of phytoalexin (an antimicrobial agent), repair and reinforcement of damaged membranes and cell walls, and synthesis of structural barriers (McLaughlin and Wimmer, 1999). Furthermore, maintenance of membrane integrity promote also cold tolerance (membrane regulates water extrusion from the cytoplasm during cold hardening, as well as resistance to cellular dehydration during the formation of extra cellular ice crystals) (Levitt; Guy cited by McLaughlin and Wimmer, 1999).

Calcium also have other functions as activator of several enzymes (including amylase), by acting as second messenger often modifies the functions of various growth hormones and is involved in some manner in nitrogen metabolism. Faust (cited by Pallardy, 2008) indicates that some calcium deficiency disorders depend on the tissue nitrogen concentration, when the nitrogen/calcium ratio (based on element mass) was 10, metabolic disorders did not develop and when the ratio was 30, metabolic disorders were common. Calcium deficiency results in injury to meristematic regions and present symptoms as decreased root growth, chlorosis and necrosis of leaves and different fruit disorders (Pallardy, 2008).

In cell walls the calcium is found in large quantities as calcium pectate and apparently influences cell wall elasticity (Pallardy, 2008). Also could be found as exchangeable calcium at the surface of cell walls and membranes or deposited in the form of organic salts in cell vacuoles. Other calcium forms in the tree are as calcium phosphate and calcium oxalate. The general distribution of calcium forms tend to be 50% pectate calcium (basically in cell walls), 25% water soluble calcium, 15% bound with phosphate and the rest between calcium oxalate and other minor forms. In some cases the oxalate calcium form can be much larger (Binkley, 1993) (Fisher and Binkley, 1999). Saltberg *et al*. (2006) agree with this concept mentioning that a large part of the calcium present in wood can be in the form of calcium oxalate. In a study conducted by these authors in industrial eucalyptus wood chips it was found that 16% of calcium was present as calcium oxalate, but in a eucalyptus log analyzed sample 57% of the calcium was in that form. Beyond the latter value may not be representative, it shows the great variability that can exist in calcium oxalate content in eucalyptus wood (Saltberg *et al.* 2006).

The formation of calcium oxalate has been attributed to various functional needs. Gourlay and Grime cited by Zambrano *et al*. (2009) suggest that are the result of detoxification rooting medium for high calcium concentration, harmful to the cell, such as in soils with excessive calcium content. On the other hand Graustein *et al*., Malajczuk and Cromack, Entry *et al*. and Cummings *et al*. cited by Zambrano *et al*. (2009) mentioned formation of calcium oxalate as a store minerals mechanism in the plant tissue to ensure normal growth in limiting mineral soils. Authors as Franceschi and Webb cited by Zambrano *et al*. (2009) report that calcium oxalate are not inert calcium reservoirs since it can be redissolved and function as source of calcium into the cell.

Other authors attribute different functions to calcium oxalate, for example Saltz and Ward cited by Zambrano *et al*. (2009) claim that calcium oxalate formation is a plant strategy defense against herbivores organisms; regulate concentration of intracellular calcium (Franceschi cited by Zambrano *et al*., 2009); act in the detoxification of various substances like heavy metals and oxalic acid in the cell (Silva *et al*. and Mazen cited by Zambrano *et al*., 2009); and hypothetically, calcium oxalate in the eucalyptus roots and ectomycorrhizae can play a role in detoxification of toxic elements in the soil, such as aluminum (Zambrano *et al*., 2009). In the study about formation of calcium oxalate crystal induced by ectomycorrhizal fungi conducted by Zambrano *et al*. (2009), the authors observed that 52.6% of the ectomycorrhizal showed abundant calcium oxalate accumulation while in the not colonized roots the accumulation frequency was substantially lower (17.5%), indicating that mycorrhizal fungi-eucalyptus association induce calcium storing under the calcium oxalate form in host plant root system. This suggests an important role of ectomycorrhizal fungi in the plant calcium acquisition in soils with low availability of this element (Zambrano *et al*., 2009).

Surplus of calcium is accumulating as calcium oxalate crystals in cell vacuoles in leaves and woody tissue (Pallardy, 2008). According to Foelkel (2011) calcium oxalate usually occur in the parenchyma and extractive bags, therefore they are more difficult to solubilized, extracted or removed (by acid leaching).

3.2. PHOSPHORUS

Phosphorus in trees is involved in reproduction and growth plant, in root development and good fruit formation (Lugo, cited by Pozo Peñalosa, 2005). Moreover, the element phosphorus is a constituent of nucleoproteins and phospholipids, and also plays an important role in energy transfer in plants (Pallardy, 2008).

Once the phosphorus is absorbed by the tree, one or two of the ends of phosphate group is attached to the carbon chains forming single bonds (ester) or double (diester). From here phosphorus develops an important role in tree energy transformations, as well as in the synthesis of proteins and nucleotides and even in the cell replication process (Binkley, 1993)

(Fisher and Binkley, 1999). The phosphate in trees may appear in free form or bound to sugars and lipids. Phospholipids are essential constituents of the cell membrane. The important role played by phosphorus in the energy transformation in cells, occurs from the ATP molecule (adenosine triphosphate) (Binkley, 1993). By means of anhydride bonds phosphate groups are joined together, then by breaking a phosphate group from the ATP molecule (forming ADP, adenosine diphosphate) a high amount of energy from those mentioned bond is released (Binkley, 1993) (Fisher and Binkley, 1999).

Phosphorus compounds in tree present a high mobility, which allows that a significant phosphorus amount present in leaves is reabsorbed before abscission. In plant cells, phosphorus undergoes very dynamic transformations but it is estimated that practically 50% of this element is in inorganic form in the plant, being able to reduce this proportion to 25% in severe phosphorus deficiencies cases (Binkley, 1993). At become limiting the phosphorus supply, leaves can hold approximately 20% of this element in lipids, 40% in nucleic acids, 20% simple esters and 20% as free inorganic phosphate. When increasing the phosphorus supply, the largest proportional increase will take place in inorganic phosphorus (which may reach 50% of total phosphorus in leaves), being also able to find a smaller increase in lipids and esters, detrimental to the proportion in nucleic acid (Fisher and Binkley, 1999). Phosphorus deficiency could cause severe stunting of young forest trees in the absence of other visible symptoms (Pallardy, 2008).

In cells with pH close to 7, most of the free phosphate is in the form of HPO_4^{-2}, moreover the pH of leaves in many instances is between 5 and 6 so that the free phosphate exists as $H_2PO_4^-$ (Binkley, 1993).

Phosphorus absorption is enhanced by the significant increase in volume soil exploration due to root-fungus association. In this way the tree can get phosphorus from places that could not do it in uninfected root systems (Grove *et al*., 1996). It is also possible to absorb the nutrient at smaller concentrations in soil solution or from phosphorus sources which could not be used in non-mycorrhizal roots (Cooper cited by Grove *et al*., 1996). Mycorrhizal fungi and roots can produce oxalic acid, which in combination with calcium ions or releasing phosphate adsorbed on iron and aluminium oxides in soil, increase phosphorus absorption (Cromack *et al*. cited by Grove *et al*., 1996). The phosphate absorbed by mycorrhizal fungi can be stored within fungal tissue as inorganic polyphosphate (Cooper cited by Grove *et al*., 1996). When phosphorus absorption from soil is insufficient to cover tree demands, phosphorus accumulated in mycorrhizae can be remobilized to the host plant (Grove *et al*., 1996).

4. CALCIUM AND PHOSPHORUS IN THE PULP MILL

4.1. GENERAL CONSIDERATIONS

Calcium and phosphorus are considered in the pulp mill as non process elements (NPE). These are defined as chemical elements that are present in the process cycle but are not essentials to the same (have no operational role) (Foelkel, 2011) (Emunds, 2010) (Salmenoja *et al*., 2009) (Tran and Vakkilainen, 2007) (Nurmesniemi *et al*., 2005).

The effects of NPE on Kraft mill operation include increased lime kiln fuel use, reduced filtration efficiency, reduced lime mud settling, increased scaling of heat exchangers, fouling and corrosion of heat transfer surfaces in the recovery boiler, and increased use of bleaching chemicals during later stages (Salmenoja *et al*., 2009).

NPE content in different mills is dependent on process configuration and operations of each, but the underlying chemistry is the same for all Kraft mills (Gu and Edwards, 2004). As these move toward a cleaner and environment friendly processes, higher degree of closure system are used (reducing effluents, closing chemicals cycles, recycling and reusing various streams and minimization of the fresh water usage), thus accumulation of NPE in Kraft mill process streams is becoming increasingly important (Foelkel, 2011) (Doldán *et al*., 2010) (Salmenoja *et al.*, 2009).

The NPE can enter in the cycle with the wood (main source), with chemical makeup, with process water, from the bleach plant, with any waste streams that are disposed of within the process (Tran and Vakkilainen, 2007), with erosion and corrosion products of metal and refractory surfaces (Dorris, G.M. cited by Richardson *et al*., 1998), waste burning in recovery boiler (e.g. biosludge), waste burning in lime kiln (e.g. sawdust wood), fuel (e.g. fuel oil in recovery boiler and lime kiln) and contaminants such as leaves, twigs, dirt, sand, water, etc. (Foelkel, 2011).
Although the concentrations in the chips may vary a lot, eucalyptus pulp mills have normally high levels of NPE, therefore special measures have to be applied to achieve a high availability of the processes. From green liquor dregs, grits, lime mud, and recovery boiler precipitator ash (ESP), NPE can be safely taken out of the process (Salmenoja *et al*., 2009).

The NPE can be classified into three general types (based on the solubility in alkaline medium) : (1) highly soluble in alkali and therefore can build up without limit (e.g. potassium and chloride); (2) partially soluble in alkali and therefore can build up to significant levels before being naturally purged by precipitation (when concentrations reach critical levels) (e.g. **phosphorus,** aluminum, and silicon); (3) highly insoluble in alkali and thus are removed

with green liquor dregs and therefore do not build up (e.g. **calcium**, magnesium and iron) (Foelkel, 2011) (Tran and Vakkilainen, 2007).
Otherwise, Foelkel (2011) uses another classification according to NPE accumulation capacity: High accumulation (potassium, aluminum, silicon and chloride); Low accumulation and easy removal (**calcium**, **phosphorus**, magnesium and manganese).

In Table 14 are shown NPE (including calcium and phosphorus) most important sources and out-puts quantification in a eucalyptus modern pulp mill (Fray Bentos, Uruguay).

Table 14. Non-process elements most important sources and out-puts quantification (g/ADt). Source: (Doldán *et al*., 2010).

Sample point	Ca	K	Cl^-	Mn	Mg	P	Al	Si
Chips (S)	2193	914	420	62	256	121	12	24
Biosludge (S)	143	17	16	14	89	41	42	197
Unbleached pulp (O)	1440	405	13	14	207	31	14	90
Purged ESP Ash (O)	1	466	342	0.1	0.4	0.2	0.1	0.9
Returned ESP Ash (R)	12	5427	3979	2	4	2	0,8	11
Lime mud from lime filter (R)	-	58	0	130	2100	5600	170	1000
Pre-coat filter (Green liquor dregs + lime mud) (O)	2049	12	2	30	209	40	35	81

(S) Source; (O) Out-put; (R) Recycle

4.2. CALCIUM

Although the calcium is a vital element in the recovery cycle (causticizing and lime kiln), the calcium that enters in wood is considered surplus and unsuitable for the plant (Foelkel, 2011) (Emunds, 2010). For this reason, all amounts of calcium entering the pulp mill with wood, bark, water and some chemical inputs (beyond sources of calcium replacement in recovery) are considered as NPE (also calcium that brings problems outside calcium cycling in the recovery system is considered NPE)

(Foelkel, 2011). The main sources of calcium are wood, make-up lime *(Salmenoja et al., 2009)* and the industrial hardness water (Foelkel, 2011). Calcium is one of the most common and abundant non-process elements, precisely because of the high content in Eucalyptus wood and bark. Particularly, the content in the bark is so significant that contamination in chips with 0.5% of bark (dry weight) can be about 5-10% of total calcium entering the pulp mill through wood chips to the digester (Foelkel, 2011).

Calcium to be a highly alkali insoluble NPE can cause scaling problems in digester screens and heating surfaces, evaporator heating surfaces and bleaching wash equipments, but it do not accumulate in the cycle because of this insoluble compound is removed in the white and green liquor clarifier or slaker (Salmenoja *et al*., 2009) (Tran and Vakkilainen, 2007) (Richardson *et al*., 1998) (Keitaanniemi and Virkola cited by Richardson *et al*., 1998). Calcium is likely to precipitate in the form of calcium carbonate in the hot surfaces since this compound presents a reversed solubility (the solubility decreases as the temperature is increased) (Guo and Severtson cited by Emunds, 2010) (Lundqvist *et al*., 2006).

In the same direction, Foelkel (2011) explain that calcium normally precipitates as $CaCO_3$ (carbonate), $CaSO_4$ (sulfate), CaC_2O_4 (oxalate), and its removal is not difficult in the purification system of white and green liquors (it can be easily filtered, decanted and removed with the residue known as dregs and grits). Kraft pulp mills use a pre-coat of the lime mud filter to facilitate filtration of this dregs and grits. Thus, there is a continuous purging of lime mud through this stage of residue filtration, therefore calcium is rarely enriched in a Kraft mill.

In the same way, Salmenoja *et al*. (2009) explain that calcium is a process element in the lime cycle and if good clarification and filtration occurs, calcium will be confined to the lime cycle. Otherwise the same author explains that the main problem in the recovery cycle with calcium (the scaling in the evaporation plant) may be significantly reduced by heating black liquor to high temperatures (so-called deactivation process).

In the case of the fiber line, another source of calcium is the residual insoluble calcium material that cannot be removed completely by decanting or filtration of the white liquor. This calcium ends up in the fiber line and recovery circuit of the black liquor. Typical white liquor has 30 to 100 ppm of soluble calcium and 70 to 100 ppm of calcium as $CaCO_3$ result of insufficient cleaning of the white liquor. This calcium can also be problematic in the digester, diffuser, washers, white liquor storage tanks and scaling and pitch in bleaching stages (Foelkel, 2011).

Among the ways to reduce calcium deposition ($CaCO_3$) are the application of chemical treatment programs, including the use of one of three kinds of products: inhibitor precipitation, dispersant or crystal modifiers (Severtson cited by Emunds, 2010).

In bleaching, calcium precipitates as calcium carbonate, phosphate, oxalate or sulfate. Its most frequent problems are the filters and pulp wash presses, showers, sieves, screens, vacuum boxes, scrubbers, pipe curves, mixers, etc. (Foelkel, 2011).

The cellulose fibers have the ability to retain the calcium cation due to their electronegative loads. Moreover, these calcium ions can be easily washed from fibers with acid solutions. In stages of acid bleaching, is a kind of ion exchange between the fibers which retain calcium cations and H + ion of the acid bleaching (Foelkel, 2011). Therefore as calcium is soluble in acidic conditions it will dissolve in acidic chlorine (C), chlorine dioxide (D), ozone (Z), chelating (Q) and acid (A) stages (Salmenoja *et al*., 2009).

Due the constant changes in pH, temperature and consistency which the cellulose pulp suspension is subjected in bleaching stages, this is one of the most attractive areas for NPE become aggressive. The best way to minimize problems caused by calcium in these stages is preventing their entry into the bleaching (Foelkel, 2011).

In a NPE study conducted by Doldán *et al*. (2010) in a eucalyptus modern pulp mill in Fray Bentos (Uruguay) the authors observed that there is not a clear enrichment of calcium in the liquor cycle (since the amount of calcium incoming with the wood chips is higher than the circulated in the black and white liquors), thus great amount of calcium pass through with the brown stock to the bleaching plant. Doldán *et al*. observed that in the acidic stages (A/D1) almost all calcium compounds are dissolved, which are therefore discharged with the acidic effluent. Beyond this, the authors also consider that calcium concentrations inside brownstock represent a high risk of scaling on washing, knotting and screening equipments (given the high amount of pulp production, even if a small fraction of total calcium precipitated as $CaCO_3$ may result in significant brownstock scaling problems).

With regard to the problems of plant closure and use of the internal streams, Andrade (2006) concluded that calcium is the most limiting NPE for the use of white water from paper machines in the washing presses in the bleaching stage (because of the scaling problems).

4.3. PHOSPHORUS

The main sources of phosphorus in the pulp mill are wood, biosludge (Doldán *et al*., 2010) (Salmenoja *et al*., 2009) and bark contamination in chips (Foelkel, 2011).

Phosphorous will tend to build up in the lime cycle and result in poor quality lime and operational problems in the lime kiln (high dead load leads to negative impacts on energy consumption) (Doldán *et al*., 2010) (Salmenoja *et al*., 2009) (Tran and Vakkilainen, 2007). Phosphorus is precipitated as calcium phosphates in white liquor, but the solubility of this compound in green liquor is much higher than in white liquor and therefore phosphorous accumulates in lime mud (Gu and Edwards, 2004). In the same direction Taylor (2007) indicates that in the lime kiln, phosphorus has been shown at several different mills to be the most significant cause of dead load.

In lime and lime mud, phosphorus can be present as calcium phosphate compounds such as hydroxylapatite: $Ca_5(PO4)_3$ (OH). The importance of phosphorus as an important dead load component is evidenced since 1 wt% phosphorus will result in a dead load of 5.4 wt% as hydroxylapatite or roughly 9 wt% for other phosphate compounds (Taylor and McGuffie, 2006). In the same direction Foelkel (2011) mentioned that 1% phosphorus in lime is equivalent to losing about 5% of useful lime. This is because the molar ratio between phosphorus and $Ca_3(PO_4)_2$ (calcium phosphate) is 62:310 or therefore 1:5.

In the Figure 13 is shown a general diagram with sources, routes and out-puts for magnesium**, phosphorus**, aluminium and silica.

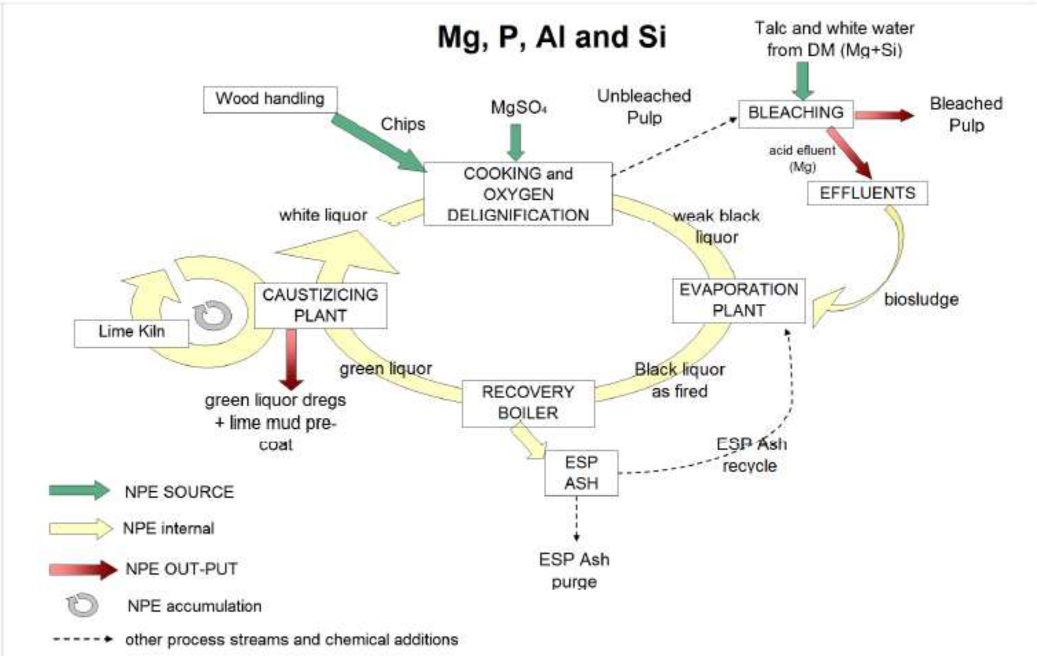


Figure 13. Magnesium, phosphorus, aluminium and silica sources, routes and out-puts general diagram. Source: Doldán *et al*., (2010).

A simple and effective way to control phosphorus in the recovery system is applying lime mud as the pre-coat of the dregs filter (Gu and Edwards, 2004). Salmenoja *et al*. (2009) indicate that phosphorus can be purged out with the lime on one side and with the ash on the other (phosphorus is enriched in the precipitator ash from lime kiln). Foelkel (2011) explain that phosphorus can be purged from the system as lime mud or through the dregs and grits removal. Doldán *et al*. (2010) agree with previous authors mention that the only output routes of phosphorus from the lime cycle are the lime mud pre-coat filter for dregs and ESP ashes from the lime kiln but phosphorus can also be controlled by purging the lime mud.

In Figure 14 are shown the levels of phosphorus in lime mud observed in a study of management of NPE in eucalyptus Kraft pulp mills *(Salmenoja et al., 2009).*

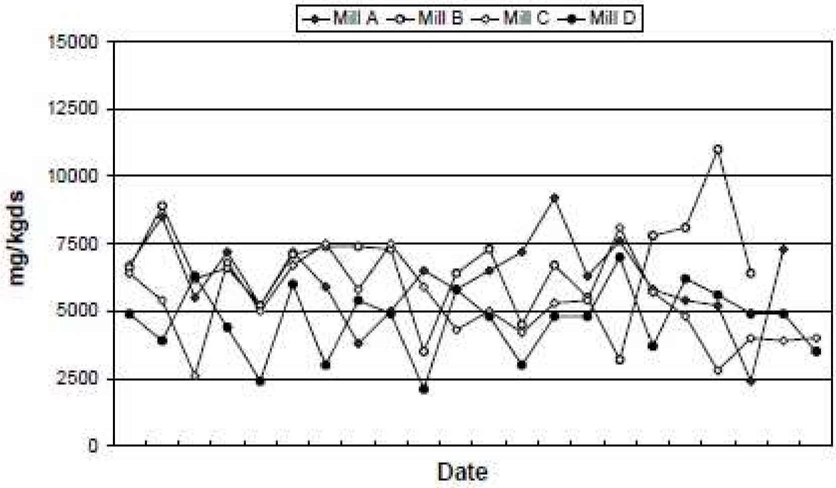


Figure 14. Lime mud phosphorus content in four Kraft pulp mills. Source: Salmenoja *et al*. (2009).

Salmenoja *et al*. (2009) explain that the variation of phosphorus in the mills is larger than with the other NPE and the level in lime mud seems to be between 2500 and 7500 mg/kgds. However, this author mentions that no special problems due phosphorous have been encountered at the mills.

5. EFFECTS OF CALCIUM IN THE KRAFT PULP DELIGNIFICATION

Are well known the problems caused by NPE in several areas of the pulp mill. Recently, some studies (Saltberg *et al.* (2009), Moreira *et al.* (2008), Moreira (2006) *and* Lundqvist *et al*. (2006)) indicate that in certain tree species the cooking process could be affected by some of this wood NPE too.

Calcium ions lead to an increase in the amount of substances (most probably lignin and lignin-carbohydrate complexes) in the pulp that contribute to the kappa number. Moreover, calcium ions have been found to coagulate lignin molecules in solution in pH 9 to 13 (Sundin and Hartler

2000). Gustavsson *et al*. cited by Sundin and Hartler (2000) found that a lower residual alkali concentration in the cook gave higher calcium content in the pulp. These authors infer that dissolved lignin is coagulated by calcium on fibers also in the cook.

Saltberg *et al*. (2009) studied the effect of calcium on delignification in birch (*Betula pendula*), aspen (*Populus tremula*) and eucalyptus (*Eucalyptus globulus*). Birch and aspen material originated from Sweden and eucalyptus from Uruguay. Delignification includes both chemical degradation and physical solubilisation of lignin. It was suggested that calcium ions decrease Kraft delignification rate by formation of calcium-lignin interaction, which lead to decrease solubility of lignin during the cook. This study discusses various treatments which modify the “availability” of calcium and therefore interfere with calcium-lignin interactions and their effect on the delignification.

One of trials was remove calcium from wood chips by acidic leaching pretreatment. Other treatments consisted in alter the solubility of calcium with the addition of carbonate or DTPA (diethylenetriaminepentaacetic acid) to the cooking liquor, and the impregnation of the wood chips with a sodium oxalate solution. The way to proceed to modify the solubility is different, while carbonate promotes the precipitation of calcium in the form of calcium carbonate, the DTPA forms soluble complexes with calcium in the black liquor. On the other side due to poorly soluble calcium oxalate formation the impregnation of wood chips with oxalate keep the loss of calcium in the impregnation at a minimum.

All these procedures were compared to each other and against a reference (impregnated with deionized water prior to cooking). It is worth noting that the deionized water impregnation gave a certain decrease in chips calcium content (most notorious for birch and aspen than for eucalyptus). The results are shown in the Figure 15.

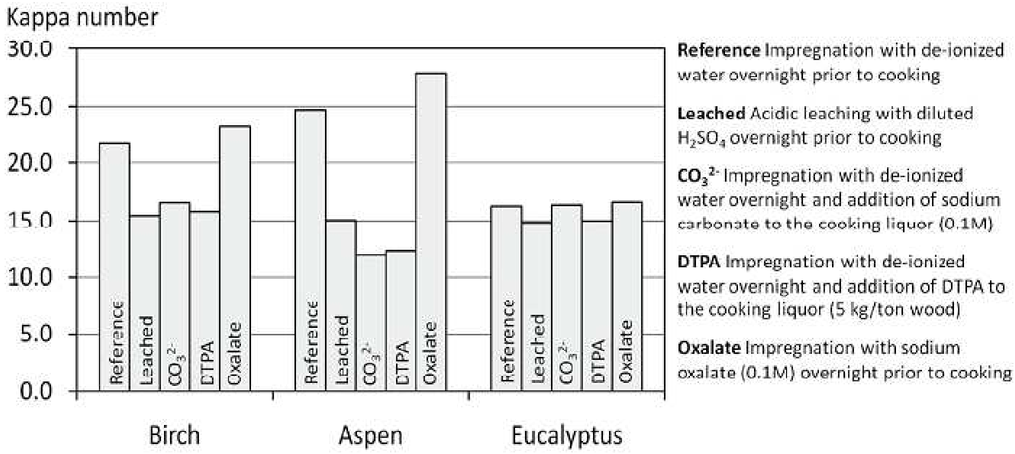


Figure 15. Influence of different procedures on kappa number after Kraft cooking of birch, aspen and eucalyptus chips. The white liquor used was carbonate-free except in the experiments labeled CO_3^{-2}. Source: Saltberg *et al*. (2009).

Figure 15 shows that the addition of carbonate and DTPA to birch cooking liquors had about the same important effect on delignification as acidic leaching, and in the case of aspen was even larger. Thus, the retarding effect of calcium on Kraft delignification is decreased by the addition of carbonate or DTPA in these two species.

In the treatment with sodium oxalate, almost all calcium was retained in the chips and this practice resulted in higher kappa number than the reference. This reinforces the idea that a higher content of calcium in birch and aspen chips retards the rate of delignification. In this case Saltberg *et al*. (2009) indicate that the presence of calcium oxalate will not counteract the calcium effect on the rate of delignification due to calcium oxalate is poorly soluble at room temperature, but at elevated temperatures, the solubility increases.

In the case of eucalyptus only small variations between the different treatments were found. Both the Kappa number and Klason lignin showed very similar results between different cooking. These results are consistent with the opinion of Salmenoja *et al*. (2009) who mentions that the calcium behavior in eucalyptus pulping and recovery may differ to other typical wood pulping raw materials, because of different calcium-binding organic black liquor compounds formation. Saltberg *et al*. meanwhile proposed different explanations for these behaviors. Firstly, the removal of calcium in the acidic leaching was only 32% from original content (significantly lower than aspen and birch with 65 and 60% respectively). This is consistent with the results obtained by Lundqvist *et al*. (2006) and Saltberg *et al*. (2006) who using the same method observed that the removal of calcium was significantly slower from *Eucalyptus globulus* than from *Betula pendula* (but differs with the results obtained by Moreira (2006) who obtained a removal of calcium in acid leaching close to 65% in *Eucalyptus* spp.). This difference in the removal of calcium between the species could explain in some way the small differences between reference, leached and oxalate (Saltberg *et al*., 2009).

On the other hand, precipitation of calcium carbonate is more limited in eucalyptus cooking so the black liquor will have higher content of calcium. This in part is explained because gallic acid and ellagic acid present in the black liquor have a propensity to form soluble calcium complexes (Lidén *et al.* cited by Saltberg *et al*., 2009). Also it is known that gallic acid and ellagic acid undergo decarboxylation reactions under Kraft pulping conditions which can partly explain the higher carbonate content in eucalyptus (Hemingway and Hillis cited by Saltberg *et al*., 2009). Furthermore phenolic substances formed from gallic acid and ellagic acid should also have a strong tendency to form complexes with calcium (Frederick and Grace cited by Saltberg *et al*., 2009). Saltberg *et al*. thus explains that the liberation of gallic acid and ellagic acid during eucalyptus Kraft cooking may affect the behavior of calcium during pulping and the impact of calcium on the solubilisation of lignin.

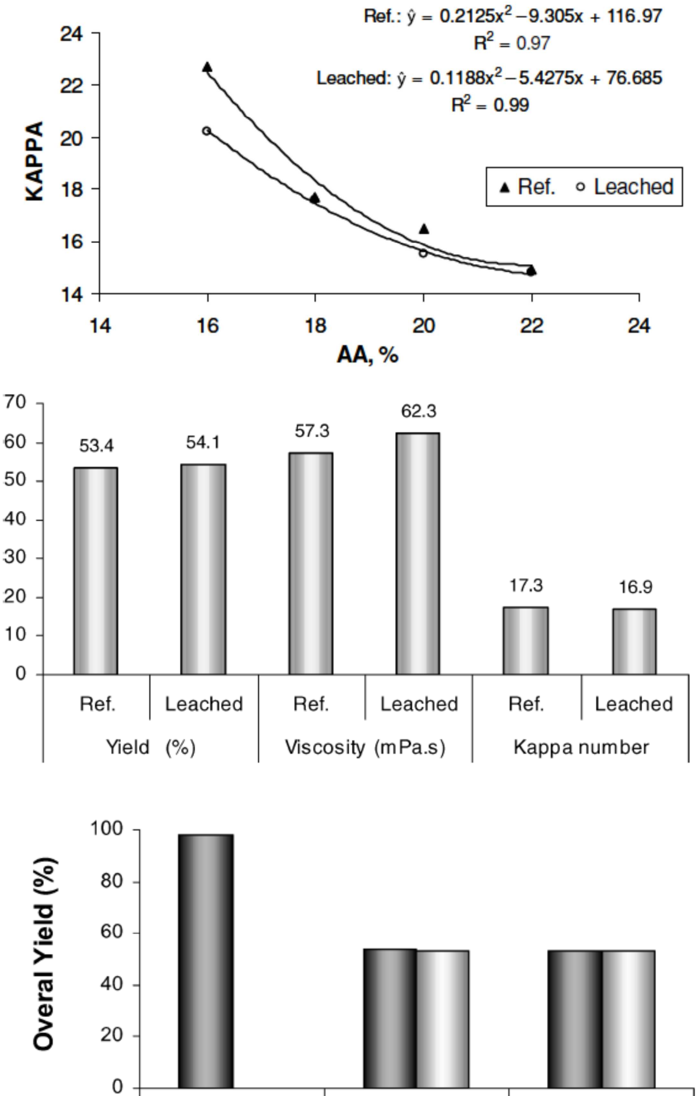
Saltberg *et al*. mentioned also the structure of xylan and the syringyl/guaiacyl ratio as features that make delignification in birch and aspen pulping probably more restricted than in the case of eucalyptus pulping. This differences influence the solubilisation of lignin during Kraft cooking, but may also influence the magnitude of the calcium effect has on the rate of delignification. In addition Saltberg *et al*. speculated that dissolved xylan in eucalyptus cooking with its higher content of uronic acids could have a higher ability to form complexes with calcium in the black liquor and thereby also the capability to eliminate the calcium effect.

In a further test, birch and eucalyptus were cooked together in the same autoclave. The results showed that the delignification of birch chips was enhanced when the cooking was performed together with eucalyptus chips. Therefore Saltberg *et al*. explain that the dissolved wood components from the eucalyptus wood may form complexes with calcium ions which may thereby prevent the negative effects exerted by calcium on the delignification of birch wood chips.

Saltberg *et al*. then conclude that the presence of calcium in Kraft cooking of aspen and birch can decrease the delignification rate. While due to the substances with calcium-chelating properties released from eucalyptus during Kraft cooking delignification, no major effect of calcium on the delignification rate are observed in this species.

Lundqvist *et al*. (2006) in a previous similar study in two of the same species *Betula pendula* and *Eucalyptus globulus*, obtained the same results as Saltberg *et al*. (2009) given that with acidic leaching of birch chips treatment prior to cooking resulted in a significant increase in the rate of delignification, but it had no effect in the case of eucalyptus. Should be noted that researchers who worked on the Saltberg *et al*. study also formed part in the previous one.

Another study was conducted by Moreira (Moreira (2006) and Moreira *et al*. (2008)) about the effect of acid leaching of *Eucalyptus* spp. wood on Kraft pulping and pulp bleachability. In Figure 16 are shown the results obtained in this research.



	Leaching	Cooking	Total
Leached	98.2	54.1	53.1
Ref.	0	53.4	53.4

Figure 16. Effect of the active alkali (AA) charge (% as NaOH) on pulp kappa number for reference and acid leached chips, Kraft cooking results for reference and acid leached chips and overall yields across chip leaching and Kraft cooking (Ref: pulp from untreated chips; Leached: pulp from acid leached chips). Source: Moreira *et al*. (2008).

In this case calcium removal in eucalyptus acid leaching was close to 65%, which was significantly higher than the above studies.

The acid leached chips had a lower pH than the reference before the cooking process and since the acid is responsible for consuming active alkali, Moreira *et al*. expected a higher alkali requirement by the acid leached sample but it did not happen. Otherwise, for a given kappa number, a lower demand of active alkali was observed in leached chips in relation to the reference (Figure 16). The authors explain this behavior because the removal of NPE (especially calcium) and organic materials from the wood chips during acid leaching given that these materials may consume significant amounts of alkali. On the other hand Moreira *et al*. mention that the breakage of wood lignin-carbohydrate bonds in the acid treatment may also explain the lower active alkali demand in the cooking.

Since the pulp derived from leached chips showed higher yield and viscosity than the pulp from reference chips (for similar kappa number) (Figure 16), Moreira *et al*. report that apparently the Kraft cooking is more selective for acid leached chips, given a possible explanation due to the calcium removal in the leaching process. Lundqvist *et al.* cited by Moreira *et al*. (2008) mentioned that the rate of delignification and the selectivity of the Kraft cooking process is hampering by calcium presence (it should be noted that Lundqvist used birch, not eucalyptus in that work cited by Moreira).

Otherwise, if overall process is take into account (acid leaching and cooking process), it can be observed that the cooking yield increase due to chip leaching effect (53.4% versus 54.1%) are offset by the weight losses (1.8%) in the previous acid leaching stage, resulting in a overall yield of 53.1% to acid leaching chip and 53.4% to the reference (Figure 16).

Moreira *et al*. (2008) then conclude that acid leaching slightly increased cooking yield, delignification efficiency, and selectivity, but overall process yield, including weight losses across acid leaching and cooking, was similar for reference and acid leached chips. Beyond this, the authors explain that more recent acid leaching studies (not yet published) using a different liquor to wood ratio (3.5/1) result in yield losses of 0.8% after leaching, significantly lower that in this case (1.8%) derivates from a 10/1 liquor to wood ratio (apparently too high and harmful to yield).

In a previous publication on the same study (Moreira, 2006) the author calculates the expected brown pulp calcium content (from chips calcium removal proportion in acid leaching and Kraft cooking yield). These expected values were 283 ppm of calcium to the reference and 99 ppm of calcium to the brown pulp from acid leaching chips. However the real values measured in the brown pulp were 2324 ppm calcium in the reference pulp and 2267 ppm calcium in the pulp resulting of the acid leaching chips. Based in this fact, Moreira (2006) explains that there was contamination with calcium during cooking, probably coming from equipment and the water used.

6. CONCLUSIONS OF THE LITERATURE REVIEW

The nutrient content in any forestry plantation in general and in *Eucalyptus* genus in particular depends on several factors, among which are: the species, genotype, plantation age, plantation silvicultural management, site quality (fertility, porosity, soil moisture, etc.) and climatic conditions.

The *Eucalyptus* genus because of its high growth rate is presented as great soil nutrients demanding but considerable nutrient content variations exist between different eucalyptus species and also within the same species.

Minerals are found in tree in amounts that vary considerably depending on the part of tree under study. With older age the biomass proportion in stem will be larger at the expense of the branches, leaves, bark and roots proportion.

Nutrient utilization efficiency increases with increasing rotation age (greater biomass produced per unit of nutrient). Generally it can be say that wood is very efficient in the use of phosphorus, and leaves and bark are very inefficient in the use of nitrogen and calcium respectively. Calcium behaves contrary to other nutrient, increasing accumulation with increasing age of tree. Nutrient retranslocation from senescing or dead tissue (leaves, heartwood or bark) to growing tissues is one of the ways to increase utilization efficiency of limited nutrients by trees. The retranslocation importance depends on the mobility of each nutrient.

In both uruguayan and foreign works calcium is the nutrient most notoriously extracted by trees, followed by potassium and nitrogen, magnesium and finally phosphorus. Also in both uruguayan and foreign works calcium was the most variability nutrient within tree, being found in very high concentrations in bark and significantly smaller in logs. On the other hand phosphorus showed larger concentrations in leaves and smaller but similar to each other compartments.

Calcium has generally larger concentrations in all compartments in uruguayan works than in foreign works and although in both cases is wood compartment that presents smallest concentrations for all nutrient, it is observed except for calcium and magnesium smaller nutrient concentration in uruguayan works for this compartment.

There are different views about the nutrient distribution along stem in both uruguayan and foreign works founded different results depending on species, assessed nutrient and study site.

Most attention in the soil nutrients study should focus on the A horizon, since it is in the eucalyptus forested soil surface where there are the highest organic matter, nutrients and roots concentrations. Also is important to consider the nutrient amount in rooting depth. Furthermore, there are many complicated interactions among various mineral nutrients, therefore one element can modify absorption and utilization of others.

The forest priority soils in Uruguay are those lands with forestry aptness that by their conditions of soil, aptitude, weather, location and other characteristics are unsuitable for any other use or permanent and profitable purpose. These soils have low nutrient availability for being very acid, with low levels of bases, medium to light texture and low organic matter content.

Soils assigned to forest production in Uruguay are distributed in the following physiographic areas: midwest sedimentary region (Littoral), northeast sedimentary region (Tacuarembó-Rivera) and the crystalline sierras (east zone of the country), each of which presents a geological substrate, macro relief and soil associations particular of each. Within the littoral zone there are variations between the characteristics of differents soils. Also in the crystalline sierras region can be observed important variations between soils, since their characteristics depend on the type of rock on which were formed. On the other hand the Tacuarembó-Rivera zone presents the smallest variability between soils compared to the other zones.

In general terms the Tacuarembó-Rivera zone present noticeably smaller bases contents in soil compared to the east and littoral zone. These characteristics however are not an impediment to development of forest. The Rivera and Tacuarembó Units are include within the classification according to forest aptitude as a class I (land very apt for implantation of artificial forests). Chapicuy and Algorta Units belonging to the littoral forest area also are found in this category. Evaluation criteria in this kind of classification include the chemical properties but also, morphological, physical and associated characteristics such as slope, rockiness and stoniness.

In Brazil plantations tend to occupy low fertility soils as occurs in Uruguay. However, forestry priority soils in our country appear as noticeably more fertile. The levels of exchangeable bases are about 10 times larger and the base saturation of about 5 times larger in forest soils of our country compared to Brazil. These data indicate that in general terms, in uruguayan soils there are smaller number of limiting nutrients than in brazilian soils. For this reason the plantations in Brazil almost always require fertilizer applications to support the high biomass production. This practice, although it can also be used in Uruguay, it is known that technological packages in our country need less nutrient amount than those used in Brazil soils. Studies conducted in the main production areas of our country concluded that there would be no clear limitations to growth of trees in practically none of studied sites and it is suggest that forest nutrition is generally not critical in Uruguay.

Each nutrient has different specific functions within tree and these affect their mobility in the same, calcium is a nutrient that has low mobility and phosphorus on the contrary is considered as a mobile nutrient within tree.

Calcium is important in adding stability and structural integrity to biological tissues, is essential in plant defense against disease and environmental factors, and plays an important regulatory role in many processes. The general distribution of calcium forms tend to be 50% pectate calcium (basically in cell walls), 25% water soluble calcium, 15% bound with phosphate and the rest between calcium oxalate and other minor forms. In some cases the oxalate calcium form can be much larger.

Phosphorus plays an important role in energy transfer in plants, is a constituent of nucleoproteins and phospholipids and is involved in reproduction and growth plant. In plant cells, phosphorus undergoes very dynamic transformations but it is estimated that practically 50% of this element is in inorganic form in the plant.

Because of the high content in eucalyptus wood calcium is one of the most common and abundant NPE, other calcium sources are make-up lime, the industrial hardness water and bark contamination in chips. Calcium to be a highly alkali insoluble NPE can cause scaling problems in digester screens and heating surfaces, evaporator heating surfaces and bleaching wash equipments, but it do not accumulate in the cycle because of this insoluble compound is removed in the white and green liquor clarifier or slaker.

The main phosphorus sources in pulp mill are wood, biosludge and bark contamination in chips. Phosphorous will tend to build up in the lime cycle and result in poor quality lime and operational problems in the lime kiln (high dead load leads to negative impacts on energy consumption).

Some studies indicate that in certain tree species the cooking process could be affected by calcium content. It was suggested that calcium ions decrease Kraft delignification rate by formation of calcium-lignin interaction, which lead to decrease solubility of lignin during the cook. The different treatments used to modify the “availability” of calcium (remove calcium from wood chips by acidic leaching, alter the solubility of calcium with the addition of carbonate or DTPA to the cooking liquor, and the impregnation of wood chips with a sodium oxalate solution) reinforced the idea that a higher content of calcium in birch and aspen chips decrease the delignification rate but in the case of eucalyptus only small variations between the different treatments were found. Formation of different bindings between calcium and substances released from eucalyptus during Kraft cooking delignification is exposed as explanation for the absence or reduction of the calcium effect in this species.

EXPERIMENTAL PART

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Calcium effect on the Kraft pulp delignification of *Eucalyptus spp.*

Ismael Fariña,* [a] Ulla Jansson,[b] María Noel Cabrera,[c] Javier Doldán[d]

Previous studies indicate that in *Populus tremula* and *Betula pendula* the cooking process could be affected by calcium content. It is suggested that calcium ions decrease Kraft delignification rate by formation of calcium-lignin interaction, which lead to decrease solubility of lignin during the process. In *Eucalyptus globulus*, formation of different bindings between calcium and substances released from this species during Kraft cooking delignification is exposed as explanation for the absence or reduction of the calcium effect. The *Eucalyptus* genus in Uruguay is considered a heavy consumer of soil nutrients due to its high growing rate, even though appreciable variations in nutrient content exists between different *Eucalyptus* species and within the same species. This work studies the effect of calcium on the Kraft delignification of five *Eucalyptus dunnii*, four *Eucalyptus globulus* and three *Eucalyptus grandis* of different age, soil type and geographical Uruguayan areas. The results suggest that there is a detrimental influence of calcium on the performance of the Kraft process in the *Eucalyptus* genus since higher wood calcium content gives lower yield at constant Kappa number, and higher Kappa number and lower ISO brightness at constant cooking conditions. Important differences among species were found in wood calcium content, *E. dunnii* presented higher values and a wider range than *E. globulus* and *E. grandis*, so the calcium detrimental effect in Kraft process is clearer observed in *E. dunnii* samples.

Keywords: Kraft pulping, Calcium, Eucalyptus

*Contact information: a: Departamento Forestal, Laboratorio Tecnológico del Uruguay, Montevideo-Uruguay, ifarina@latu.org.uy; b: Stora Enso Biomaterials, Karlstad Sweden, Ulla.Jansson@storaenso.com; c: Ingeniería de Procesos Forestales, Instituto de Ingeniería Química, Facultad de Ingeniería-UDELAR, ncabrera@fing.edu.uy; d: Departamento Forestal, Laboratorio Tecnológico del Uruguay, Montevideo-Uruguay, jdoldan@latu.org.uy.*Corresponding author:.*

INTRODUCTION

A study conducted by Saltberg *et al.* (2009) indicate that in *Populus tremula* and *Betula pendula* the cooking process could be affected by calcium presence. It is suggested that calcium ions decrease Kraft delignification rate by formation of calcium-lignin interaction, which lead to decrease solubility of lignin during the process. In *Eucalyptus globulus*, formation of different bindings between calcium and substances released from this species during Kraft cooking delignification is exposed as explanation for the absence or reduction of the calcium effect. Lidén *et al.* and Frederick and Grace (both cited by Saltberg *et al.* (2009)) mention that the presence of gallic acid, ellagic acid and phenolic substances (formed from these acids) in the eucalyptus black liquor have a propensity to form calcium complexes. In addition to this, Saltberg *et al.* (2009) speculated that dissolved xylan in eucalyptus cooking (with high content of uronic acids) could have an important ability to form complexes with calcium in the black liquor and thereby also the capability to eliminate the calcium effect. These concepts are consistent with the opinion of Salmenoja *et al.* (2009) who mentions that calcium behavior in eucalyptus pulping and recovery may differ to other typical wood pulping raw materials, because of different calcium-binding organic black liquor compounds formation. Lundqvist *et al.* (2006) in a previous work obtained the same results as Saltberg *et al*. (2009) for samples of *Betula pendula* and *Eucalyptus globulus.* They perform an acid leaching prior to cooking, with the aim of reduce the content of calcium and other non process elements, this resulted in a significant increase in the rate of delignification of *Betula pendula*, but it had no effect in the case of *Eucalyptus globulus*. Meanwhile Moreira (2006) and Moreira *et al.* (2008) conducted a study about the effect of acid leaching of *Eucalyptus spp.* wood on Kraft pulping and conclude that acid leaching slightly increased cooking yield, delignification efficiency, and selectivity, but overall process yield was similar for reference and acid leached chips, including weight losses across acid leaching and cooking.

The Eucalyptus genus in Uruguay because of its high growth rate is presented as great soil nutrients demanding, but considerable nutrient content variations can exist between different eucalyptus species and also within the same species. Calcium is the nutrient most extracted by trees, but its amounts vary considerably depending on the part of tree, being found in very high concentrations in bark and significantly smaller in logs (Foelkel, 2011; Hernández *et al.*, 2009; Gonzalez 2008; Foelkel, 2005; Freitas *et al.*, 2004; Schumacher *et al.*, 2001; Brañas *et al.*, 2000). This work studies the effect of calcium on the Kraft pulp delignification of *Eucalyptus spp.*

EXPERIMENTAL

Materials and Methods

For this study 12 samples of 3 important eucalyptus species in Kraft pulping industry were selected (5 *Eucalyptus dunnii*, 4 *Eucalyptus globulus* and 3 *Eucalyptus grandis*). In order to obtain the greatest possible wood calcium content variation, samples of different ages, soils (Coneat groups: National Commission of Land Agro-economic Study) and Uruguayan geographical areas were selected. In the Table 1 is shown the information about trees.

Table 1. Information about the samples used in this work.

Code	Species	Age (years)	Soil Type (Coneat)	Geografical area
DU-4	*E. dunnii*	14	9.1	Litoral north
DU-8	*E. dunnii*	14	9.3	Litoral north
DU-9	*E. dunnii*	10	9.3	Litoral south
DU-24	*E. dunnii*	14	2.21	East centre
DU-28	*E. dunnii*	14	9.1	Litoral north
GL-6	*E. globulus*	14	9.3	Litoral north
GL-12	*E. globulus*	10	9.3	Centre
GL-14	*E. globulus*	14	2.21	East centre
GL-17	*E. globulus*	10	2.21	East
GR-1	*E. grandis*	8	9.3	Litoral south
GR-3	*E. grandis*	16	9.3	Litoral north
GR-25	*E. grandis*	14	2.21	East centre

Each sample is composed of 10 trees cut to one sixth of commercial height from where it was obtained a log of a meter long from each one. The logs were sawn, chipped, homogenized, dried below 20% moisture and stored for posterior studies.

The Kraft cookings were performed in a rotative autoclave with four capsules of 1.5 liters capacity each. With the aim to improve the liquor impregnation during the Kraft process, the chips were immersed in water at 80°C for 30 minutes prior to cooking. The constant cooking factors utilized were:

- Amount of dry chips: 200 grams
- Chips water impregnation: 30 minutes at 80 ºC
- Max. Temperature: 155 ºC
- Time to reach Max. Temperature: 45 minutes
- Time at Max. Temperature: depend on H factor
- Sulphidity: 34%
- Liquor to Wood Ratio: 3.5

The Table 2 shows the variable cooking conditions used in the Kraft process.

Table 2. Variable cooking conditions used in this work.

Cooking conditions				
Specie	**H-factor**	**Efective Alcali (%) as NaOH**	**Alternative H-factor**	**Alternative Efective Alcali (%) as NaOH**
E. globulus	365	14.5		
	365	15.0		
	500	17.5		
E. grandis	365	15.0		
	500	17.5		
	600	18.5		
E. dunnii	365	15.0	700	18.5
	500	17.5		
	600	18.5		

Each sample was processed in 3 different Kraft cooking conditions (H factor and effective alkali) looking for a Kappa number near to 18 (normally used in mills) in the intermediate condition, and upper and lower Kappa number in the "lighter" and "harder" cooking conditions respectively. Due to the characteristics of each species the cooking conditions to obtain the target Kappa number were different for the 3 species. It is known that E. globulus requires lighter cooking conditions than E. grandis and E. dunnii but, in order to compare, the HF 500/EA 17.5% cooking condition was chosen in E. globulus to have a common condition for all species.

Samples of black liquor were taken after the Kraft cooking for ICP (Inductively Coupled Plasma Optical Emission Spectrometry) and residual alkali (according to SCAN-N 33:94) measurement. The resultant pulp was washed in cloth bags with softened (calcium free) water and disintegrated in pulper to 20,000 revolutions. After that, a pulp sample was obtained for ICP measurement. The rest of pulp was processed in a Somerville screening apparatus (according to internal Latu standard ITR.PFO.023).

The total yield was calculated and the Kappa number was determinate according to standard Tappi 236 om-06.

To determinate the amount of calcium in each sample an Optima 4300 DV Perkin Elmer Instruments ICP was utilized, performed according to Latu internal ITR ESPEC 043 based on ISO 11885. The chips samples were milled in 2 mills (first coarse grinding and then fine). Previously ICP measurement, milled wood, pulp and black liquor were processed in nitric acid and peroxide digestions, all in duplicate, based on AWPA standard A-04 digestion method 2, SCAN-N 22:96 and internal Stora Enso

Karlstad Research Centre standard. Given the characteristics of the ICP equipment and treatments necessary to process the samples, determinations of calcium have an uncertainty of 5 percent (this will be shown in the Figures with the error bars). These calculations are based on "Quantifying Uncertainty in Analytical Measurement", EURACHEM / CITAC Guide CG 4, Second Edition, 2000, with 95% confidence, k=2.

The Klason lignin was measured in all wood samples by Near Infrared Spectroscopy (NIR, the equipment was calibrated for this test using standard Tappi T 222 om-02 in the conventional determination). The ISO brightness (according to internal Latu standard PEC.PFO.005 based on UNIT-NM-ISO 2470:2001) were determinate for all pulp samples. The hexenuronic acid (according to standard Tappi 282 pm 07) was measured in pulps resulting from the cooking condition H Factor 500 and effective alkali 17.5%.

RESULTS AND DISCUSSION

In Table 3 are presented the results of calcium wood contents of samples utilized in this work.

Table 3. Calcium wood content by species, age, soil type and geographical area.

Code	Species	Age (years)	Soil Type (Coneat)	Geografical area	Ca in wood (mg/kg)
DU-4	*E. dunnii*	14	9.1	Litoral north	1809
DU-8	*E. dunnii*	14	9.3	Litoral north	3658
DU-9	*E. dunnii*	10	9.3	Litoral south	4275
DU-24	*E. dunnii*	14	2.21	East centre	2133
DU-28	*E. dunnii*	14	9.1	Litoral north	2607
GL-6	*E. globulus*	14	9.3	Litoral north	934
GL-12	*E. globulus*	10	9.3	Centre	1358
GL-14	*E. globulus*	14	2.21	East centre	911
GL-17	*E. globulus*	10	2.21	East	926
GR-1	*E. grandis*	8	9.3	Litoral south	919
GR-3	*E. grandis*	16	9.3	Litoral north	938
GR-25	*E. grandis*	14	2.21	East centre	746

Table 3 shows an important variation among species and within the same species in wood calcium content in our country. *E. dunnii* presented more wood calcium content and more variability than *E. grandis* and *E. globulus*. In the three species under study the amount of calcium in wood shows to be closely related to soil type (CONEAT). The trees on 9.3 soils show higher calcium content than others soils.

In reference to the Kraft cooking results, residual alkali at the end of process has impact on resulting yield and Kappa number, for this reason is important to take it into account and compare different samples that they have a residual alkali within a limited range.

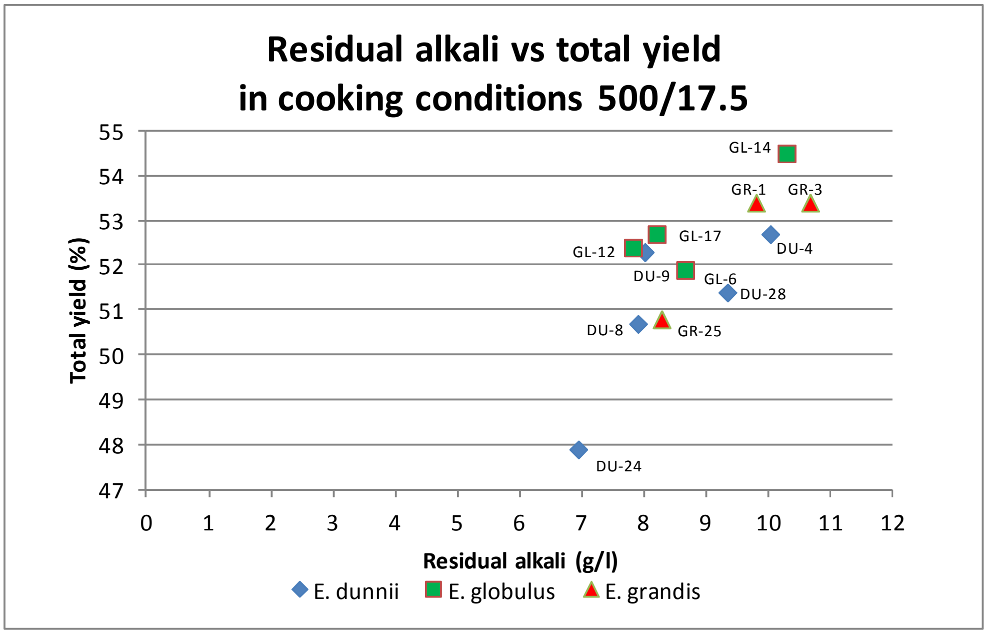

Figure 1. Residual alkali vs. total yield in HF 500/EA 17.5 cooking conditions for all species.

Figure 1 shows that the values of residual alkali for each species are within a limited range in the different samples. In Figure 2 is shown the total yield (at Kappa number 18 calculated on the basis of the three cooking of each sample) vs. wood calcium content.

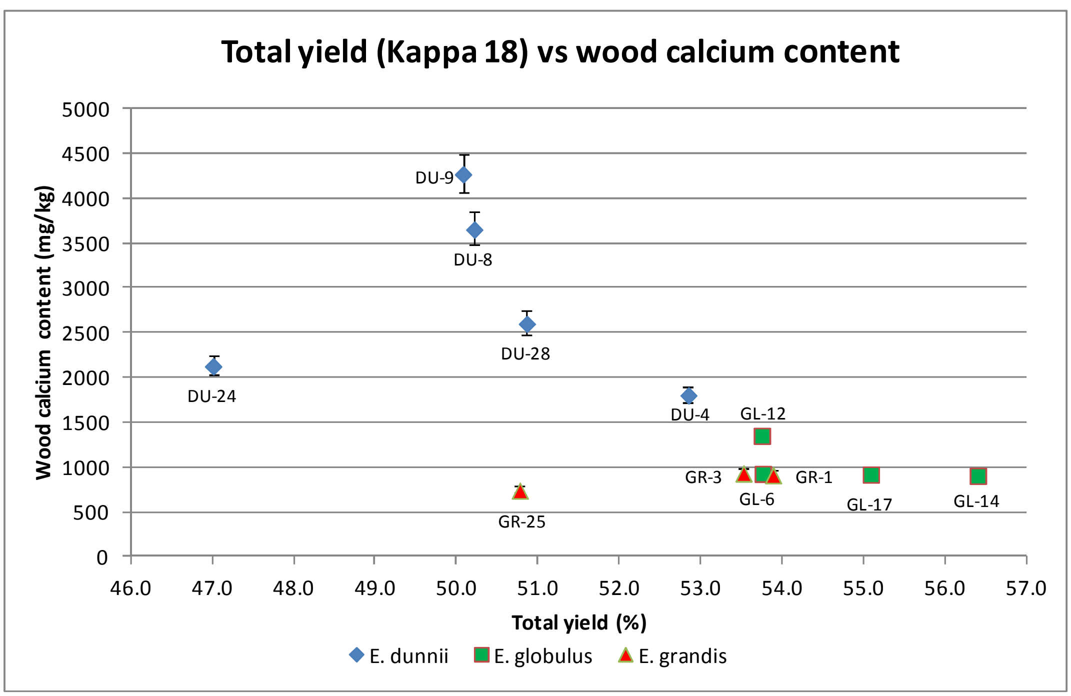

Figure 2. Total yield (Kappa number 18) vs. wood calcium content for the three species.

As expected, in Figure 2 is observed that *E. globulus* showed higher pulp yield average than the other species at the same Kappa number. Furthermore there is a tendency, higher wood calcium content gives lower yield at constant Kappa number. 2 of the 12 samples clearly deviate from this behavior (samples DU-24 and GR-25). The sample DU-9 did not reach Kappa number 18 even in the most extreme cooking conditions (HF 700/EA 18.5) used in this work. The data in this sample is obtained by extrapolation, so if we will applied more severe conditions to reach Kappa 18, the yield may be somewhat different from figure 2 (probably lower).

In Figure 3 is presented the relation between wood calcium content and Kappa number obtained in the HF 500/EA 17.5% cooking condition (the only condition used in all species).

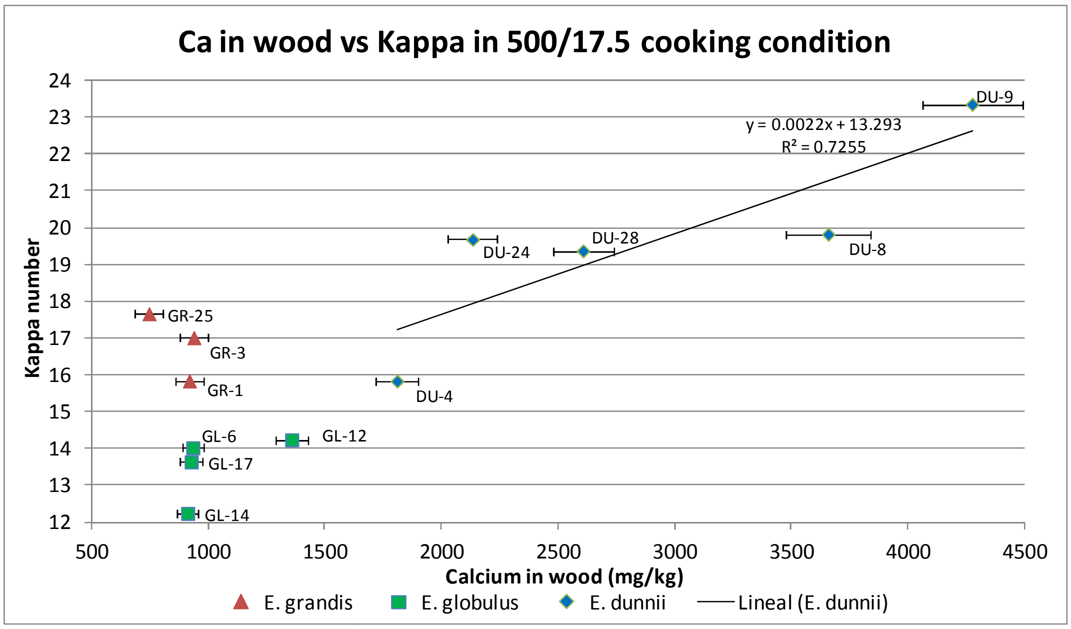

Figure 3. Calcium in wood vs. Kappa number in HF 500/EA 17.5% cooking condition.

Figure 3 shows that *E. dunnii* presented higher Kappa number average at constant cooking conditions than *E. grandis* and the latter higher than *E. globulus*. Moreover is observed that higher wood calcium content gives higher Kappa number at constant cooking conditions (HF 500/EA 17.5%). As in wood calcium content, *E. dunnii* presented a wider Kappa number range than *E. globulus* and E. *grandis*. In the latter two species with smaller wood calcium range, the impact on Kappa number is not so clear.

On the other hand the HF 500/EA 17.5% cooking conditions is too hard for *E. globulus* so the potential calcium cooking effect is not observed so clearly in this cooking condition. Therefore in the Figure 4 are presented the Kappa number obtained in the HF 365/EA 15.0% cooking condition in function of the calcium content in wood (in this condition *E. globulus* present Kappa number near to 18).

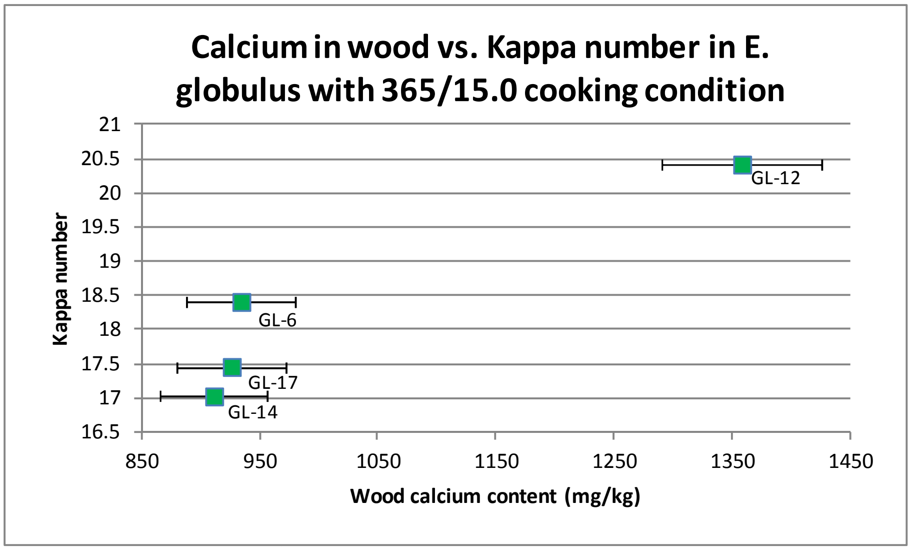

Figure 4. *E. globulus* wood calcium content vs. Kappa number in HF 365/EA 15.0% cooking condition.

In Figure 4 is observed that the samples GL-6, GL-14 and GL-17 present comparable wood calcium content (can be considered equal considering the ICP error measurement) while sample GL-12 with a bigger calcium content obtained higher Kappa number than the first at the same cooking conditions. The residual alkali in *E. globulus* samples are also in a narrow range for this cooking conditions (GL-6 3.48 g/l, GL-12 4.01 g/l, GL-14 4.47 g/l and GL-17 4.01 g/l).

In the next table and figures are presented wood and pulp characteristics of the samples used in this work.

Table 4. Calcium in wood, Kappa number, total yield, basic gravity and Klason lignin in wood of the samples used in this work.

Species - code	Ca in wood (mg/kg)	Nº Kappa in 500/17.5 condition	Total yield kappa 18 (%)	Basic Gravity in chips (g/cm^3)	Klason lignin (%±0.4)
DU-4	1809	15.83	52.8	0.521	22.1
DU-8	3658	19.82	50.2	0.513	22.1
DU-9	4275	23.35	50.1	0.518	22.2
DU-24	2133	19.68	47.0	0.464	24.4
DU-28	2607	19.37	50.9	0.530	21.7
GL-6	934	14.02	53.8	0.529	22.4
GL-12	1358	14.24	53.7	0.529	22.1
GL-14	911	12.24	56.4	0.561	22.4
GL-17	926	13.64	55.1	0.527	22.1
GR-1	919	15.84	53.9	0.402	23.8
GR-3	938	17.01	53.5	0.398	24.9
GR-25	746	17.66	50.8	0.377	25.8

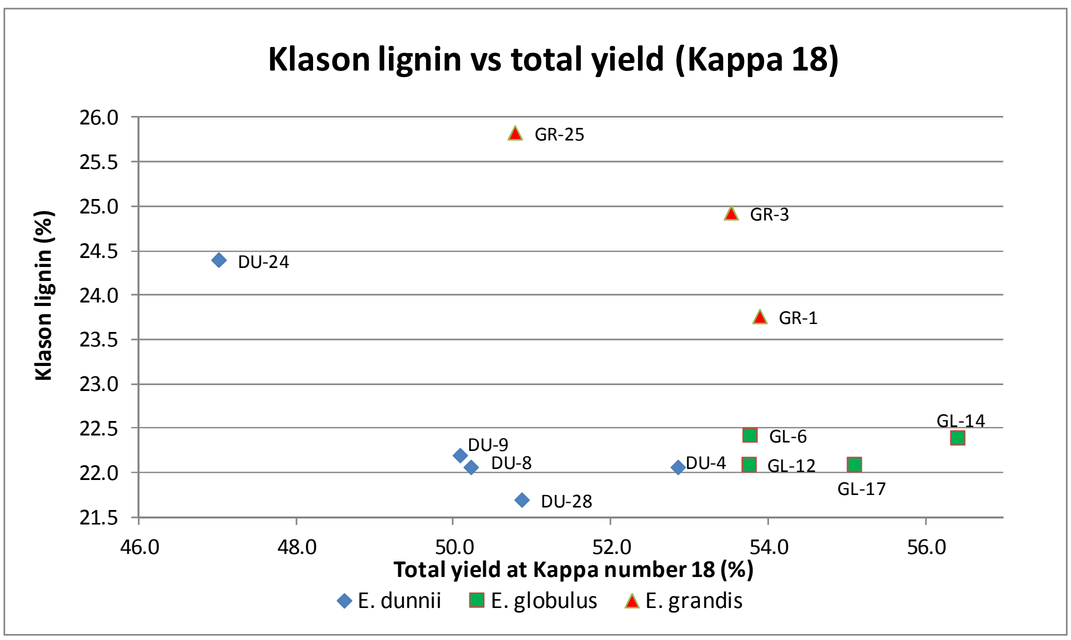

Figure 5. Klason lignin vs. total yield (Kappa number 18) for *E. globulus*, *E. dunnii* and *E. grandis*.

E. globulus and *E. dunnii* present a reduced Klason lignin range (except for the sample DU-24) while *E. grandis* that has higher values for this parameter than the other 2 species, show that the samples with higher Klason lignin have lower total yield. An interesting observation is that the 2 samples that clearly deviate from tendency where higher wood calcium content gives lower yield at constant Kappa number (DU-24 and GR-25 in figure 2) present the highest Klason lignin values in their species, which may explain such behavior. Also these two samples showed the lowest yield of its species (both samples come from east center geographical area, soil type coneat 2.21 and are 14 years old).

If we leave out from discussing the Klason lignin factor, the Kappa number differences could be explained by the wood calcium content. The next figure shows the behavior of *E. dunnii* samples without DU-24 sample.

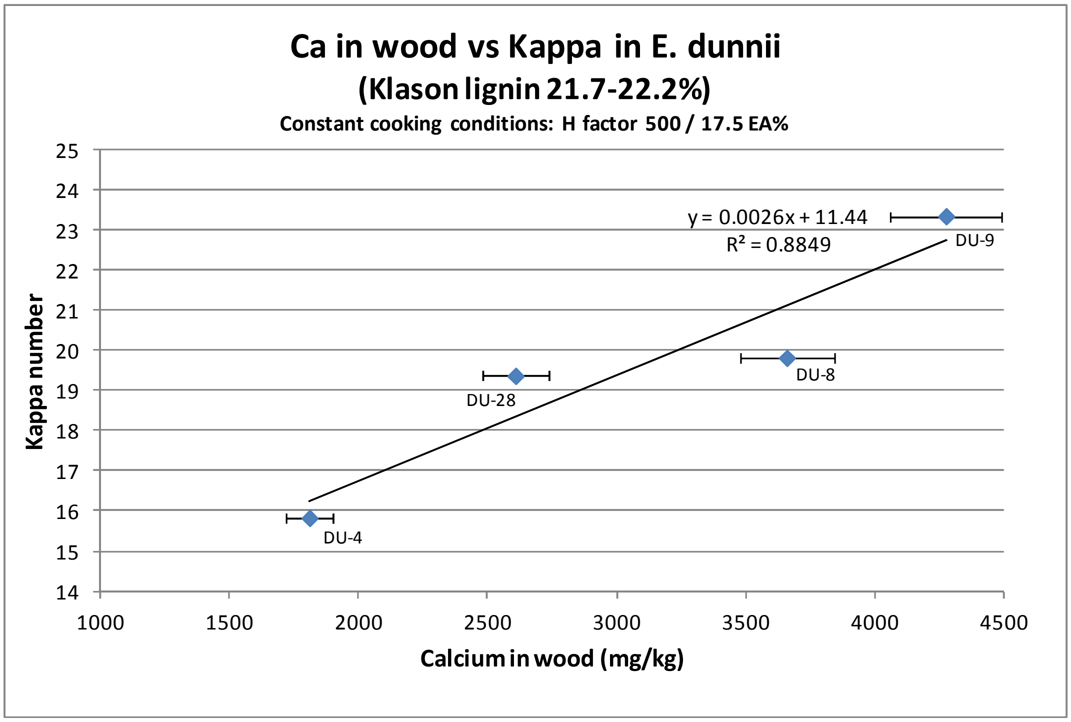

Figure 6. Wood calcium content vs. Kappa number in *E. dunnii* with similar Klason lignin at constant cooking conditions.

In figure 6 it is noted that when comparing the sample with a similar Klason lignin graphical adjustment improves (R^2 in Figure 3 including sample DU-24 was 0.7255).

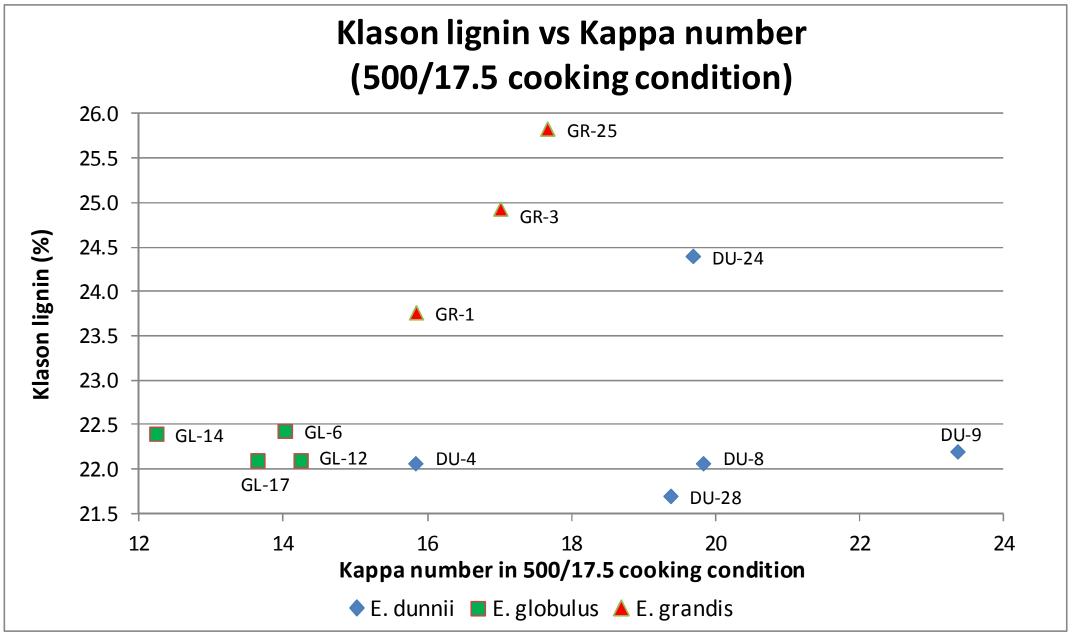

Figure 7. Klason lignin vs. Kappa number in HF 500/EA 17.5% cooking condition.

Figure 7 shows that Klason lignin vs. Kappa number do not have a clear trend, except for *E. grandis* where higher Klason lignin (%) results in higher Kappa number at constant cooking conditions. Klason lignin in *E. globulus* and *E. dunnii* present a small range except for DU-24, so as mentioned above differences in kappa number within this two species could be explain by the wood calcium content. To complement these data it would be interesting in future research, to study the chemical structure of lignin (e.g. syringyl/guaiacyl ratio) present in each sample.

Kappa number may be affected by the presence of hexenuronic acids and thus not represent residual lignin content in pulp appropriately. It is important to take into account when considering for instance a sample with a high Kappa number that the value is due to the residual lignin and not to the presence of hexenuronic acids.

In the next table are presented hexenuronic acids content, Kappa number and Klason lignin of the samples used in this work.

Table 5. Hexenuronic acids, Kappa number and Klason lignin of the samples used in this work.

Species - Code	Cooking condition	Hexenuronic acids C (umol/g)	Kappa number	Klason lignin (%±0.4)
DU-4	500 / 17.5	71.5	15.83	22.1
DU-8	500 / 17.5	74.4	19.82	22.1
DU-9	500 / 17.5	70.4	23.35	22.2
DU-24	500 / 17.5	79.4	19.68	24.4
DU-28	500 / 17.5	80.8	19.37	21.7
GL-6	500 / 17.5	69.7	14.02	22.4
GL-12	500 / 17.5	72.8	14.24	22.1
GL-14	500 / 17.5	69.5	12.24	22.4
GL-17	500 / 17.5	70.1	13.64	22.1
GR-1	500 / 17.5	88.6	15.84	23.8
GR-3	500 / 17.5	81.1	17.01	24.9
GR-25	500 / 17.5	93.7	17.66	25.8

As in Klason lignin, *E. grandis* presented the highest values of hexenuronic acids. Anyway do not show a clear trend between Kappa number and hexenuronic acids for any species. For example samples DU-4 and DU-9 with the lowest and highest Kappa number values respectively, show a similarly hexenuronic acids content. So the high Kappa number of sample DU-9 would not be explained by this factor. On the other hand if we compare e.g. DU-8 and DU-28 with a similar Kappa number we see that DU-28 could potentially have slightly less residual lignin in pulp than DU-8 but these differences do not seem substantial and do not change the conclusions about the figures shown above.

No important differences are observed in the hexenuronic acids content between samples of *E. globulus* in this cooking condition. It should be noted that in the case of this species it would be more appropriate to measure hexenuronic acids in the pulp resulting from the cooking condition 365/15 as is shown in Figure 4. Anyway, considering that all samples of *E. globulus* have very similar Klason lignin values (Table 5) we can infer that the Kappa number value of sample GL-12 could be explained by their wood calcium content (Figure 4).

The pulp ISO brightness depends on the residual lignin (among other factors), thus this parameter could be used as another reference of the performance of the laboratory cooking process. The Figure 8 shows ISO brightness vs. wood calcium content in the same cooking conditions as in Figure 3. In that figure it was observed for *E. dunnii* that the samples with higher calcium content had higher Kappa number values (hence higher residual lignin).

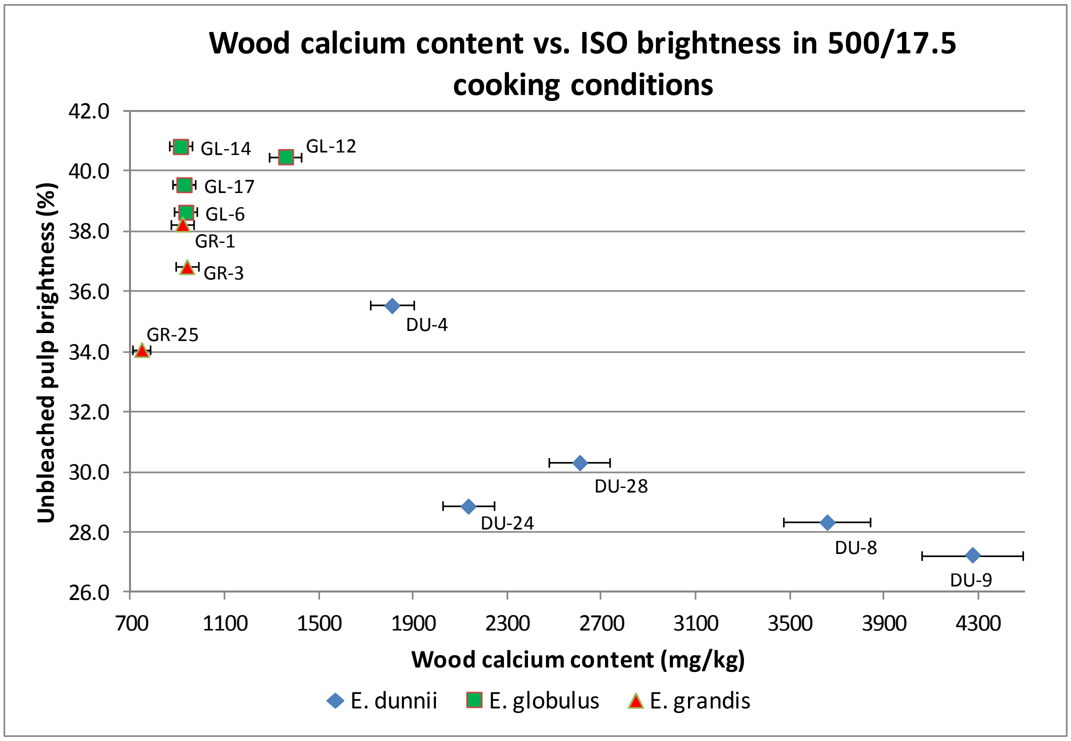

Figure 8. ISO brightness vs. wood calcium content in HF 500/EA 17.5% cooking condition.

In the same sense Figure 9 presents the ISO brightness vs. Kappa number in HF 500/EA 17.5% cooking condition.

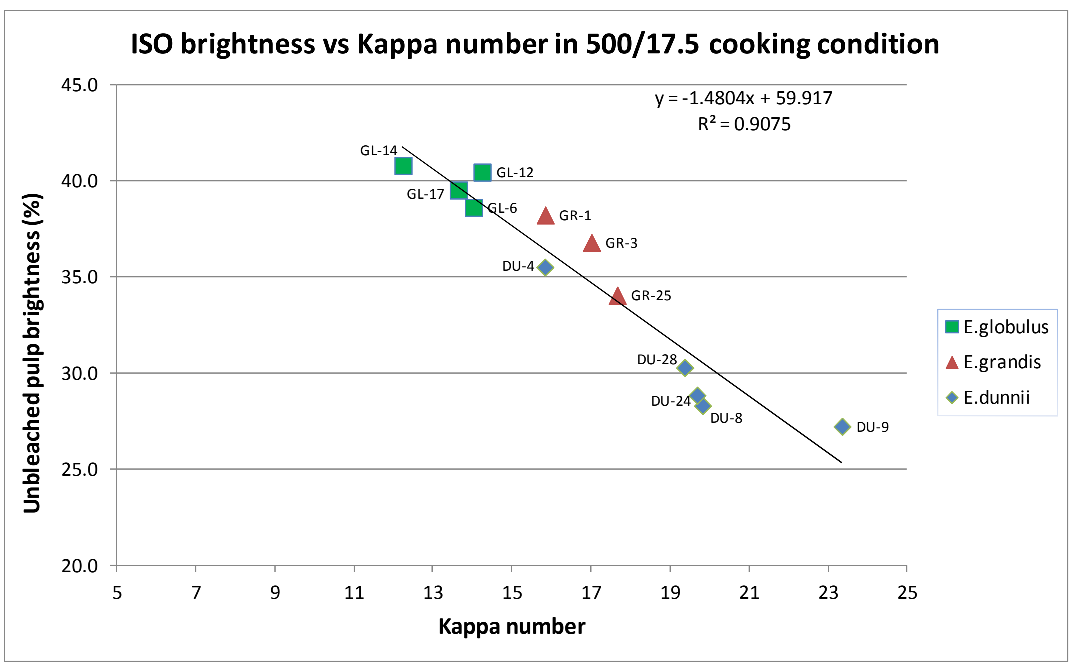

Figure 9. ISO brightness vs. Kappa number in HF 500/EA 17.5% cooking condition.

Figure 8 shows a trend, where the higher the wood calcium content the lower the ISO brightness at the same cooking conditions. This seems reasonable since as mentioned above, the ISO brightness depends largely on residual lignin in the pulp. So, wood calcium content influence the residual lignin and thus in an underlying way the ISO brightness too. This could also be an indirect negative consequence of calcium for the production of bleached pulp. Once again two examples which deviate from this behavior are those with most Klason lignin in their respective species (DU-24 and GR-25). These results seem indicate again that there is a detrimental influence of calcium on the performance of the Kraft process in the genus Eucalyptus.

Figure 9 shows very good correlation between ISO brightness and Kappa number which confirms the mentioned above about dependence of ISO brightness by the residual lignin content.

Figures 10 to 15 show the Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition under different scenarios of species, age and soil (Coneat groups).

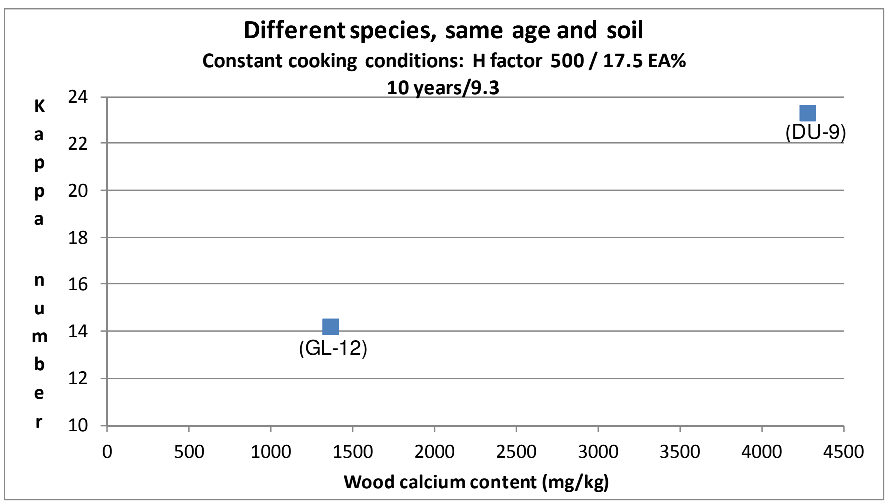

Figure 10. Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition for different species, same age and soil.

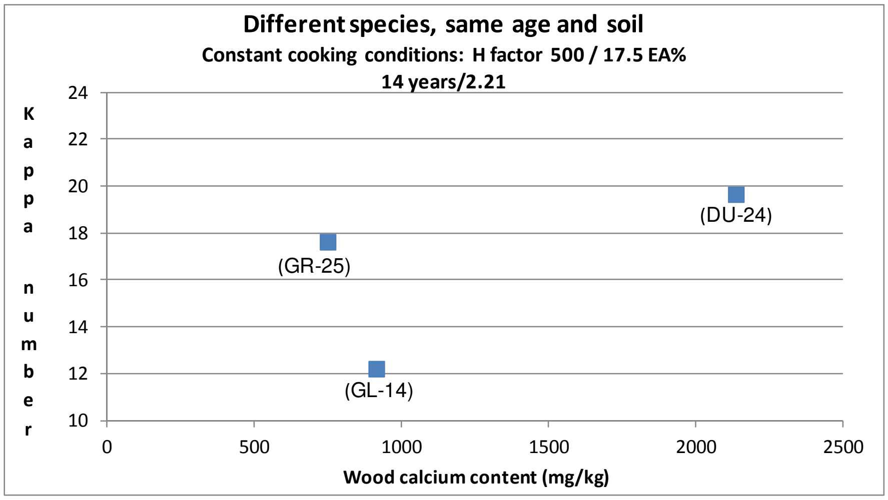

Figure 11. Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition for different species, same age and soil.

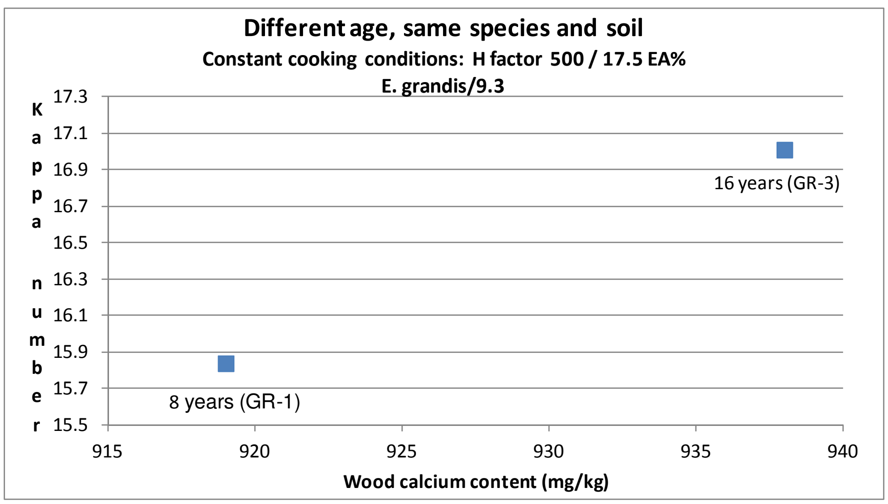

Figure 12. Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition for different age, same species and soil.

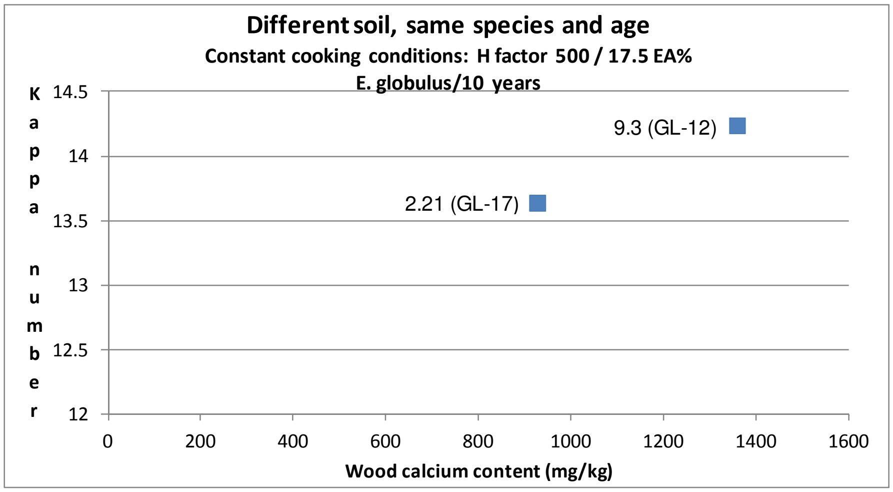

Figure 13. Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition for different soil, same species and age.

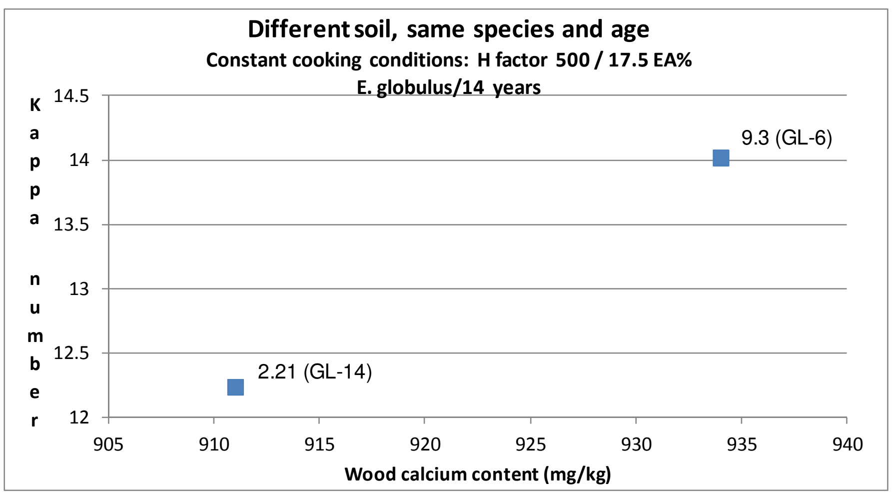

Figure 14. Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition for different soil, same species and age.

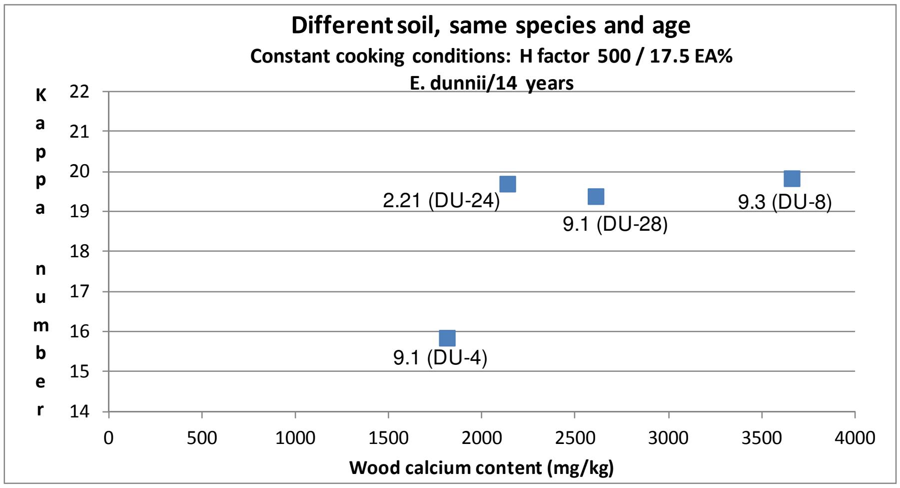

Figure 15. Kappa number vs. wood calcium content in HF 500/EA 17.5% cooking condition for different soil, same species and age.

Figures 10 to 15 show several examples where higher wood calcium content, independently of species, age or soil (Coneat groups) gives higher kappa number at constant cooking conditions (with the exceptions of samples DU-24 and GR-25 above explained).

In the introduction were mentioned different studies in eucalyptus were no major effect of calcium on Kraft cooking delignification rate were observed. The results obtained in the present work on the contrary show that the presence of calcium in eucalyptus Kraft cooking decreases the delignification rate. Saltberg *et al.* (2009) although not observed this behavior in eucalyptus, observed it in aspen and birch, explaining it by formation of calcium-lignin interaction which leads to decrease solubility of lignin during the cooking. This explanation according to the results obtained in the present work could be applied to eucalyptus too.
The decrease in the delignification rate due to calcium presence is clearly observed in *E. dunnii* where were found samples with important differences in wood calcium content. On the other hand, samples of *E. grandis* and *E. globulus* had significantly lower wood calcium content than *E. dunnii* and also less variability between samples within the species, so the effect of calcium could not be observed in the same degree.
It should be noted that in the works mentioned in the introduction was used mostly *E. globulus*, with wood calcium content in all cases similar or lower than those obtained for the samples of *E. globulus* in the present study.

Although all phenomena mentioned in Saltberg *et al.* (2009) work that explains the calcium effect elimination in eucalyptus (due to presence of substances that have a propensity to form calcium complexes like dissolved xylan, gallic acid, ellagic acid and phenolic substances) may occur in this species, its effect would appear may become important in samples with relatively low wood calcium content (as *E. grandis* and *E. globulus* in this case), but in samples with high wood calcium content (as can occur in *E. dunnii*) these phenomena do not appear to be strong enough to counteract the "calcium effect" in a significantly way.

CONCLUSIONS

1. The results seem to indicate that there is a detrimental influence of calcium on the performance of the Kraft process in the Eucalyptus genus (higher wood calcium content gives: lower yield at constant Kappa number, and higher Kappa number and lower ISO brightness at constant cooking conditions).
2. *E. dunnii* showed more wood calcium content and more variability than *E. grandis* and *E. globulus*, confirming the great difference that can exist between different eucalyptus species and also within the same species in this parameter. Due to this the calcium detrimental effect in Kraft process is clearer observed in *E. dunnii* species.
3. Within each one of the three species under study the amount of calcium in wood shows to be closely related to soil type (CONEAT groups), finding on 9.3 soils trees with higher wood calcium content than in others soils.

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