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Nitrogen in wood and its fate in kraft pulping – a review

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Summary

The present review focused on the content of nitrogen in the Nordic pine, spruce and birch trees (stemwood), as well as on the nature of organic nitrogen constituents and their behaviour in the kraft process, especially in the fibreline. For comparison, a lot of material was also collected for other softwood and hardwood materials, but the corresponding concentrations are not tabulated in detail.

During the comprehensive literature searches it became evident that there is a huge amount of information available on nitrogen content in dozens of different softwood and hardwood species covering numerous industrially important genera. It also became clear that the studies cover all different tree parts, including twigs and branches, bark, roots, and needles. For the Nordic wood species, the nitrogen content in stemwood usually varies from c. 0.05 to 0.15%, although somewhat higher amounts have also been frequently reported. The reasons for the reported differences are also discussed.

Most of nitrogen in wood is present in the form of proteins or free amino acids. They are almost completely dissolved in black liquor during pulping, with simultaneous degradation to ammonia and organic nitrogen compounds, such cyclic compounds and amino acids. During black liquor evaporation, ammonia and some organic nitrogen compounds are separated to the condensates and rectified methanol. Nitrogen entering the recovery boiler with the black liquor is converted during combustion to gaseous N2, NO, and cyanate (OCN–) in the smelt. Cyanate originating from the smelt is slowly but completely converted into ammonia during green liquor handling and white liquor preparation.

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Contents

1. Introduction

During the past 20-30 years, the knowledge on the fate of wood-derived nitrogen at kraft pulp mills and on the factors affecting (and reducing) nitrogen oxide emissions has significantly increased. It still looks, however, that there is not yet solid reliable information available on all the correlations between the nitrogen content in wood and black liquor, and the nitrogen oxide emissions. The creation of these correlations has apparently been hampered by varying data available (from literature and different laboratories) on the nitrogen content, both in wood raw material and black liquors.

Therefore, the current review work was planned to cover the available literature and other potential information sources on the following questions: nitrogen content in stemwood or pulp mill chips of the key Nordic wood raw materials (pine, spruce and birch), the chemical nature of the wood nitrogen, and the behaviour of nitrogen at the kraft pulp mills (covering both fibrelines and recovery lines).

The material for the current review was based on two different sets: 1) comprehensive collection of literature on wood nitrogen, collected at KCL during 2000–2002 as part of the Rempulp EU project, and 2) further literature searches that especially focused on the new material published during the past 15 years. For the searches, different databases and information sources available at VTT were used, strengthened by comprehensive searches with the help of Scopus and Google Scholar websites.

It can be mentioned here that the elemental composition of wood began to attract chemists during the second half of the 19th century. One of the first investigators was König, who in 1861 found that wood losses some of its nitrogen by copper sulphate treatment (but no exact figures were given). More precise data was later reported by Schroeder (1874), Gottlieb (1883), and Hartig (1888). According to the pioneering study by Schroeder (1874), spruce and other woods should contain less than 0.3% of nitrogen. Slightly lower nitrogen figures were reported by Gottlieb (1883), whose numbers have turned out to be in a good agreement with the best of the current data.

Today, there is a lot of wood nitrogen related information available, created for largely varying purposes. These have varied from industrial wood uses (e.g. Antikainen et al. 2004) to various environmental questions, biomass nutrient recycling, and numerous other needs. As a result, the data is typically heterogeneous and challenging to review and analyse; different analytical methods that have been applied can also easily make solid conclusions challenging.

2. Nitrogen in wood – content and distribution

2.1 Nitrogen in softwood

During the comprehensive literature searches it became evident that there is a huge amount of information available on nitrogen content in dozens of different softwood species covering numerous industrially important genera, including pines, spruces, firs, larches, hemlocks, cypresses and many others. It also became clear that the studies cover all different tree parts, including twigs and branches, bark, roots, and needles. Furthermore, it is evident that practically taken all the main softwood species contain equally low amounts of nitrogen in mature stemwood, as the figures above >0.2–0.3% have only seldom been reported. As will be shown later by selected examples, the highest nitrogen contents are typically found only in the outer layers of sapwood.

Due to the availability of the vast amount of published data, the present Section will mainly focus on the main Nordic softwood species, Scots pine (Pinus sylvestris) and Norway spruce (Picea abies). For comparison, however, selected data on other pine and spruce species will also be provided, strengthened by examples on other types of softwood species. The currently available information on wood nitrogen does not focus only on the total nitrogen content. In addition, there is detailed information available on the distribution of nitrogen in different parts of stemwood. This type of variation will also be demonstrated below, with the help of selected examples.

For the nitrogen content of Scots pine (Table 1) and Norway spruce (Table 2), most of the figures reported during the past 100 years have remained below 0.15%. In only a few cases any figures on the levels of >0.15% have been published. The highest figures for both pine (0.24%) and spruce (0.25%) are derived from the Swedish Ecocyclic pulp mill project (Anon. 1999) and may be explained by a systematically different analytical approach. For the comparisons, it is important to notice that all the figures from a pioneering Norwegian study (Gislerud and Tveite 1973) are from wholetree (stemwood with bark) samples.

There is an interesting difference between the data reported for pine and spruce. Namely, nearly all the figures for pine are below 0.1%, whereas for spruce two different data sets can be recognised: those around from c. 0,04 to 0,08%, and those going clearly above 0.1% (up to 0.16-0.18%). No unambiguous explanation for that can now be given, and for example, no apparent differences could be recognised in the applied analytical methods to readily explain the differences.

For many of the reported nitrogen content figures there are ranges given, for a number of reasons. For example, Gislerud and Tveite (1973), Varhimo (1988), Häsänen & Huttunen (1989) and Hedenberg (1996) have studied wood samples from several geographical areas. On the other hand, Nickel (1960), Siltala (1988), Boutelje et al. (1990) and many others have provided figures from different parts of the logs. There is also variation in the nitrogen content caused by the use of different levels of fertilisation, e.g. those by Ingerslev (1999), Anttonen et al. (2002) and Kaakinen et al. (2007, 2009). In some cases, the fertilisation was shown to have only minor impacts on the wood nitrogen contents. In addition to the cited examples, many other investigations (not cited) report on the impact of fertilisation on the trees, by providing figures for N as kg/ha, without specific data on the nitrogen content in wood. Later in this Section, selected examples are given to further demonstrate the extent of this type of variations.

Table 1. Nitrogen content (%) of Scots pine, according to the main Nordic and other European sources.

Nordic studies		
Content (%)	Topic addressed, comments	Reference
0,07-0,13	Stemwood samples with bark, several Norwegian sites	Gislerud & Tveite 1973
0,05	Softwood chips from a Swedish mill	Magnusson et al. 1979, 1980
0,04	Effect of fertilisation on peatland	Paavilainen 1980
0,04-0,06	Pulp wood composition, samples from five regions	Varhimo 1988
c. 0,05-0,1	Distribution of nutrients in different tree parts	Siltala 1988
c. 0,05-0,1	English paper based on Siltala's M.Sc. thesis	Helmisaari and Siltala 1989
0,06-0,07	Effect on fertilisation on two Finnish regions	Finér 1989
0,05-0,08	Samples from five different Finnish regions	Häsänen & Huttunen 1989
0,04-0,08	N distribution in several Swedish planks, effect of drying	Boutelje 1990
0,04-0,19	Extension of Boutelje's (1990) work with planks	Theander et al. 1993
0,06	Fate of N in wood drying	Terziev 1995
0,05-0,08	Samples from three Swedish pulp mills	Hedenberg 1996
0,09-0,11	Samples from three Swedish locations	Terziev et al. 1997
0,05	Fate of nitrogen at pulp mills	Telkkinen 1996, 1999
0,07	Heating values of mature trees	Nurmi 1997
0,12-0,24	Swedish Ecocylic pulp mill project (1990s)	Anon. 1999
0,04	Fate of nitrogen in pulping	Niemelä & Ulmgren 2002
0,11	Softwood chips from a Swedish mill	Niemelä et al. 2003
c. 0,05	N content in stump wood (change during decay)	Palvianen et al. 2010

Other European studies		
Content (%)	Topic addressed, comments	Reference
0,13	Composition of wood	Schwalbe & Becker 1919
0,13	Mature sapwood (0,9% in newly-formed wood)	Allsop & Misra 1940
0,07	N content in several wood species	Ovington 1957
0,08-0,1	Nutrient distribution in trees	Wright and Will 1958
0,05-0,09	N and protein contents across the stem	Nickel 1960
0,08-0,11	N and protein contents across the stem	Becker 1962
0,06-0,09	Amino acids and proteins in sapwood and heartwood	Laidlaw & Smith 1965
0,03-0,08	N content in very old pine trees (>100 years)	Popović 1966
0,07-0,1	N content in outer sapwood, seasonal variation	Bletchly 1969
c. 0,04-0,1	N content along the radius of the stems	King et al. 1974
0,05-0,08	N content and distribution, protein compositions	Adelsberger & Petrowitz 1976
0,07	N content (average figures in wood and bark)	Marutsky & Roffael 1977
0,06	N content analysed by chemiluminescence	Keller & Nussbaumer 1993

Nickel (1960) investigated nitrogen and protein contents in a 100-year-old Scots pine wood and found a steep decrease from the utmost sapwood towards the heartwood, followed by a small rise in the inner heartwood zone towards the centre (Fig. 1). Orman and Will (1960) found a similar distribution pattern in a 26-year-old radiata pine. Becker (1962) investigated in detail nitrogen content (expressed as proteins by multiplying with 6.25) in Scots pine and Norway spruce (Fig. 2). His results support (and widen) those from the earlier investigations.

Table 2. Nitrogen content (%) of Norway spruce, according to the main Nordic and other European sources. *Becker (1962) used the old name P. excelsa for Norway spruce.

Nordic studies		
Content (%)	Topic addressed, comments	Reference
0,1-0,15	Optimal nitrogen levels in spruce trees (field trials)	Tamm 1968
0,07-0,17	Stemwood samples with bark, several Norwegian sites	Gislerud & Tveite 1973
0,04-0,05	Pulp wood composition, samples from three regions	Varhimo 1988
0,03	N content in wood and some other tree parts	Westernark et al. 1986
0,06	Effect on fertilisation on one Finnish region	Finér 1989
0,05-0,07	N distribution in two Swedish planks, effect of drying	Boutelje 1990
0,04-0,05	Samples from four Swedish pulp mills	Hedenberg 1996
0,05	Fate of nitrogen at pulp mills	Telkkinen 1996, 1999
0,04	Heating values of mature trees	Nurmi 1997
0,12-0,25	Swedish Ecocylic pulp mill project (1990s)	Anon. 1999
0,09-0,13	Effect on fertilisation (in Denmark)	Ingerslev 1999
0,06-0,11	Effect on fertilisation (in Sweden)	Anttonen et al. 2002
0,08-0,15	Effect on fertilisation (in Finland)	Kaakinen et al. 2007
0,14-0,16	Effect on fertilisation (in Sweden)	Kaakinen et al. 2009
c. 0,07	N content in stump wood (change during decay)	Palviainen et al. 2010

Other European studies		
Content (%)	Topic addressed, comments	Reference
0,04	Composition of wood	Gottlieb 1883
0,11	Composition of wood	Schwalbe & Becker 1919
0,18	Composition of wood	König & Becker 1919
0,07-0,10	N content in several wood species	Ovington 1957
0,04-0,08	N and protein contents across the stem*	Becker 1962
0,04-0,09	N content over the stem in several wood species	Merrill and Cowling 1966a
c. 0,04-0,08	N content along the radius of the stems	King et al. 1974
0,07	N content (average figures in wood and bark)	Marutsky & Roffael 1977
0,07	N content analysed by chemiluminescence	Keller & Nussbaumer 1993

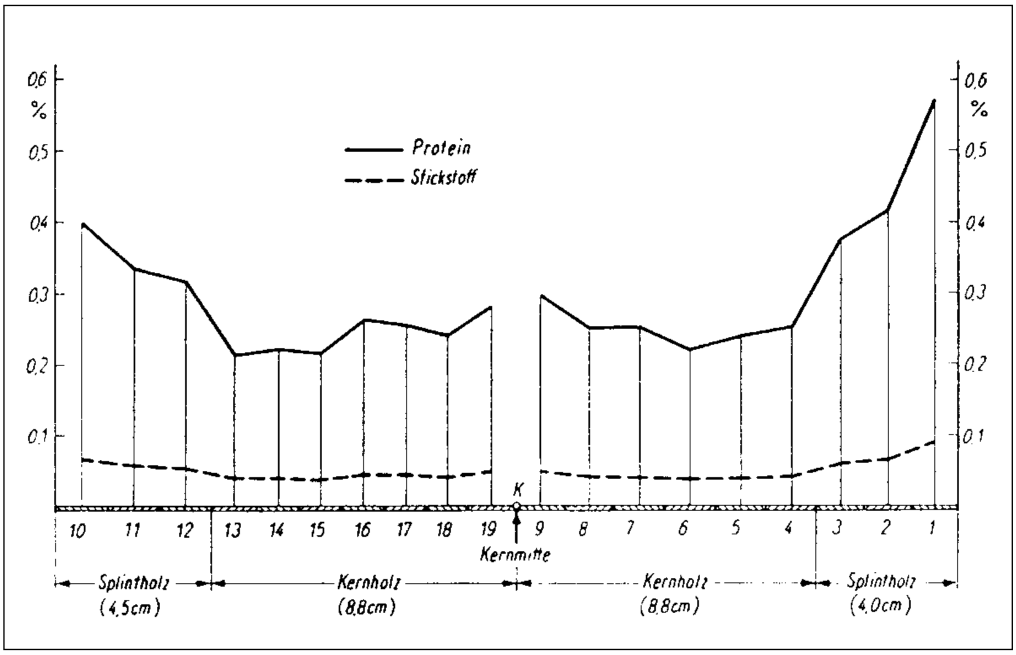


Fig. 1. Nitrogen and protein concentrations in a 100-year-old Scots pine (Nickel 1960).

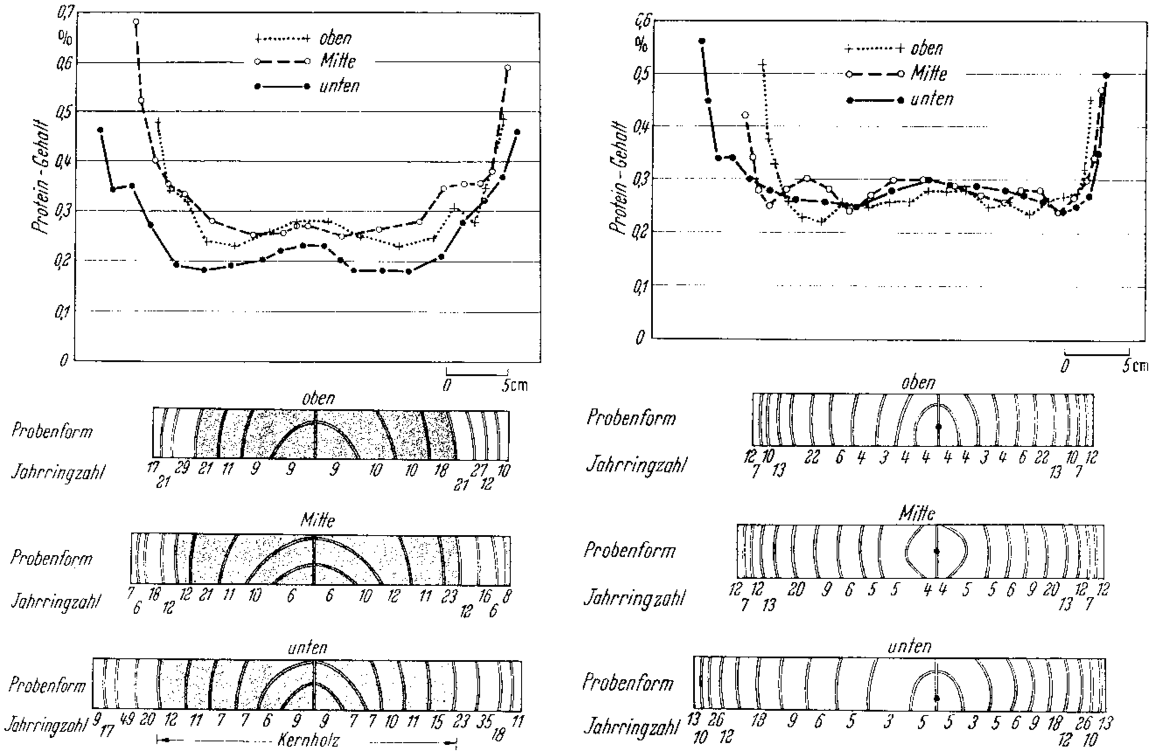


Fig. 2. Protein concentrations over cross sections in Scots pine (left) and Norway spruce (named as Picea excelsa, right) at three different heights (oben, Mitte, unten) corresponding to 2.5, 5, and 7.5 metres (Becker 1962). Similar distribution was also found (figure not reproduced) for a noble fir (Abies pectinata).

Apparently one of the most comprehensive of the above-mentioned distribution-related studies is that by Siltala (1988). In his M.Sc. Thesis, he investigated distribution of nitrogen in pine seedlings, young trees, and mature trees, paying attention to xylem, inner bark, outer bark, seasonal changes, and soil fertilisation (Figs. 3–8). The major results from the Siltala's Thesis are also published in a scientific paper by Helmisaari and Siltala (1989).

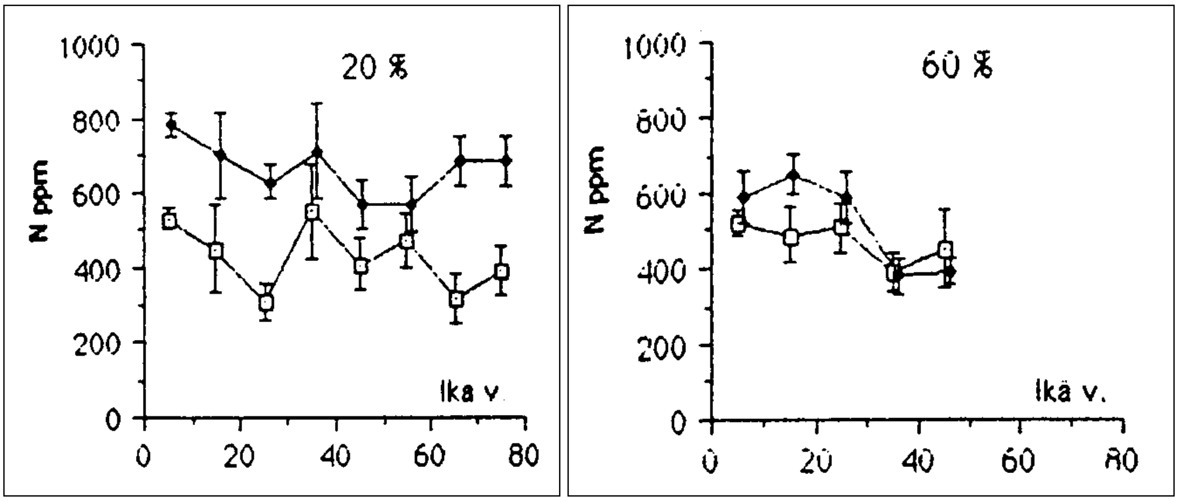


Fig. 3. Horizontal distribution of nitrogen in pine wood (xylem) at relative heights of 20% and 60%, according to Siltala (1988). *Ikä* refers to number of growth rings; • indicates pine grown in a fertilised area; and ☐ refers to pine grown in a non-fertilised area.

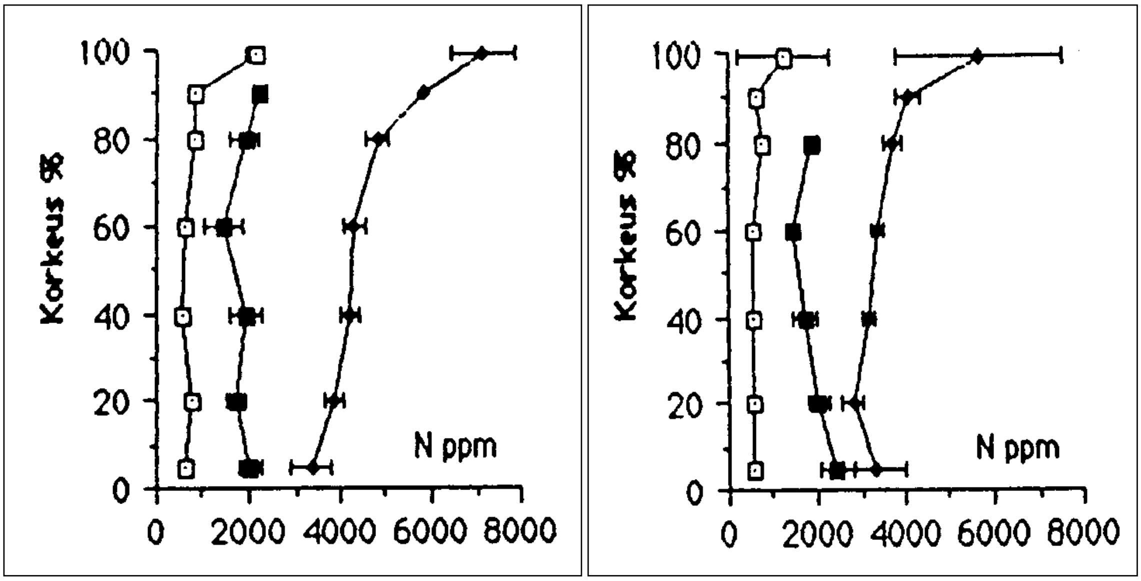


Fig. 4. Vertical distribution of nitrogen in pine wood grown in a fertilised (left) and non-fertilised (right) area, according to Siltala (1988). *Korkeus* refers to relative tree height; ☐ indicates xylem; ■ indicates inner bark, and • indicates outer bark.

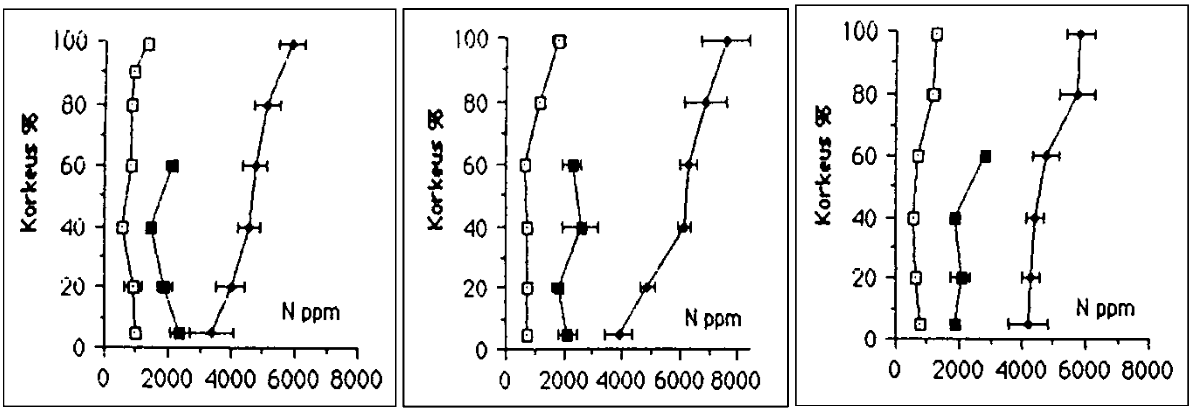


Fig. 5. Vertical distribution of nitrogen in pine wood grown in different localities, according to Siltala (1988). Symbols as in Fig. 3.

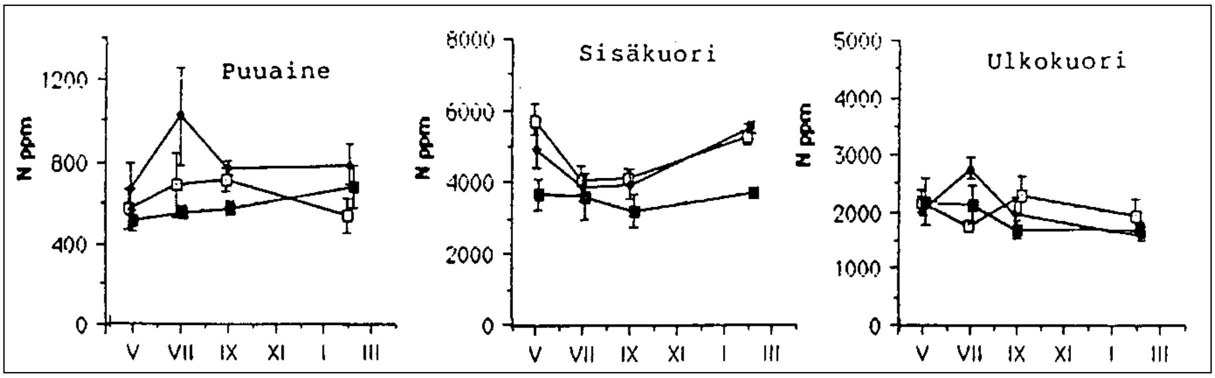


Fig. 6. Seasonal variation of nitrogen content in pine wood xylem (left), inner bark (middle), and outer bark (right), according to Siltala (1988). ☐ indicates seedlings; ■ indicates young forest, and • indicates mature trees.

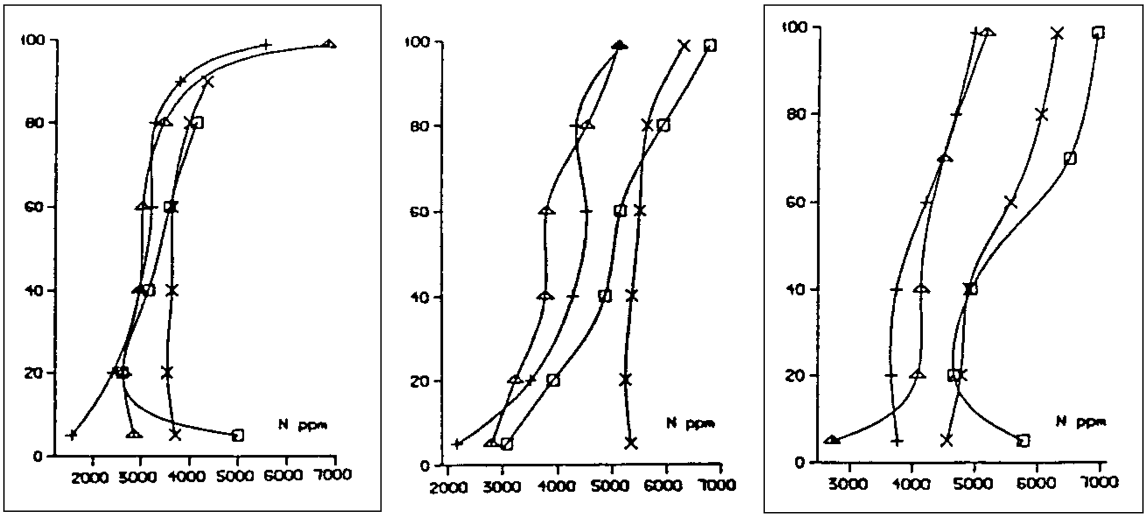


Fig. 7. Seasonal variation in vertical nitrogen content in inner bark of pine: mature trees (left), young trees (middle), and seedlings (right), according to Siltala (1988). Sampling in February (□), May (☐), July (⊗), and September (+).

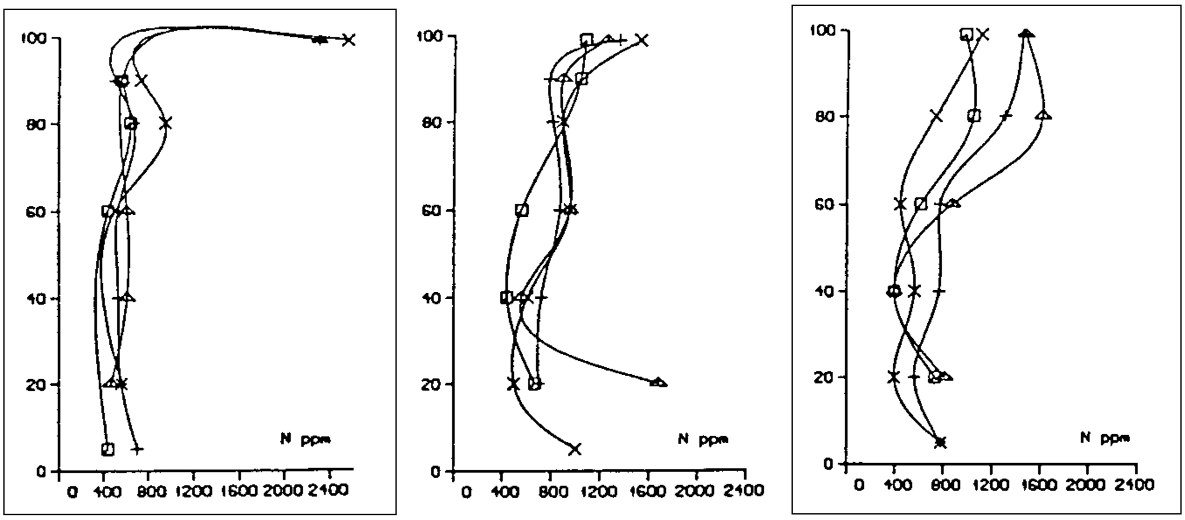
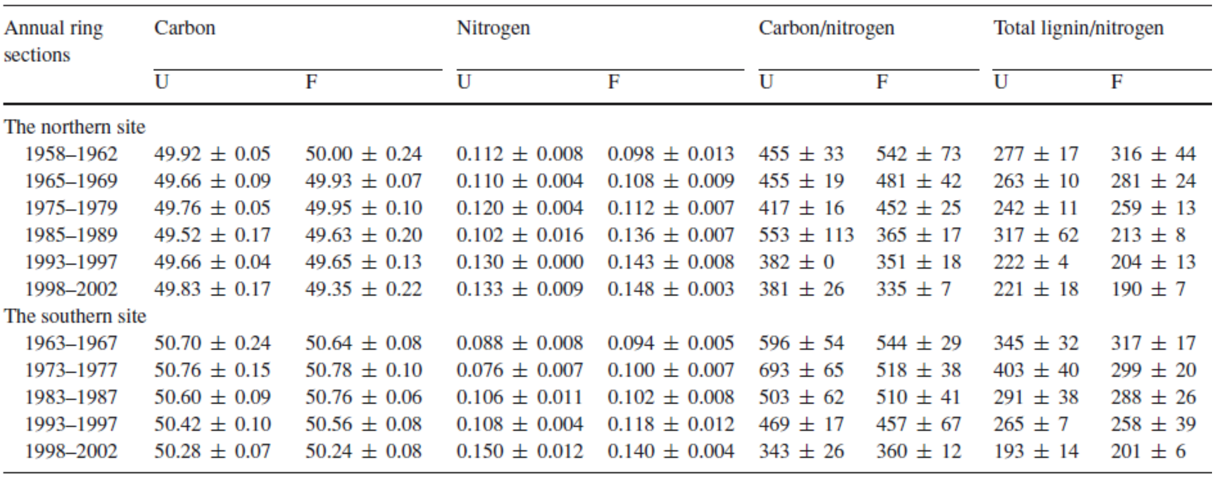


Fig. 8. Seasonal variation in vertical nitrogen content in outer sapwood of pine: mature trees (left), young trees (middle), and seedlings (right), according to Siltala (1988). Sampling in February (□), May (☐), July (⊗), and September (+).

The above Siltala's (1988) figures for Scots pine clearly confirm earlier findings on higher nitrogen content in wood bark, and also reveal some seasonal variation. This type of variation is, however, much more typical for hardwood. Bletchly (1969) has also provided data on seasonal variation (between 0.07 and 0.1%) in nitrogen content of Scots pine sapwood.

Results from a highly interesting study were published by Kaakinen et al (2007) some years ago, including measurements on the effects of nitrogen-fertilisation on the nitrogen content of Norway spruce on two locations in Finland. They studied "the effect of long-term nitrogen fertilisation on wood chemistry at two boreal sites in Finland: the northern site (Kemijärvi) and the southern site (Heinola). N-fertilisation was repeated in five-year intervals from the 1960s. The trees that had been planted in 1938 and 1954, in the northern and the southern site, respectively, were harvested in October 2002. Altogether 20 trees, in five different size classes, either unfertilised or fertilised, were felled. Wood sections at breast height, consisting of five consecutive annual rings, from six (Kemijärvi) or five (Heinola) points with different distances from the pith were examined. Differences in growth between the northern and southern sites were marked in favour of the southern site. In the northern site fertilisation had clearly increased the diameter growth, while in the southern site fertilisation had no effect. Nitrogen fertilisation resulted in slight changes in wood chemistry that included increased nitrogen concentrations in the northern site and extractives in the southern site (Table 3). Stem wood had higher concentrations of extractives, starch, and uronic acids, and lower concentration of cellulose, in the northern than in the southern site”.

Table 3. Wood component concentrations (% DM) and ratios from the pith to the bark in the northern site (Kemijärvi) and in the southern site (Heinola) in Finland (Kaakinen et al. 2007). U, unfertilised; F, nitrogen-fertilised.



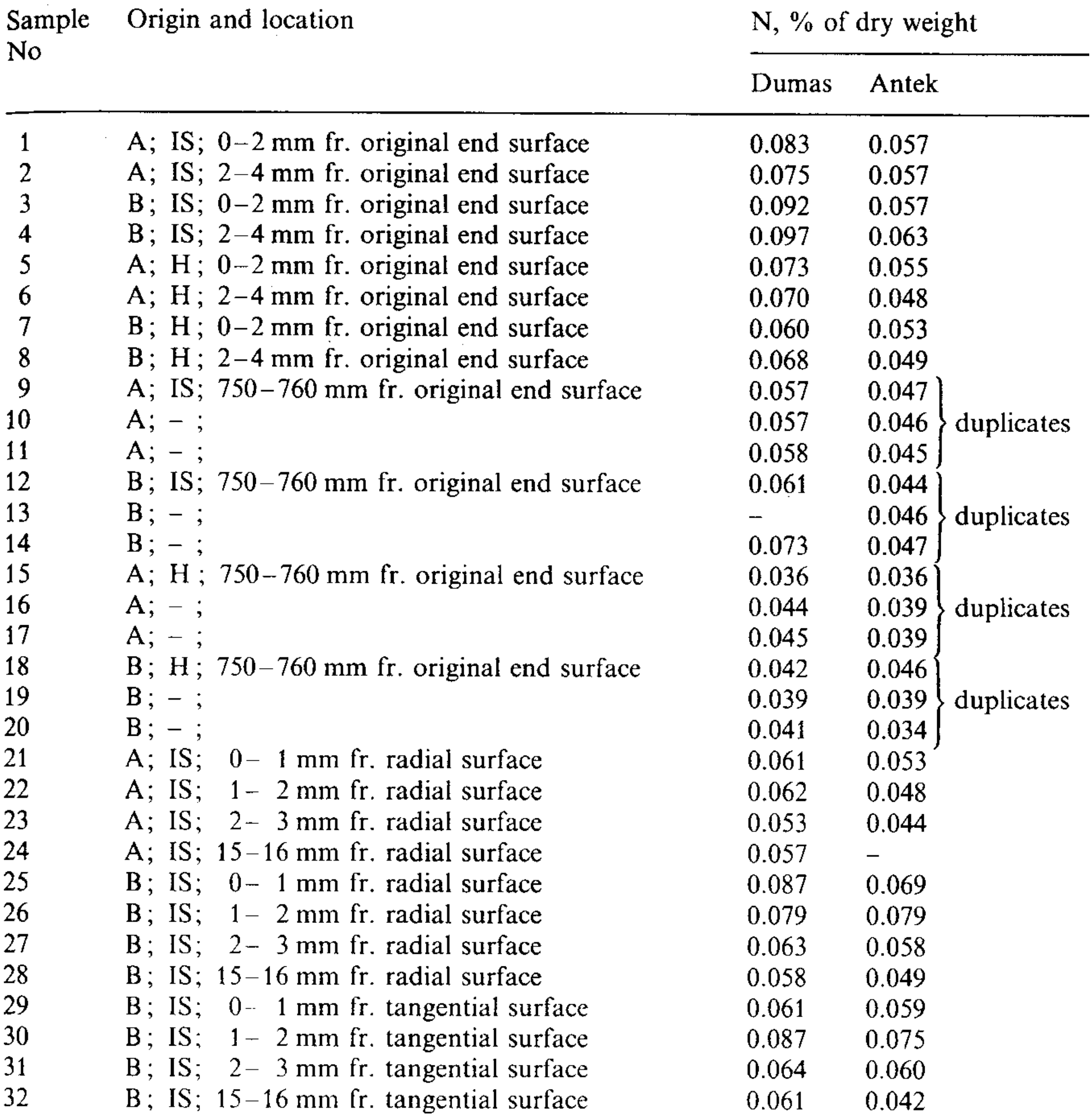
Annual ring sections	Carbon		Nitrogen		Carbon/nitrogen		Total lignin/nitrogen	
	U	F	U	F	U	F	U	F
The northern site								
1958–1962	49.92 ± 0.05	50.00 ± 0.24	0.112 ± 0.008	0.098 ± 0.013	455 ± 33	542 ± 73	277 ± 17	316 ± 44
1965–1969	49.66 ± 0.09	49.93 ± 0.07	0.110 ± 0.004	0.108 ± 0.009	455 ± 19	481 ± 42	263 ± 10	281 ± 24
1975–1979	49.76 ± 0.05	49.95 ± 0.10	0.120 ± 0.004	0.112 ± 0.007	417 ± 16	452 ± 25	242 ± 11	259 ± 13
1985–1989	49.52 ± 0.17	49.63 ± 0.20	0.102 ± 0.016	0.136 ± 0.007	553 ± 113	365 ± 17	317 ± 62	213 ± 8
1993–1997	49.66 ± 0.04	49.65 ± 0.13	0.130 ± 0.000	0.143 ± 0.008	382 ± 0	351 ± 18	222 ± 4	204 ± 13
1998–2002	49.83 ± 0.17	49.35 ± 0.22	0.133 ± 0.009	0.148 ± 0.003	381 ± 26	335 ± 7	221 ± 18	190 ± 7
The southern site								
1963–1967	50.70 ± 0.24	50.64 ± 0.08	0.088 ± 0.008	0.094 ± 0.005	596 ± 54	544 ± 29	345 ± 32	317 ± 17
1973–1977	50.76 ± 0.15	50.78 ± 0.10	0.076 ± 0.007	0.100 ± 0.007	693 ± 65	518 ± 38	403 ± 40	299 ± 20
1983–1987	50.60 ± 0.09	50.76 ± 0.06	0.106 ± 0.011	0.102 ± 0.008	503 ± 62	510 ± 41	291 ± 38	288 ± 26
1993–1997	50.42 ± 0.10	50.56 ± 0.08	0.108 ± 0.004	0.118 ± 0.012	469 ± 17	457 ± 67	265 ± 7	258 ± 39
1998–2002	50.28 ± 0.07	50.24 ± 0.08	0.150 ± 0.012	0.140 ± 0.004	343 ± 26	360 ± 12	193 ± 14	201 ± 6

Kaakinen et al. (2009) also compared the properties and composition of control and nutrient optimised Norway spruce stems, grown in Sweden. The reported nitrogen contents were 0.14 and 0.16% for the control and nutrient optimised samples, respectively. Anttonen et al. (2002) also studied in Sweden the impacts of optimal fertilization of chemistry of spruce and found the wood nitrogen increase from 0.06 to 1.1%

Other type of data on concentrations and distribution of nitrogen in pines comes from several studies on the effect of drying on nitrogen compounds. For example, Boutelje (1990) analysed a large number of pine plank samples (at different locations) with both Antek and Dumas methods (Table 4). The latter method always gave somewhat higher nitrogen figures. The results are also discussed by Theander et al. (1993).

The above studies, substantiated by that of King et al. (1974), also reveal some re-distribution of nitrogen during drying. This was studied in more detail by Terziev (1995) and Kreber et al. (1998). A selected example (Fig. 9) shows the tendencies of (soluble) nitrogen to migrate from deeper layers towards the surface, particularly during kiln drying. There is also some stain formation, believed to be caused by Maillard-type reactions between amino acids and carbohydrates. This has also been evidenced in a more detailed study of the nitrogen compounds (Donald et al. 2000).

Table 4. Nitrogen content in 32 samples taken from two Scots pine planks (A and B), demonstrating variation of nitrogen content within wood raw material (according to Boutelje 1990). IS, inner sapwood; H, heartwood. See the original work for the sampling details and for the effects of drying on the nitrogen content. The original work also gives some nitrogen concentrations for Norway spruce.



Sample No	Origin and location	N, % of dry weight		
		Dumas	Antek	
1	A; IS; 0–2 mm fr. original end surface	0.083	0.057	
2	A; IS; 2–4 mm fr. original end surface	0.075	0.057	
3	B; IS; 0–2 mm fr. original end surface	0.092	0.057	
4	B; IS; 2–4 mm fr. original end surface	0.097	0.063	
5	A; H; 0–2 mm fr. original end surface	0.073	0.055	
6	A; H; 2–4 mm fr. original end surface	0.070	0.048	
7	B; H; 0–2 mm fr. original end surface	0.060	0.053	
8	B; H; 2–4 mm fr. original end surface	0.068	0.049	
9	A; IS; 750–760 mm fr. original end surface	0.057	0.047	duplicates
10	A; – ;	0.057	0.046	
11	A; – ;	0.058	0.045	
12	B; IS; 750–760 mm fr. original end surface	0.061	0.044	duplicates
13	B; – ;	–	0.046	
14	B; – ;	0.073	0.047	
15	A; H; 750–760 mm fr. original end surface	0.036	0.036	duplicates
16	A; – ;	0.044	0.039	
17	A; – ;	0.045	0.039	
18	B; H; 750–760 mm fr. original end surface	0.042	0.046	duplicates
19	B; – ;	0.039	0.039	
20	B; – ;	0.041	0.034	
21	A; IS; 0– 1 mm fr. radial surface	0.061	0.053	
22	A; IS; 1– 2 mm fr. radial surface	0.062	0.048	
23	A; IS; 2– 3 mm fr. radial surface	0.053	0.044	
24	A; IS; 15–16 mm fr. radial surface	0.057	–	
25	B; IS; 0– 1 mm fr. radial surface	0.087	0.069	
26	B; IS; 1– 2 mm fr. radial surface	0.079	0.079	
27	B; IS; 2– 3 mm fr. radial surface	0.063	0.058	
28	B; IS; 15–16 mm fr. radial surface	0.058	0.049	
29	B; IS; 0– 1 mm fr. tangential surface	0.061	0.059	
30	B; IS; 1– 2 mm fr. tangential surface	0.087	0.075	
31	B; IS; 2– 3 mm fr. tangential surface	0.064	0.060	
32	B; IS; 15–16 mm fr. tangential surface	0.061	0.042	

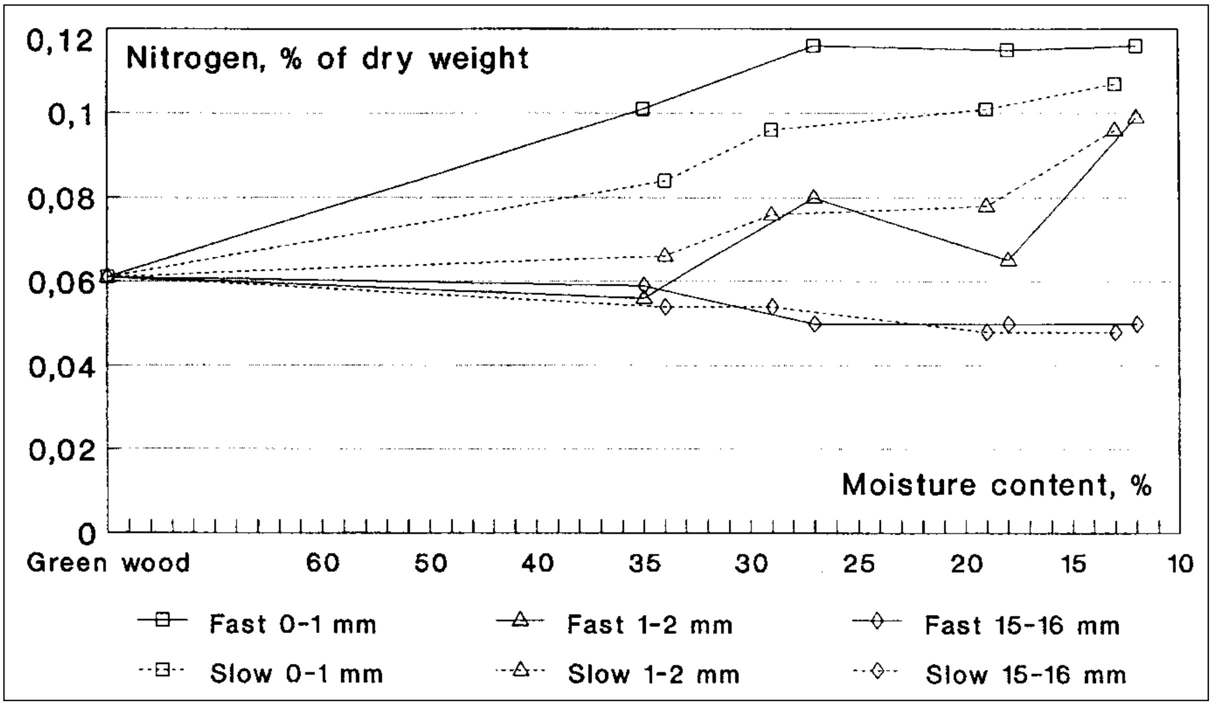


Fig. 9. Concentration of nitrogen in unedged planks of Scots pine during kiln drying at 80 C, as a function of moisture content. (Terziev 1995). Note the increase of nitrogen content in the surface layers, as a result of nitrogen migration from deeper layers. Similar tend was not found during air drying (see the original publication for that).

As already pointed out in the beginning of this Section, other pine and spruce species (as well as softwoods from other genera) all seem to have very similar or even equal nitrogen contents. In this context it is not justified to provide detailed summaries on such investigations. For the potential need of further information on this question, the following references can be recommended as representative examples:

- Meerts (2002) has summarised contents of nitrogen and other nutrients for nearly 100 different wood species, including >20 softwoods. For comparison, the summary tables from this study are provided in Appendix 1.
- A large number of papers report the nitrogen contents of c. 0.04-0.12% for several foreign pine species, such as contorta, echinata, elliottii, nigra, lambertiana, monticola, palustris, ponderosa, taeda, radiata and strobus (e.g. Allison et al. 1963, Ovington 1957, Wright and Will 1958, Orman and Will 1960, Young and Guinn 1966, Cowling and Merrill 1966, Merill and Cowling 1966a, 1966b, Ziegler 1968, Haas and Kremer 1964, Young 1971, Birk and Vitousek 1986, Wong and Wilkes 1988, Madgwick and Frederick 1988, McDonald et al. 2000, Martin et al. 2015).
- Similar (usually c. 0.05–0.15%) nitrogen contents have been reported for numerous foreign spruce, fir, larch and hemlock species (for example by Allison et al. 1963, Ovington 1957, Young and Guinn 1966, Ziegler 1968, Haas and Kremer 1964, Young 1971, and Martin et al. 2015).

2.2 Nitrogen in hardwood

For the content of nitrogen in the Nordic birch wood, there is clearly less information available than for softwood (Table 5). The scattered data reveals the concentration ranges very similar than those in softwood, covering a few examples showing values below 0.1%, and several examples with somewhat higher figures. The highest reported figures seem to be just under 0.2%. The figure of 0.18% by Palviainen et al. refers to birch stumpwood. For other birch species (alba, papyrifera, and alleghaniensis), nitrogen contents from 0.05 to 0.14% have bee reported (Ovington 1957, Young and Guinn 1966, and Martin et al. 2015).

Data collected by Meerts (2002) for dozens of different hardwood species includes only a few examples of any species with the nitrogen content of c. 0.2–0.25% or higher, more typical ranges being around 0.05–0.17%. It thus looks that the Nordic birch species represent typical nitrogen content among many other hardwood genera. In the total dataset by Meerts, the average values for nitrogen were 0.08% and 0.11% in all softwood and hardwood (heartwood) materials, respectively. It may be added here that the typical Eucalyptus wood nitrogen contents were around 0.1–0.15%.

Table 5. Nitrogen content (%) in birch (Betula pendula/verrucosa), according to the main Nordic and European studies.

Nordic studies		
Content (%)	Topic addressed, comments	Reference
0,06-0,15	Stemwood samples with bark, several Norwegian sites	Gislerud & Tveite 1973
0,11-0,19	Nutrient balances in birch trees	Mälkönen & Saarsalmi 1982
0,08-0,11	Pulp wood composition, samples from four regions	Varhimo 1988
0,08-0,1	Fate of nitrogen at pulp mills	Telkkinen 1996, 1999
0,07-0,08	Samples from three Swedish pulp mills	Hedenberg 1996
0,04-0,07	Heating values of mature trees	Nurmi 1997
0,06	Fate of nitrogen in pulping	Niemelä and Ulmgren 2002
0,13	Fate of nitrogen in pulping	Niemelä et al. 2003
c. 0,18	N content in stump wood (change during decay)	Palviainen et al. 2010
0.2	Several short rotation wood species (1-12 years old)	Pesonen et al. 2014

Other European studies		
Content (%)	Topic addressed, comments	Reference
0,1	Composition of wood	Gottlieb 1883
0,12	Composition of wood	Schwalbe & Becker 1919
0,19	Composition of wood	König & Becker 1919
0,14-0,15	N content in several wood species	Ovington 1957
0,14	N content (average figures in wood and bark)	Marutzky & Raffael 1977

As can be seen in Table 5, there is surprisingly little published data available on the nitrogen content of birch wood chips collected at the pulp mills. Hedenberg (1996) has analysed samples from three Swedish pulp mills, showing nearly identical nitrogen contents. The figures reported by Varhimo (1988) for pulpwood samples from four Finnish locations are in a good agreement with Hedenberg's data. In any case, it has been frequently found (e.g. Aho et al. 1994a, Forssén et al. 1999, Kymäläinen 2001, Salmenoja 2009) that hardwood black liquors contain slightly or significantly more nitrogen than softwood black liquors.

2.3 Nitrogen in wood bark

It has already been mentioned that sapwood typically contains more nitrogen than heartwood. Highest nitrogen contents are clearly found, however, in bark (especially in inner bark, phloem) and in cambium between the inner bark and wood (e.g. Anderson and Pigman 1947, Thornber and Northcote 1961, Merrill and Cowling 1966a, Cowling 1970, Grozdits and Ifju 1973; see Fig. 10). As a good representative example on the nitrogen content in the main Nordic (Finnish) wood bark, a summary table from Nurmi (1997) is reproduced (Table 6). Similar data for pine, spruce and birch bark nitrogen has also been reported by Hedenberg (1996), using material from several Swedish pulp mills. In addition, similar data on bark nitrogen contents has been provided for a large number of other softwood and hardwood species, for example by Young and Guinn (1966), Young (1971) and Martin et al. (2015).

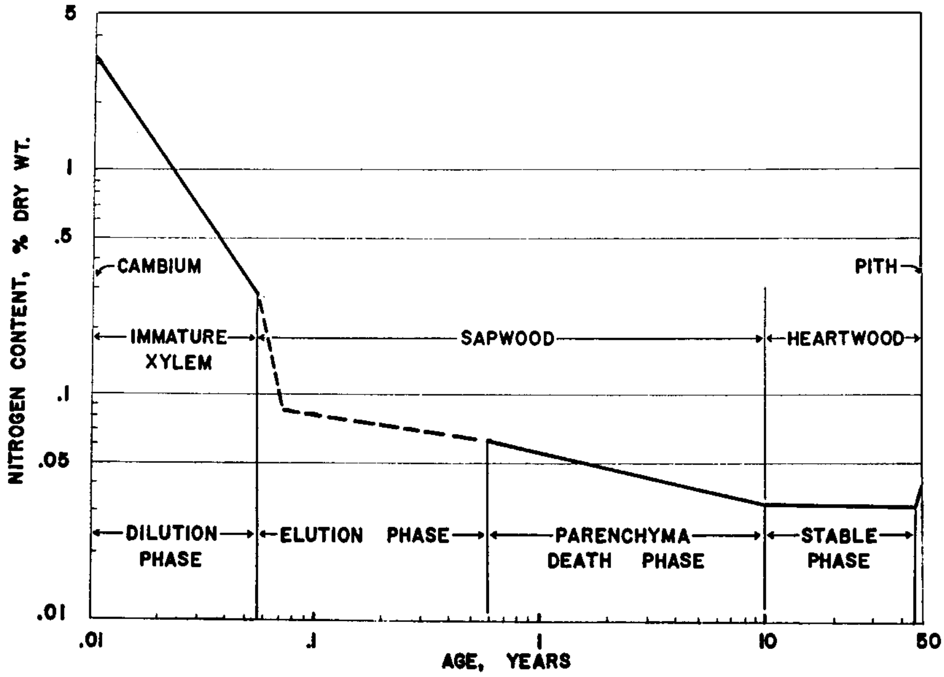


Fig. 10. Hypothetical graph of changes in nitrogen content during various stages in the maturation and aging of tissues within the xylem cylinder of typical softwood and hardwood tree stems (Merrill and Cowling 1966a).

Table 6 Content of carbon, hydrogen and nitrogen in different parts of the main Finnish softwood and hardwood species (Nurmi 1997).

Element/ Species	Wood				Inner bark		Outer bark		All bark		Foliage
	Stem	Branches	Stump	Roots	Stem	Branches > 5mm	Stem	Branches > 5mm	Branches < 5mm	Roots	
Carbon, % of dry weight											
P. sylvestris	52.70	55.59	58.49	54.08	51.86	52.32	54.88	54.72	55.07	55.59	50.49
P. abies	51.48	52.84	52.69	54.08	52.04	48.84	55.54	55.90	54.95	52.32	51.50
B. pubescens	51.68	52.68	51.52	52.67	51.08	51.68	72.77	70.62	54.88	53.28	51.50
B. pendula	51.92	52.37	51.2	51.52	52.44	52.46	72.24	70.24	53.02	54.94	51.00
A. incana	52.72	51.61	51.78	52.24	54.61	54.14	65.07	60.71	55.31	55.11	52.60
A. glutinosa	51.78	51.54	49.02	50.94	53.08	53.33	59.07	60.71	56.34	53.96	50.69
P. tremula	51.86	51.50	51.44	50.70	51.86	50.99	55.70	52.85	52.43	54.19	51.40
Hydrogen, % of dry weight											
P. sylvestris	6.46	6.39	7.07	6.38	5.81	5.60	5.52	5.66	5.77	4.89	6.37
P. abies	6.32	6.52	6.25	6.36	5.79	5.39	5.66	5.46	5.64	5.32	5.78
B. pubescens	6.28	6.38	6.32	6.22	5.63	5.77	9.21	8.93	6.24	5.19	5.84
B. pendula	6.21	6.45	6.15	6.31	5.81	5.79	9.24	9.00	5.87	5.28	6.13
A. incana	6.34	6.33	6.16	6.26	6.07	5.88	7.49	7.08	6.13	5.73	5.89
A. glutinosa	6.23	6.35	6.07	6.15	5.72	5.77	6.03	7.13	6.34	5.52	5.94
P. tremula	6.32	6.28	6.18	6.17	5.88	5.80	6.44	6.33	5.80	5.41	5.90
Nitrogen, % of dry weight											
P. sylvestris	0.07	0.08	0.05	0.08	0.54	0.53	0.25	0.25	0.73	0.37	1.07
P. abies	0.04	0.09	0.08	0.12	0.61	0.39	0.39	0.4	0.53	0.41	0.89
B. pubescens	0.07	0.17	0.08	0.24	0.38	0.39	0.32	0.32	0.65	0.49	1.99
B. pendula	0.04	0.16	0.07	0.17	0.38	0.51	0.33	0.38	0.82	0.61	1.61
A. incana	0.18	0.21	0.22	0.28	0.75	0.91	0.99	1.22	1.45	1.22	3.21
A. glutinosa	0.2	0.33	0.24	0.53	1.17	1.19	0.98	1.14	1.44	1.3	2.7
P. tremula	0.02	0.14	0.13	0.37	1.13	0.91	0.49	0.46	0.75	1.21	1.95

2.4 Nature of nitrogen compounds in wood

There should be no doubt that majority of wood nitrogen is bound to proteins, although free amino acids are apparently also always present. Lower amounts of miscellaneous organic nitrogen compounds have also been reported, and in addition, some inorganic compounds (ammonia and nitrate) can be found as essential nitrogen sources (Rennenberg et al. 1998, 2010). The existing literature on wood amino acids and proteins is relatively extensive (Lists 1–2), covering a large number of different tree species and indicating that typical, major plant amino acids also play key roles in trees.

List 1. Studies on characterisation conifer proteins and free amino acids.

Holmes and Kurth (1961), Barnes (1963), Fukuda (1963), Laidlaw and Smith (1965), Durzan and Steward (1967), Hodges et al. (1968), Ziegler (1968), Clark and Mills (1970), Adelsberger and Petrowitz (1976), Butcher and Fountain (1987), Fukuda et al. (1988), Wetzel and Greenwood (1989), Roberts et al. (1991), Harms and Sauter (1992), Pietiläinen and Lähdesmäki (1995), Lähdesmäki and Pietiläinen (1996), Donald et al. (2000), Sudachkova et al. (2000), Hafrén (2007).

List 2. Examples of studies on characterisation of hardwood proteins and amino acids.

Mittler (1953), Reuter and Wolffgang (1954), Reuter (1957), Bollard (1957), Mugg (1959), Lamport and Northcote (1960), Barnes (1963), Dickson (1989), Dietrchs and Funke (1967), Sauter (1981), Titus and Kang (1982), Cleve et al. (1988), Putman et al. (1989, 1991), Wetzel and Greenwood (1991a, 1991b), Harms and Sauter (1992), Sauter and van Cleve (1994), Stepien et al. (1992, 1994), Close (1996), Sauter and Wellenkamp (1998), Sauter et al. (1989, 1999).

During the past years and decades, more and more attention has been paid to the roles and characterisation of different cell wall proteins in wood (List 3), as more advanced isolation and analysis techniques have been developed. For example, Gion et al. (2005) have identified 175 proteins in a wood forming tissue of maritima pine and found them play a role in either defence (19.4%), carbohydrates (16.6%) and amino acid (14.9%) metabolisms, genes and proteins expression (13.1%), cytoskeleton (8%), cell wall biosynthesis (5.7%), secondary (5.1%) and primary (4%) metabolisms. Westermark et al. (1986) have shown that protein content in the middle lamella fraction of spruce wood was 1.1%, compared to 0.2% in whole wood.

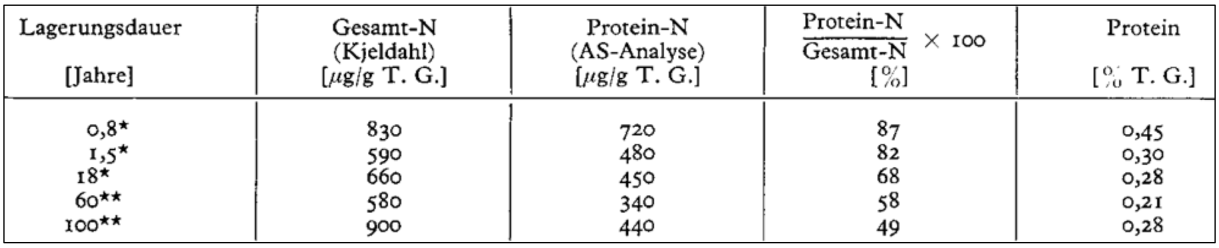
List 3. Studies on protein-lignin complexes, protein-polysaccharide complexes and cell wall proteins in wood.

Heath et al. (1971), Whitmore (1982), Dill et al. (1984), Westermark et al. (1986), Fukuda et al. (1988), Bao et al. (1992), Karácsonyi et al. (1996, 1998), Loopstra (2000), Gion et al. (2005), Hornatowska (2005), Makarova et al. (2015), Costa and Plazanet (2016), Fleming et al. (2016).

A few examples will be provided to demonstrate more detailed amino acid composition of total or individual wood proteins. In a pioneering study, by Adelsberger and Petrowitz (1976) analysed total nitrogen and protein in different parts of Scotch pine wood stem, and confirmed the dominating role of proteins compared to the total nitrogen (Tables 7–8). Of the listed amino acids, hydroxyproline produces a specific compound (pyrrole) during kraft pulping that can be found in black liquors, condensates, and rectified methanol.

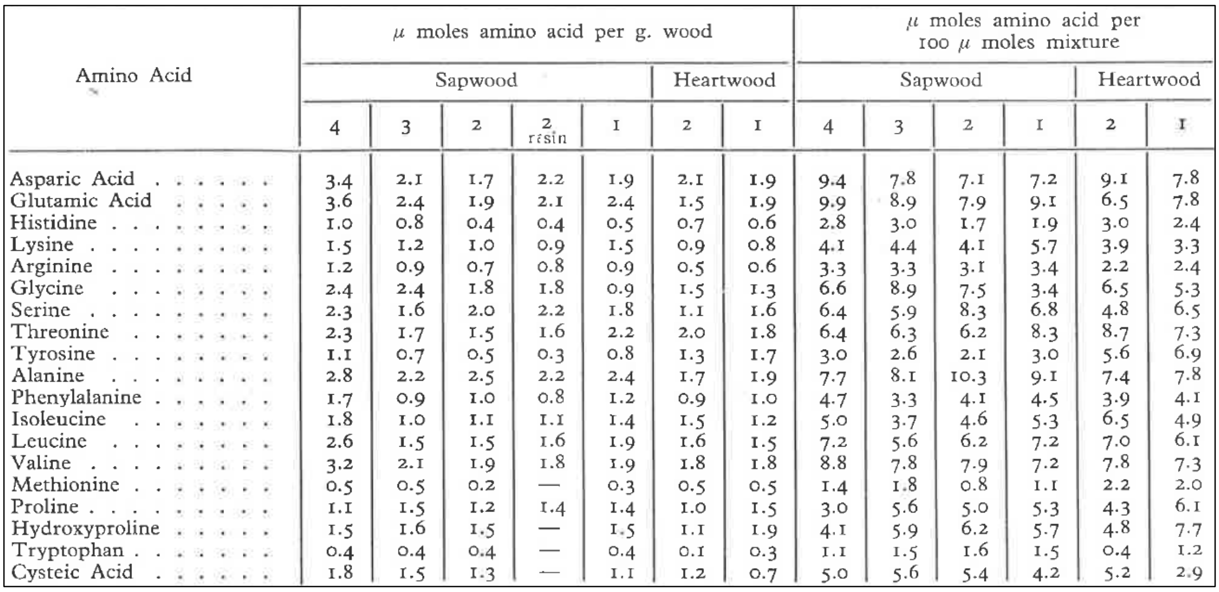
In another example (Table 9), Scurfield and Nicholls (1970) have analysed amino acid compositions for several Eucalyptus species. No similar studies on birch wood proteins could readily be found, but it is justified to assume that the same amino acids could be found, possibly in (slightly) different shares.

Table 7. Concentrations of total nitrogen and protein-nitrogen in different annual growth rings of a Scots pine wood stem (Adelsberger and Petrowitz 1976).



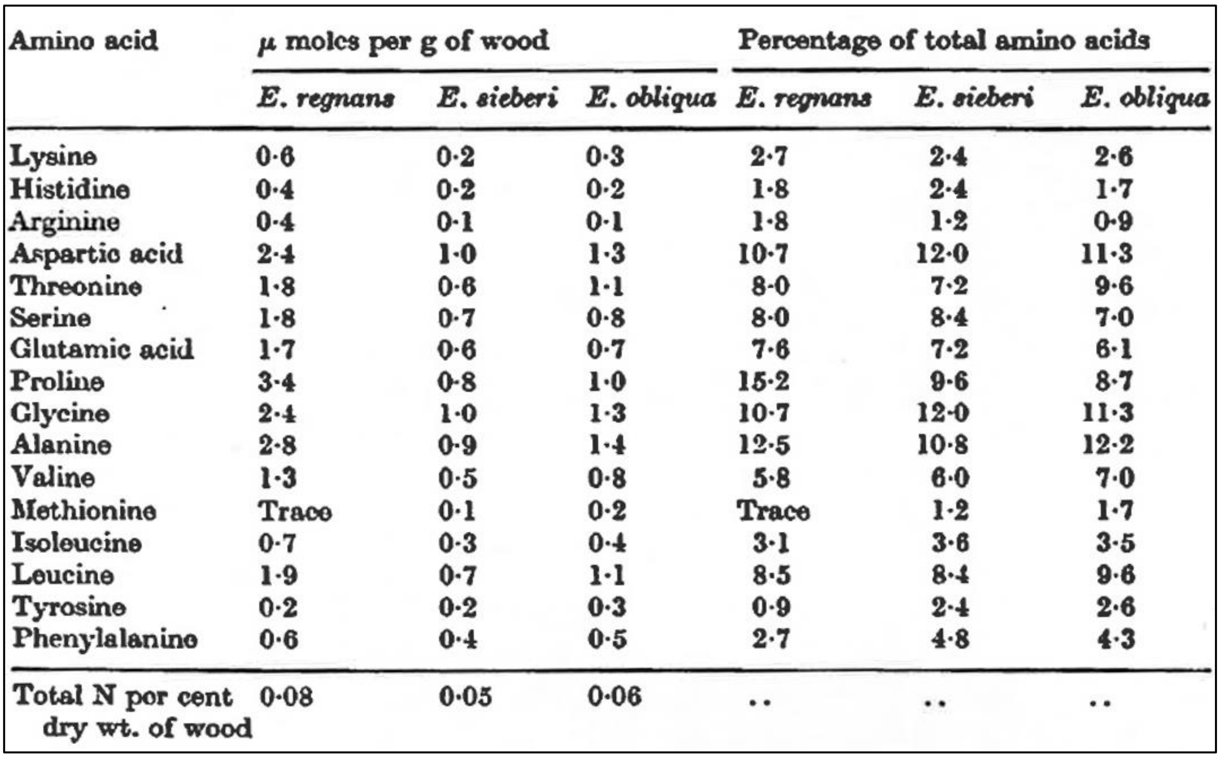
Lagerungsdauer [Jahre]	Gesamt-N (Kjeldahl) [μg/g T. G.]	Protein-N (AS-Analyse) [μg/g T. G.]	$\frac{\text{Protein-N}}{\text{Gesamt-N}} \times 100$ [%]	Protein [% T. G.]
0,8*	830	720	87	0,45
1,5*	590	480	82	0,30
18*	660	450	68	0,28
60**	580	340	58	0,21
100**	900	440	49	0,28

Table 8. Amino acid composition of Scots pine proteins, according to Adelsberger and Petrowitz (1976).



Amino Acid	μ moles amino acid per g. wood							μ moles amino acid per 100 μ moles mixture					
	Sapwood					Heartwood		Sapwood				Heartwood	
	4	3	2	2 resin	1	2	1	4	3	2	1	2	1
Asparic Acid	3.4	2.1	1.7	2.2	1.9	2.1	1.9	9.4	7.8	7.1	7.2	9.1	7.8
Glutamic Acid	3.6	2.4	1.9	2.1	2.4	1.5	1.9	9.9	8.9	7.9	9.1	6.5	7.8
Histidine	1.0	0.8	0.4	0.4	0.5	0.7	0.6	2.8	3.0	1.7	1.9	3.0	2.4
Lysine	1.5	1.2	1.0	0.9	1.5	0.9	0.8	4.1	4.4	4.1	5.7	3.9	3.3
Arginine	1.2	0.9	0.7	0.8	0.9	0.5	0.6	3.3	3.3	3.1	3.4	2.2	2.4
Glycine	2.4	2.4	1.8	1.8	0.9	1.5	1.3	6.6	8.9	7.5	3.4	6.5	5.3
Serine	2.3	1.6	2.0	2.2	1.8	1.1	1.6	6.4	5.9	8.3	6.8	4.8	6.5
Threonine	2.3	1.7	1.5	1.6	2.2	2.0	1.8	6.4	6.3	6.2	8.3	8.7	7.3
Tyrosine	1.1	0.7	0.5	0.3	0.8	1.3	1.7	3.0	2.6	2.1	3.0	5.6	6.9
Alanine	2.8	2.2	2.5	2.2	2.4	1.7	1.9	7.7	8.1	10.3	9.1	7.4	7.8
Phenylalanine	1.7	0.9	1.0	0.8	1.2	0.9	1.0	4.7	3.3	4.1	4.5	3.9	4.1
Isoleucine	1.8	1.0	1.1	1.1	1.4	1.5	1.2	5.0	3.7	4.6	5.3	6.5	4.9
Leucine	2.6	1.5	1.5	1.6	1.9	1.6	1.5	7.2	5.6	6.2	7.2	7.0	6.1
Valine	3.2	2.1	1.9	1.8	1.9	1.8	1.8	8.8	7.8	7.9	7.2	7.8	7.3
Methionine	0.5	0.5	0.2	—	0.3	0.5	0.5	1.4	1.8	0.8	1.1	2.2	2.0
Proline	1.1	1.5	1.2	1.4	1.4	1.0	1.5	3.0	5.6	5.0	5.3	4.3	6.1
Hydroxyproline	1.5	1.6	1.5	—	1.5	1.1	1.9	4.1	5.9	6.2	5.7	4.8	7.7
Tryptophan	0.4	0.4	0.4	—	0.4	0.1	0.3	1.1	1.5	1.6	1.5	0.4	1.2
Cysteic Acid	1.8	1.5	1.3	—	1.1	1.2	0.7	5.0	5.6	5.4	4.2	5.2	2.9

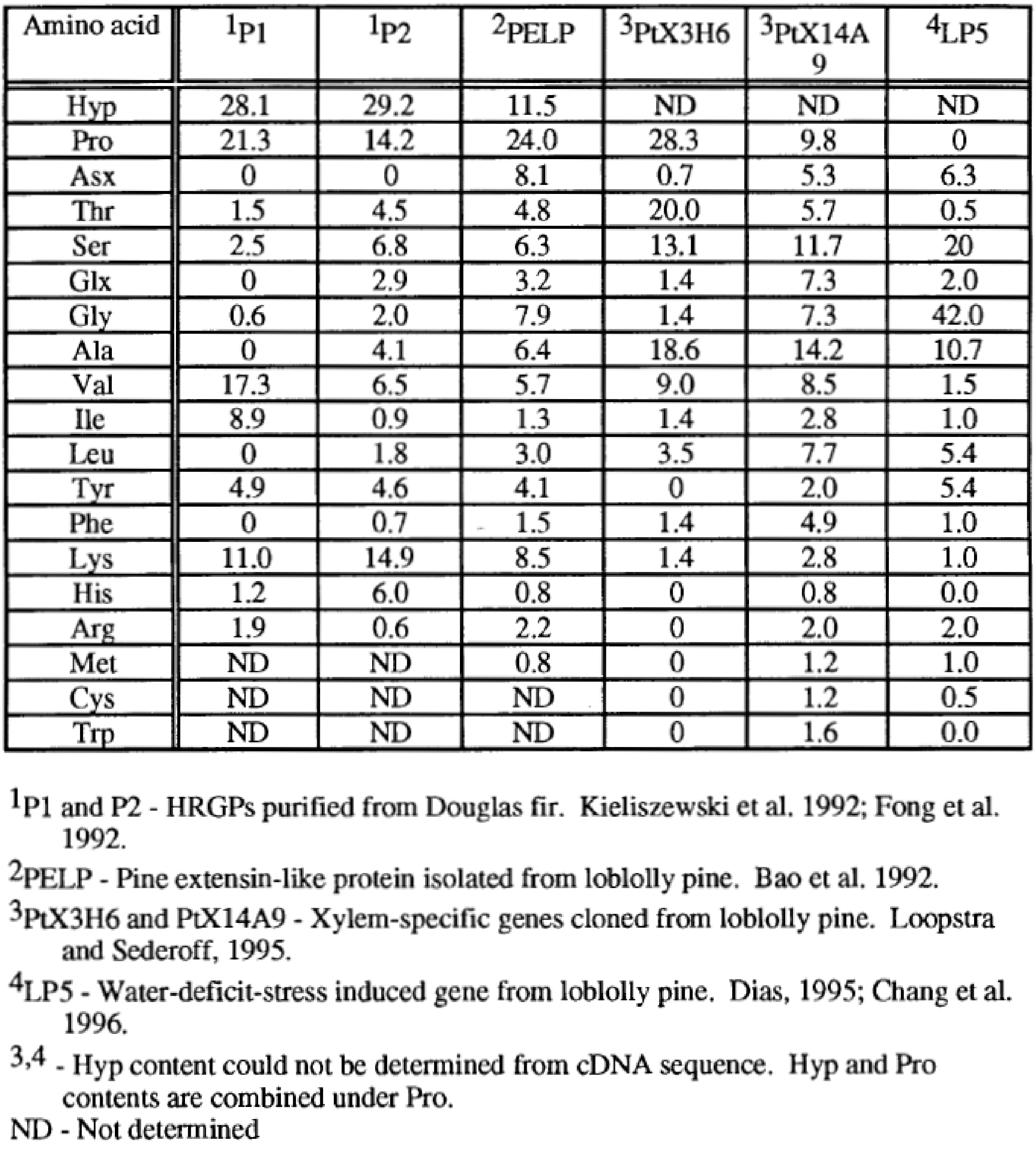
Table 9. Amino acid composition of heartwood of selected Eucalyptus species, according to Scurfield and Nicholls (1970).



Amino acid	μ moles per g of wood			Percentage of total amino acids		
	E. regnans	*E. sieberi*	*E. obliqua*	*E. regnans*	*E. sieberi*	*E. obliqua*
Lysine	0·6	0·2	0·3	2·7	2·4	2·6
Histidine	0·4	0·2	0·2	1·8	2·4	1·7
Arginine	0·4	0·1	0·1	1·8	1·2	0·9
Aspartic acid	2·4	1·0	1·3	10·7	12·0	11·3
Threonine	1·8	0·6	1·1	8·0	7·2	9·6
Serine	1·8	0·7	0·8	8·0	8·4	7·0
Glutamic acid	1·7	0·6	0·7	7·6	7·2	6·1
Proline	3·4	0·8	1·0	15·2	9·6	8·7
Glycine	2·4	1·0	1·3	10·7	12·0	11·3
Alanine	2·8	0·9	1·4	12·5	10·8	12·2
Valine	1·3	0·5	0·8	5·8	6·0	7·0
Methionine	Trace	0·1	0·2	Trace	1·2	1·7
Isoleucine	0·7	0·3	0·4	3·1	3·6	3·5
Leucine	1·9	0·7	1·1	8·5	8·4	9·6
Tyrosine	0·2	0·2	0·3	0·9	2·4	2·6
Phenylalanine	0·6	0·4	0·5	2·7	4·8	4·3
Total N per cent dry wt. of wood	0·08	0·05	0·06	..	..	..

More recently, amino acid composition of several separate proteins from different softwood species have been determined. For example, Loopstra (2000) has reviewed earlier material from douglas fir and loblolly pine (Table 10) and Karácsonoyi et al. (1996, 1998) have characterised polysaccharide-proteins from Norway spruce

Table 10. Amino acid compositions of six conifer cell wall proteins (Loopstra 2000).



Amino acid	[1]P1	[1]P2	[2]PELP	[3]PtX3H6	[3]PtX14A9	[4]LP5
Hyp	28.1	29.2	11.5	ND	ND	ND
Pro	21.3	14.2	24.0	28.3	9.8	0
Asx	0	0	8.1	0.7	5.3	6.3
Thr	1.5	4.5	4.8	20.0	5.7	0.5
Ser	2.5	6.8	6.3	13.1	11.7	20
Glx	0	2.9	3.2	1.4	7.3	2.0
Gly	0.6	2.0	7.9	1.4	7.3	42.0
Ala	0	4.1	6.4	18.6	14.2	10.7
Val	17.3	6.5	5.7	9.0	8.5	1.5
Ile	8.9	0.9	1.3	1.4	2.8	1.0
Leu	0	1.8	3.0	3.5	7.7	5.4
Tyr	4.9	4.6	4.1	0	2.0	5.4
Phe	0	0.7	1.5	1.4	4.9	1.0
Lys	11.0	14.9	8.5	1.4	2.8	1.0
His	1.2	6.0	0.8	0	0.8	0.0
Arg	1.9	0.6	2.2	0	2.0	2.0
Met	ND	ND	0.8	0	1.2	1.0
Cys	ND	ND	ND	0	1.2	0.5
Trp	ND	ND	ND	0	1.6	0.0

[1] P1 and P2 - HRGPs purified from Douglas fir. Kieliszewski et al. 1992; Fong et al. 1992.

[2] PELP - Pine extensin-like protein isolated from loblolly pine. Bao et al. 1992.

[3] PtX3H6 and PtX14A9 - Xylem-specific genes cloned from loblolly pine. Loopstra and Sederoff, 1995.

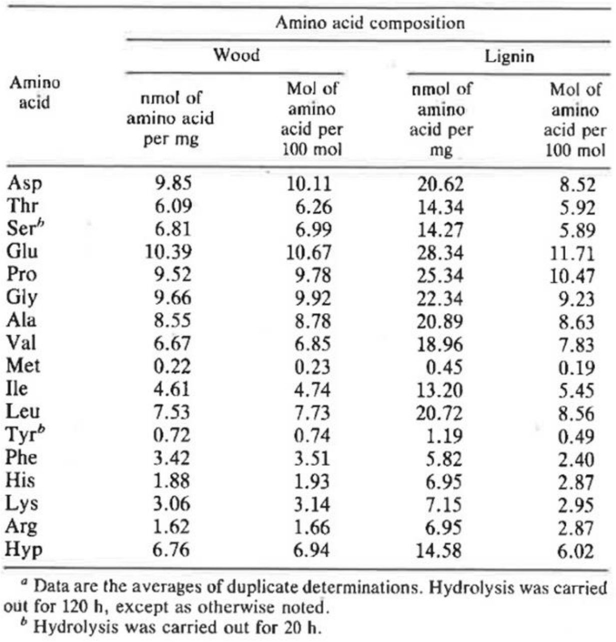
[4] LP5 - Water-deficit-stress induced gene from loblolly pine. Dias, 1995; Chang et al. 1996.

[3,4] - Hyp content could not be determined from cDNA sequence. Hyp and Pro contents are combined under Pro.

ND - Not determined

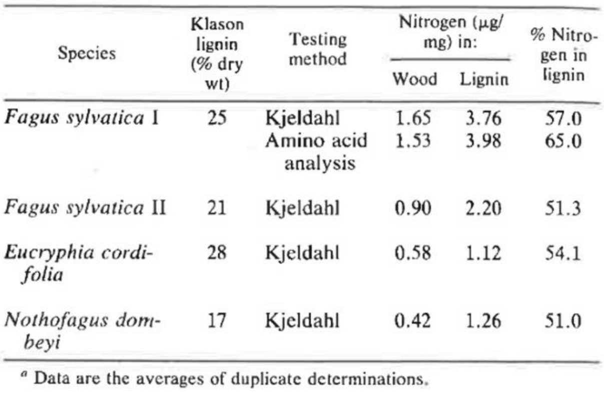
The nature of the lignin-protein linkages or complexes are still inadequately known. However, recent model compound experiments by Cong et al. (2013) and Diehl et al. (2014) have made it possible to characterise potential covalent links between lignin matrix and amino acids of the proteins. In this context it is interesting to note that Dill et al. (1984) found that c. 50% of wood (beech) nitrogen can be bound to Klason lignin (Tables 11–12). More studies would be required to establish how much of this nitrogen binding is original, and how much is generated during the acidic hydrolysis conditions.

Table 11 (left). Amino acid compositions of hydrolysates of wood and Klason lignin from beech. Table 12 (right). Nitrogen content of wood and Klason lignin of beech and two other hardwood species (Dill et al. 1984).



Amino acid	Amino acid composition			
	Wood		Lignin	
	nmol of amino acid per mg	Mol of amino acid per 100 mol	nmol of amino acid per mg	Mol of amino acid per 100 mol
Asp	9.85	10.11	20.62	8.52
Thr	6.09	6.26	14.34	5.92
Ser[b]	6.81	6.99	14.27	5.89
Glu	10.39	10.67	28.34	11.71
Pro	9.52	9.78	25.34	10.47
Gly	9.66	9.92	22.34	9.23
Ala	8.55	8.78	20.89	8.63
Val	6.67	6.85	18.96	7.83
Met	0.22	0.23	0.45	0.19
Ile	4.61	4.74	13.20	5.45
Leu	7.53	7.73	20.72	8.56
Tyr[b]	0.72	0.74	1.19	0.49
Phe	3.42	3.51	5.82	2.40
His	1.88	1.93	6.95	2.87
Lys	3.06	3.14	7.15	2.95
Arg	1.62	1.66	6.95	2.87
Hyp	6.76	6.94	14.58	6.02

[a] Data are the averages of duplicate determinations. Hydrolysis was carried out for 120 h, except as otherwise noted.
[b] Hydrolysis was carried out for 20 h.



Species	Klason lignin (% dry wt)	Testing method	Nitrogen (μg/mg) in:		% Nitrogen in lignin
			Wood	Lignin	
Fagus sylvatica I	25	Kjeldahl	1.65	3.76	57.0
		Amino acid analysis	1.53	3.98	65.0
Fagus sylvatica II	21	Kjeldahl	0.90	2.20	51.3
Eucryphia cordifolia	28	Kjeldahl	0.58	1.12	54.1
Nothofagus dombeyi	17	Kjeldahl	0.42	1.26	51.0

[a] Data are the averages of duplicate determinations.

3. Fate of wood nitrogen at kraft pulp mills

During the past decades, more and more attention has been paid to the fate of wood nitrogen and its reaction products, both in the fibreline and recovery line processes. Important recent sources of information include, among others, extensive studies at Åbo Akademi and in the 3-year EU funded project Rempulp (Reduction of air emissions at kraft pulp mills) (Niemelä et al. 2003). The Rempulp project also included the creation of nitrogen balances at three kraft pulp mills, using hardwood (birch and eucalyptus) and softwood as raw materials. In this Chapter, short summary on the nitrogen behaviour in the key process steps is given, supported by selected results mainly from the above studies. The main focus will be in the fibreline processes as they have a great impact on the generation of black liquor nitrogen.

3.1 Nitrogen in pulping

According to the current understanding, the main nitrogen reactions in the pulping stages include the following (illustrated in Figs. 11–16 and Tables 13–16):

- The nitrogen present in the wood raw material (typically 0.05–0.15%) is the main source of nitrogen found in black liquors; only marginal amounts (at most) are derived from any process chemicals such EDTA (Veverka et al. 1993, Siltala 1996).
- A substantial part of the nitrogen is dissolved from the wood chips into the cooking liquor at early pulping stages; there are no raw material-specific differences. The pulps going to oxygen delignification and bleaching contain only traces of nitrogen (Veverka et al. 1993, Niemelä and Ulmgren 2002, Niemelä et al. 2003). A Kjeldahl method has been optimised and calibrated for the accurate determination of total nitrogen in black liquors, (Niemelä and Tuominen 2005).
- The cooking conditions have only marginal effects on the overall release of nitrogen from chips.
- Approximately 10–15% of wood nitrogen is converted into ammonia during pulping, found first by Bergström and Fagerlind (1908). Model compound experiments have shown that different amino acids and proteins produce ammonia in different yield levels (e.g. 2–20%).

- The dissolved kraft lignin always contains some nitrogen; its content in lignin has been shown to be significantly higher in the beginning of the cook than in the final kraft lignin (Gellerstedt et al. 1984, Robert et al. 1984, Niemelä and Ulmgren 2002). The lignin-nitrogen is apparently derived from proteins that may be either covalently bound to lignin or just co-precipitated protein impurities. Alkaline hydrolysis reactions of the proteins during the cooks explain the reduction of the amount of nitrogen in lignin. The nature of the nitrogen compounds or links in the final kraft lignin are poorly known; lignin may also react with the liberated ammonia (Weichelt 1981, Weichelt and Khairy 1981).
- Small amounts of protein-derived amino acids can also be found in black liquors. Also, there is a small number of other (cyclic) nitrogen compounds found in black liquors, formed from different amino acids. Some of the products are specific for certain amino acids, such pyrrole derived from hydroxyproline (Niemelä 1990, Martin and Malcolm 1995, Niemelä and Ulmgren 2002, Niemelä et al. 2003). Generally, there is only relatively little information available on the alkaline degradation and hydrolysis reactions of proteins under the alkaline conditions relevant for kraft pulping. Most of the alkaline hydrolysis studies have dealt with the analysis of certain amino acids via their specific degradation products (e.g. Herzfeld 1913, Onslow 1921, Spies and Chambers 1949, McGrath 1972, Hugli and Moore 1972, Asquith and Carthew 1972, Levine 1982, Nielsen and Hurrell 1985).

Table 13. Characterisation of pine kraft black liquors from laboratory pulping at 170 °C (Niemelä and Ulmgren 2002). The rest of nitrogen (not characterised) is probably mainly in the forms of proteins and free amino acids.

Compound (fraction)	Kappa number 134	Kappa number 87.5	Kappa number 20.6
Total nitrogen, mg/L	96	170	180
Ammonium nitrogen, mg/L	7.5	13	16
Lignin, g/L	11.1	40.9	62
Nitrogen in lignin, %	0.26	0.058	0.045
Nitrogen in lignin, mg/L	29	24	28

Table 14. The extent of ammonia formation during laboratory-scale cooking of different raw materials (Niemelä et al. 2003).

Raw material	Kappa number	Total N, mg/L	Ammon. N, mg/L	Ammon. N, %
Birch	100	49.6	6.8	13.7
Birch*	15	159.7	21.7	13.6
Eucalyptus	81	66.3	8.1	12.2
Eucalyptus**	13	100.5	12.3	12.2
Pine	134	96	7.5	7.8
Pine	88	170	13	7.6
Pine	18	180	16	8.9

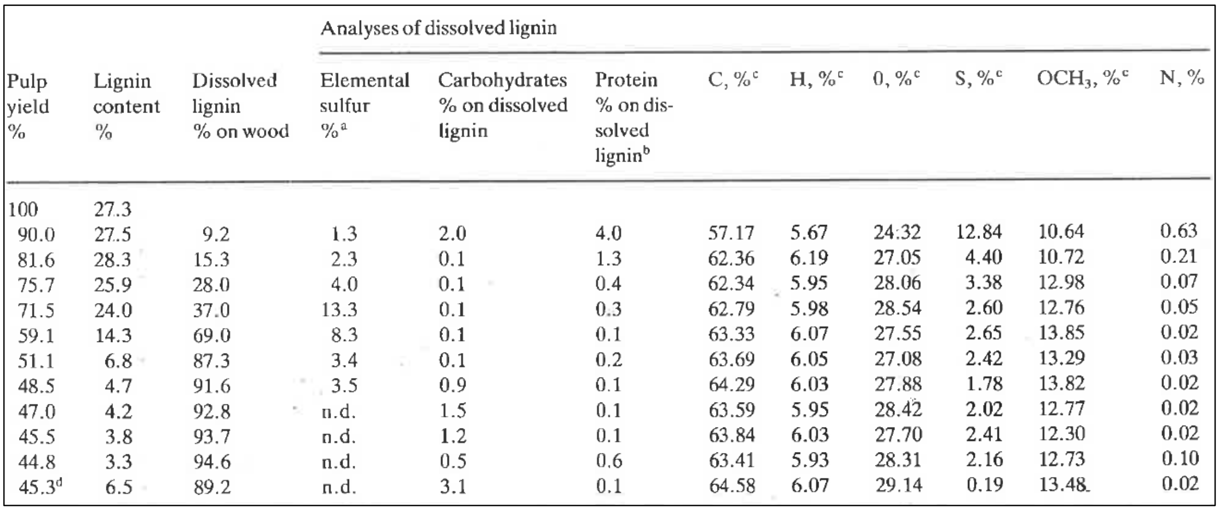
*Another final black liquor contained 162 and 24.1 mg/L of total and ammon. nitrogen, respectively.
**Another final black liquor contained 104 and 11.7 mg/L of total and ammon. nitrogen, respectively.

Table 15. The formation of ammonia (% of total nitrogen) after alkali treatment of selected model compounds at 160 or 170 °C for 30 min.

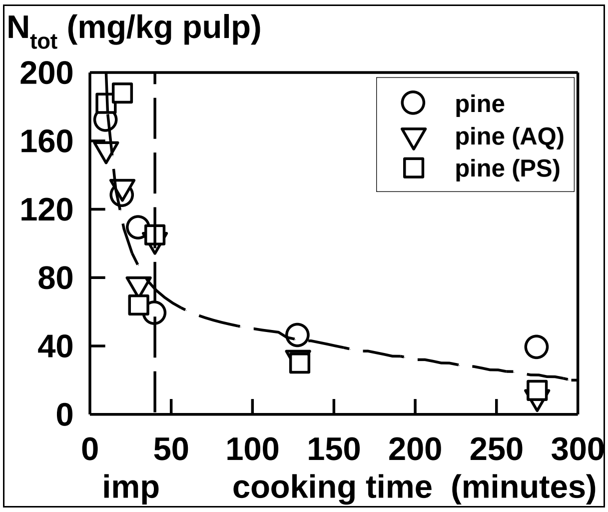
Material	160 °C, NaOH	170 °C, NaOH	170 °C, NaOH/Na_2S
4-Hydroxyproline	8.0	n.s.*	n.s.
Glycine	0.6	1.2	0.5
Serine	13.5	22.0	19.5
Valine	1.4	1.6	0.4
Aspartic acid	n.s.	7.4	n.s.
Glutamic acid	n.s.	1.4	n.s.
Proline	n.s.	2.3	n.s.
Phenylalanine	n.s.	3.6	n.s.
Lysine	n.s.	1.5	n.s.

*ns; not studied.

Table 16. Changes in the composition of dissolved lignin during kraft pulping of Scots pine (Gellerstedt el al. 1984). Note the changes in the nitrogen content of lignin.



			Analyses of dissolved lignin								
Pulp yield %	Lignin content %	Dissolved lignin % on wood	Elemental sulfur %^{a}	Carbohydrates % on dissolved lignin	Protein % on dissolved lignin^{b}	C, %^{c}	H, %^{c}	O, %^{c}	S, %^{c}	OCH_3, %^{c}	N, %
100	27.3										
90.0	27.5	9.2	1.3	2.0	4.0	57.17	5.67	24:32	12.84	10.64	0.63
81.6	28.3	15.3	2.3	0.1	1.3	62.36	6.19	27.05	4.40	10.72	0.21
75.7	25.9	28.0	4.0	0.1	0.4	62.34	5.95	28.06	3.38	12.98	0.07
71.5	24.0	37.0	13.3	0.1	0.3	62.79	5.98	28.54	2.60	12.76	0.05
59.1	14.3	69.0	8.3	0.1	0.1	63.33	6.07	27.55	2.65	13.85	0.02
51.1	6.8	87.3	3.4	0.1	0.2	63.69	6.05	27.08	2.42	13.29	0.03
48.5	4.7	91.6	3.5	0.9	0.1	64.29	6.03	27.88	1.78	13.82	0.02
47.0	4.2	92.8	n.d.	1.5	0.1	63.59	5.95	28.42	2.02	12.77	0.02
45.5	3.8	93.7	n.d.	1.2	0.1	63.84	6.03	27.70	2.41	12.30	0.02
44.8	3.3	94.6	n.d.	0.5	0.6	63.41	5.93	28.31	2.16	12.73	0.10
45.3^{d}	6.5	89.2	n.d.	3.1	0.1	64.58	6.07	29.14	0.19	13.48	0.02



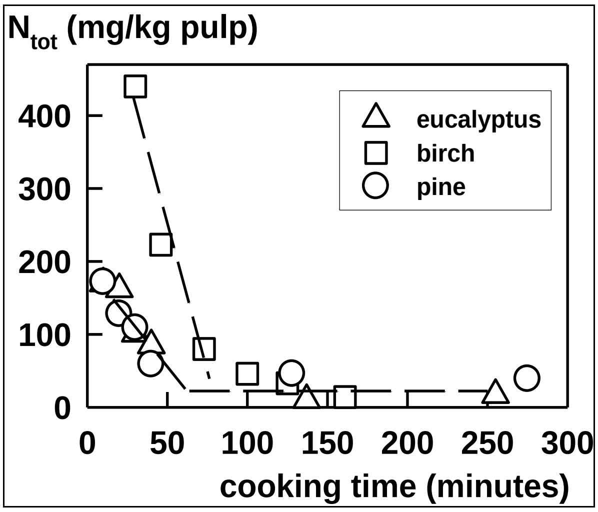
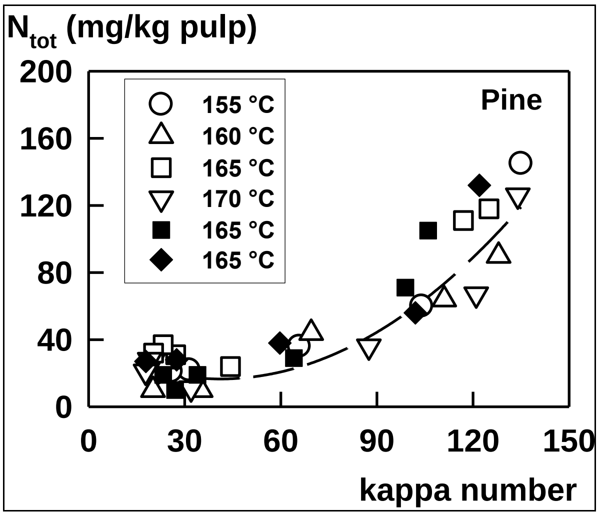


Fig. 12 (left). Release of nitrogen from wood chips vs. impregnation (imp) and cooking time for pine cooks with or without addition of anthraquinone (AQ) or polysulphide (PS), at 165 °C.
Fig. 13 (right). Release of nitrogen from wood chips versus cooking time. The temperatures for eucalyptus and birch cooks were 147 and 162 °C, respectively (Niemelä et al. 2003).



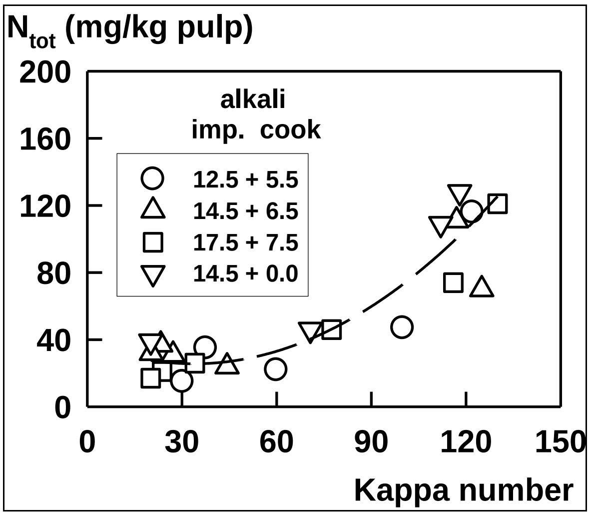


Fig. 14 (left). Release of nitrogen from pine wood vs. kappa number during cooking at different temperatures. Unfilled and filled symbols refer to the cooking experiments with synthetic and industrial white liquors, respectively.

Fig. 15 (right). Release of nitrogen from pine chips versus kappa number at different distributions of alkali charge (% of wood) between impregnation (first number) and cooking (second number). The cooking temperature was 165 °C. (Niemelä et al. 2003).

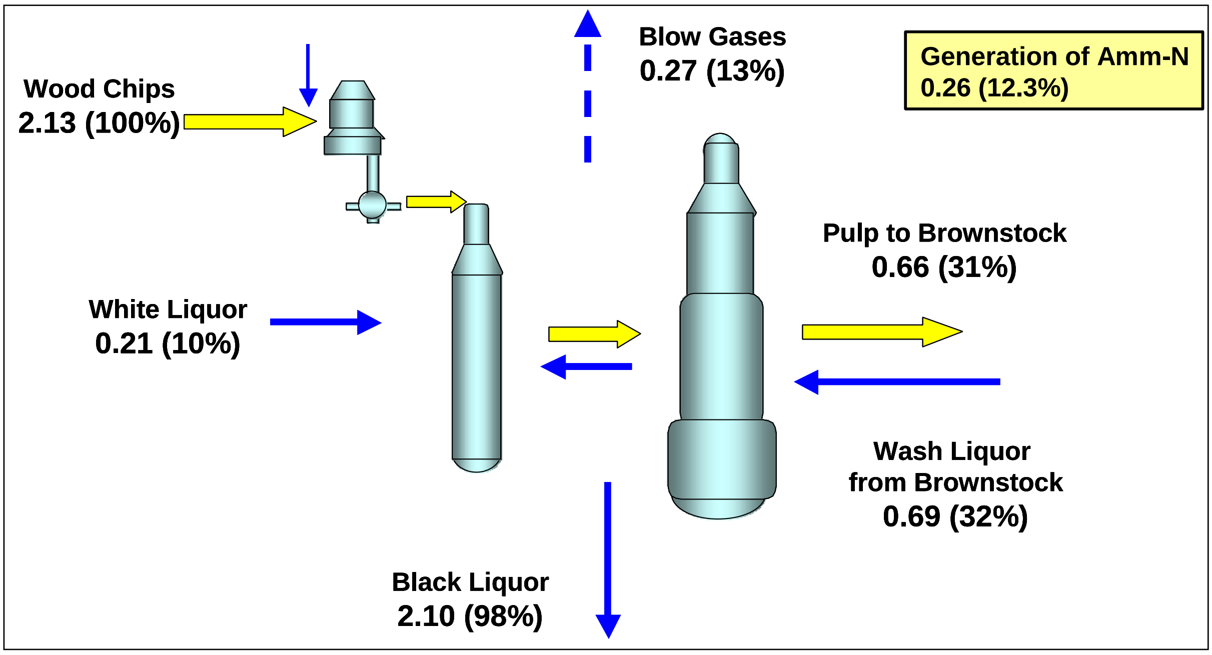
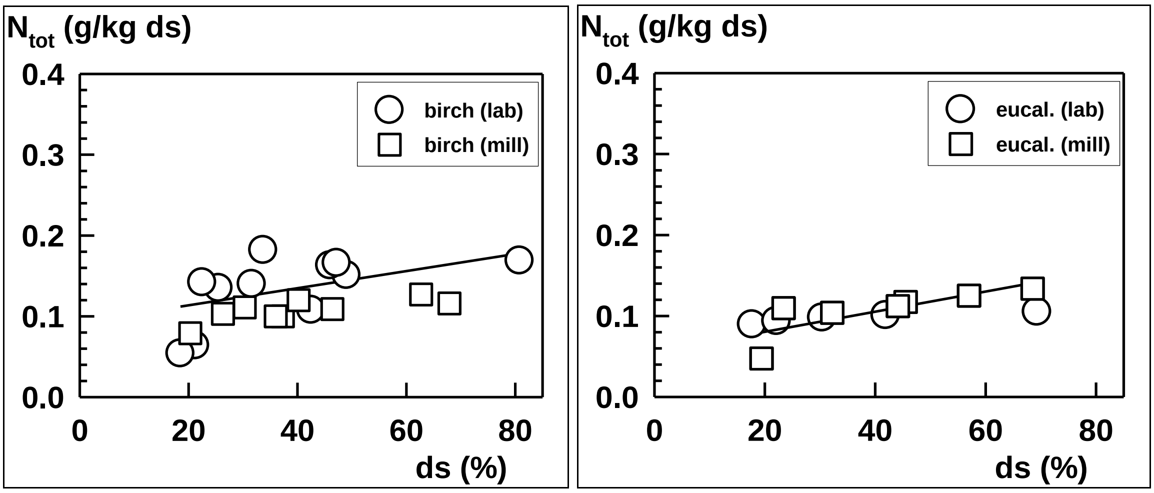


Fig. 16. Total nitrogen balances for the digester at one of the study mills (Niemelä et al. 2003). The figures are given as kg N/ton pulp and normalised to nitrogen in wood chips (100%).

3.2 Nitrogen in black liquor evaporation and condensate handling

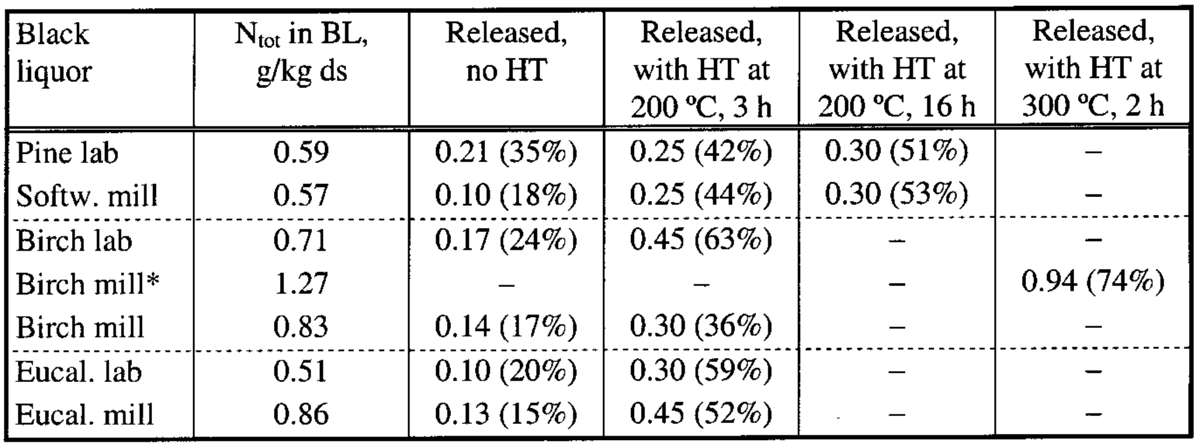
According to the current understanding, the main nitrogen steps or reactions in black liquor evaporation, condensate handling and by-products recovery include the following (illustrated in Figs. 17–18 and Tables 17–20):

- Ammonia and other volatile nitrogen compounds are readily transferred to the condensates at early evaporation stages. There is only some additional ammonia formation during later evaporation stages. Highest ammonia concentrations are naturally found in the foul condensates.
- The extent of nitrogen removal during evaporation can be increased by high-temperature black liquor treatments. The required conditions are, however, probably too drastic for full mill-scale applications. The increased formation of volatile sulphur compounds in such treatments also needs to be taken into account (Niemelä et al. 2003).
- Ammonia and other volatile nitrogen compounds are stripped off from foul condensates, and are thus also found in rectified methanol. Ammonia is always the dominating nitrogen compound in rectified methanol; approximately 85–95% of nitrogen in methanol is in the form of ammonia. The high ammonia shares are in accordance with its known tendency to be stripped off (e.g. Emilsson et al. 1997, Olsson 1999, Crawford and Someshwar 2000), and with its known high solubility in methanol (Short et al. 1983).
- Some amine-type compounds are also present in methanol but they have not yet been fully identified. Surprisingly, such compounds have not been found in other kraft pulping process streams, suggesting that they may be formed during methanol recovery (Niemelä 2004).
- Some nitrogen can also be found in crude sulphate turpentines. In the samples analysed by Niemelä et al. (2003), the figures for the total and ammonium nitrogen varied from 60 to 160 mg/L and 5 to 13 mg/L, respectively. The ammonia smell in the turpentine recovery was noticed by Knösel as early as 1876.
- Some nitrogen can also be found in crude tall oil. In the samples analysed by Niemelä et al. (2003), the figures for the total nitrogen varied from 1130 to 2700 mg/L. Very little is known on the nature of these nitrogen compounds.
- It is also noteworthy that ammonia can be separated as a by-product (from different streams). So far, this has obviously taken place globally at one mill only, in Kotka in the 1910s. The highest annual production volume was eight tons of ammonium sulphate.



Figs. 17 and 18. Total release of nitrogen into condensate during laboratory evaporation of birch and eucalyptus black liquors (versus ds). The original nitrogen contents of the liquors were 0.069% for birch lab, 0.083% for birch mill, 0.051% for eucalyptus lab, and 0.086% for eucalyptus mill (from Niemelä et al. 2003).

Table 17. Release of total nitrogen in laboratory evaporation of black liquors, with and without heat treatment. Procedure: pre-evaporation to 30–50% ds, then heat treatment (HT) and finally evaporation to about 70% ds. N released, amount of N released from the liquors in the laboratory evaporator; –, not determined. The numbers given must be considered rather rough since variations in total nitrogen concentrations in condensates under the same experimental conditions were common.



Black liquor	N_{tot} in BL, g/kg ds	Released, no HT	Released, with HT at 200 °C, 3 h	Released, with HT at 200 °C, 16 h	Released, with HT at 300 °C, 2 h
Pine lab	0.59	0.21 (35%)	0.25 (42%)	0.30 (51%)	–
Softw. mill	0.57	0.10 (18%)	0.25 (44%)	0.30 (53%)	–
Birch lab	0.71	0.17 (24%)	0.45 (63%)	–	–
Birch mill*	1.27	–	–	–	0.94 (74%)
Birch mill	0.83	0.14 (17%)	0.30 (36%)	–	–
Eucal. lab	0.51	0.10 (20%)	0.30 (59%)	–	–
Eucal. mill	0.86	0.13 (15%)	0.45 (52%)	–	–

Table 18. Rough concentration ranges of nitrogen compounds (as mg N/L) in the main condensate types at a softwood pulp mill studied by Niemelä et al. (2003).

Condensate type	Total N	Ammonium N	Pyrrole N	Other org. N
Cleanest	< 1	< 1	–	–
Semi-foul	100–170	100–150	0–5	0–5
Foul	200–350	200–330	30–60	5–25

Table 19. Nitrogen contents in the investigated methanol samples.

Origin of methanol	Total nitrogen, mg/L	Ammonium nitrogen, mg/L
Softwood mill	13,230	12,780
Hardwood mill 1	11,830	10,050
Hardwood mill 2	20,800	19,170

Table 20. Rough concentrations (mg/L) of organic nitrogen compounds (calculated as nitrogen) identified in the investigated methanol samples.

Compound (category)	Softwood mill	Hardwood mill 1	Hardwood mill 2
Pyrrole	65	20	70
1-Methylpyrrole	20	–	30
Miscellaneous heterocyclic	traces	traces	traces
Aliphatic amines	220	150	190
Total	305	170	290

3.3 Nitrogen in black liquor combustion and white liquor preparation

The comprehensive studies on the behaviour of nitrogen in black liquor combustion and white liquor preparation, especially at Åbo Akademi, are well-known and therefore not summarised in any detail in this context. A lot of detailed information is provided by Aho (1994), Aho et al. (1994a, 1994b), Forssén et al. (1997), Kymäläinen (2001), Kymäläinen et al. (1999, 2001), DeMartini (2004), DeMartini et al. (2004a, 2004b), and Vähä-Savo (2014). Additional studies from Åbo Akademi include, for example, the studies by Malm (1997) and Holmström (1999). Åbo Akademi also had a strong role in the Rempulp project (Niemelä et al. 2003).

As a result of the above studies, there is detailed data available on the reactions of nitrogen in black liquor combustion and white liquor preparation, as well as on overall nitrogen balances at kraft pulp mills operating under different conditions and using different raw materials. In Sweden, nitrogen balances at the mills have been studied by Boström et al. (1997), Stripple (1997) and Stripple and Tomani (1997). The main nitrogen reactions or related to process steps include (examples in Figs. 19–20).

- Nitrogen entering the recovery boiler with the black liquor is converted during combustion to gaseous N_2, NO, and cyanate (OCN^-) in the smelt. The combustion conditions can be controlled, for example to increase nitrogen incorporation into smelt which offers certain opportunities to force more nitrogen as ammonia to different gaseous streams (for separate handling or combustion).
- Cyanate originating from the smelt is slowly but completely converted into ammonia during green liquor handling and white liquor preparation. The kinetics shows significant mill-to-mill differences.
- Some ammonia is removed from the green and white liquors with the vent gases, but most of it returns to cooking with the white liquor. Ammonia emissions from the causticisation lines may correspond to one third of all nitrogen emissions from the recovery cycles.
- Proper handling of all non-condensable gases (NCGs), stripper off-gases or rectified methanol, and causticisation vent gases is of great importance for controlling the millwide NOx balances. The experience has shown that the recovery boilers offer the best option for the low NOx combustion of these ammonia-containing streams.
- If necessary, it is also possible to remove ammonia from stripper off-gases, methanol or vent gases before combustion. The removed ammonia could be used, for example, in selective catalytic reduction systems at recovery boilers, or as a nutrient (ammonium sulphate or phosphate) at the activated sludge plants.
- The addition of biosludge to black liquor increases its nitrogen content, but does not necessarily result in clearly higher NOx emission from the recovery boiler. Instead, it appears that the increased nitrogen content of the as-fired black liquor results in an increase in cyanate formation, both in green liquor samples and laboratory-made smelts, which then results in more ammonia in the chemical recovery cycle.
- The level of black liquor nitrogen can apparently be also affected by integration of lignin recovery processes at the mills, as certain amounts of lignin-bound nitrogen will this way be removed from the black liquors.

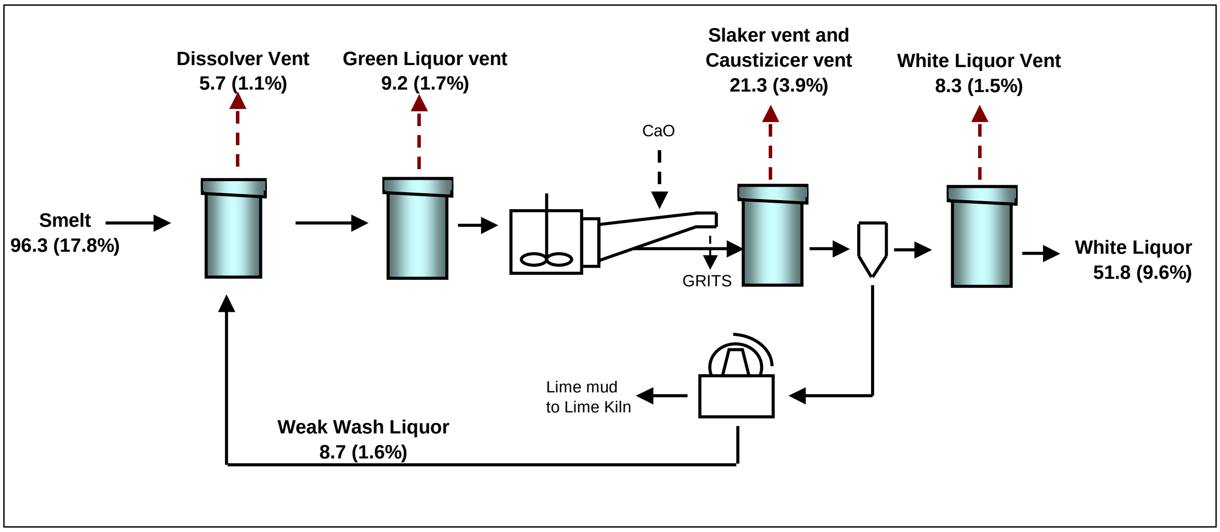


Fig. 19. Total nitrogen balance for the causticizing areas at one of the study mills (Niemelä et al. 2003). The figures are given as kg N/ton of white liquor produced, and in brackets as percent of nitrogen entering the mills with wood chips.

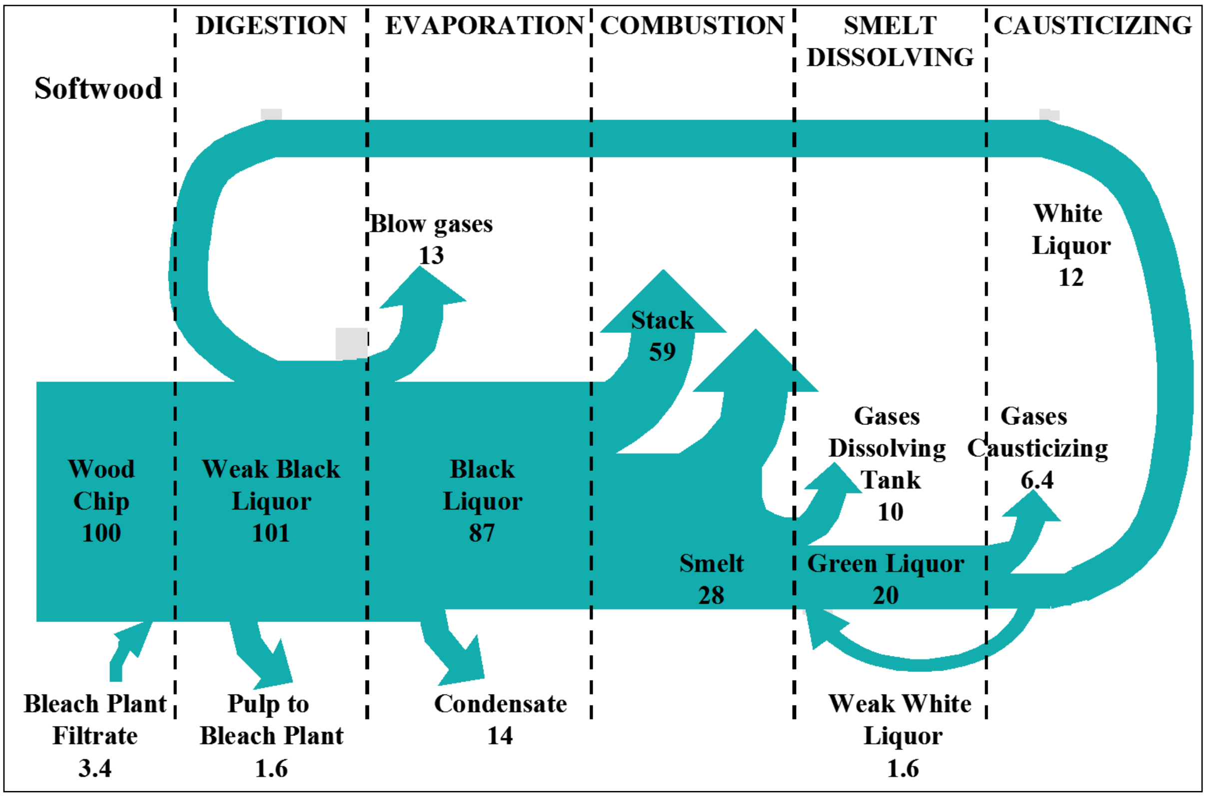


Fig. 20. Normalised total nitrogen balances for two study mills. Nitrogen intake with wood chips normalised to 100% (Niemelä et al. 2003).

4. Summary and conclusions

The present review focused on the content of nitrogen in the Nordic pine, spruce and birch trees, as well as on the nature of organic nitrogen constituents and their behaviour in the kraft process. For comparison, a lot of material was also collected addressing other softwood and hardwood materials, but the corresponding concentrations are not tabulated in detail.

During the comprehensive literature searches it became evident that there is a huge amount of information available on nitrogen content in dozens of different softwood and hardwood species covering numerous industrially important genera. It also became clear that the studies cover all different tree parts, including twigs and branches, bark, roots, and needles. Furthermore, it is evident that practically taken all the main wood species contain equally low amounts of nitrogen in mature stemwood, as the figures above >0.25–0.3% have only seldom been reported.

For the Nordic wood species, the nitrogen content in stemwood usually varies from c. 0.05 to 0.15%, although somewhat higher amounts have also been frequently reported. For the recorded variation, there are apparently many reasons, depending for example on the following factors:

- different applied analytical methods used at different laboratories
- different geographical locations, soil type, and potential fertilisation
- age of wood
- specific sampling point in wood, vs. a bulk sample
- purity of the samples, e.g. carefully sorted sample vs. industrial chips

All those factors (known or unknown) make it hard to reach sufficiently detailed or correct final conclusions on the most representative values for the nitrogen content of wood, especially for pulpwood used at the current pulp mills. This is also hampered by the fact that very little data has been published on nitrogen content of pulp mill chips. Although there is some data, as already mentioned (p. 13) on higher nitrogen content in hardwood than softwood black liquors, this is not unambiguously supported by the reported nitrogen contents in the corresponding wood raw materials. Furthermore, it is noteworthy that the reported nitrogen contents do not justify any obvious differences between the Swedish and Finnish wood materials and do not thus provide clear explanations for the differences between the reported NOx emission from the pulp mills in these countries. For further clarifications it is therefore now recommended to conduct a national sampling and analysis campaign to cover chips and black liquor samples from the domestic pulp mills, to be all analysed in the same laboratory with the same methods to produce comparable results. In this context, it might also be beneficial to analyse the black liquors for both the total and ammonium nitrogen, to further clarify potential systematic differences in the role of ammonium nitrogen between softwood and hardwood black liquors and NOx emissions. The mill sampling campaigns could also be supported by representative laboratory-scale cooking experiments and analyses. For the black liquors, for example VTT (KCL) has developed an improved Kjeldahl method (Niemelä and Tuominen 2005).

Appendix 1. Nitrogen and other nutrient concentrations (%) in a number of softwood and hardwood species (Meerts 2002). Softwoods cover genera from Abies to Tsuga.

		Concentrations in sapwood (s) and heartwood (h) (mg kg^{-1})										Heartwood/sapwood				
Species	Taxon	N_s	N_h	P_s	P_h	K_s	K_h	Ca_s	Ca_h	Mg_s	Mg_h	N	P	K	Ca	Mg
Abies firma	1					3000	2000			110	100			0.67		0.91
Abies firma	1			20	2	250	1000	300	400	100	100		0.10	4.00	1.33	1.00
Abies sacchalinensis	1					630	1000	800	1200	150	200			1.59	1.50	1.33
Callitris columellaris	1			10	10	320	230	3170	3710	460	510		1.00	0.72	1.17	1.11
Callitris hugelii	1			55	10	600	380	2960	4710	160	480		0.18	0.63	1.59	3.00
Cedrus deodara	1							1500	300						0.20	
Chamaecyparis obtusa	1					600	500	400	300	75	100			0.83	0.75	1.33
Chamaecyparis thyoides	1							600	200	80	40				0.33	0.50
Cryptomeria japonica	1							606	562	93	184				0.93	1.98
Cryptomeria japonica	1					1600	5600	1000	800	100	200			3.50	0.80	2.00
Cryptomeria japonica	1			70	5.5	375	1150	950	900	85	200		0.08	3.07	0.95	2.35
Larix decidua	1			280	30	678	140	709	600	164	167		0.11	0.21	0.85	1.02
Larix laricina	1			185	20	754	490	559	652	151	323		0.11	0.65	1.17	2.14
Larix leptolepis	1					600	200	400	200	100	50			0.33	0.50	0.50
Metasequoia glyptostroboides	1							800	450	160	100				0.56	0.63
Picea abies	1	1600	800	95	5	900	300	600	700			0.50	0.05	0.33	1.17	
Picea rubens	1					873	522	936	810	166	412			0.60	0.87	2.48
Picea rubens	1							500	800	62	60				1.60	0.97
Picea rubens	1			67	33	776	875	597	673	74	85		0.49	1.13	1.13	1.15
Pinus densiflora	1					450	250	700	900	100	200			0.56	1.29	2.00
Pinus nigra	1	950	910	94	20	900	400	570	660	180	255	0.96	0.21	0.44	1.16	1.42
Pinus rigida	1	870	970	70	20	490	240	810	1040	275	146	1.11	0.29	0.49	1.28	0.53
Pinus strobus	1	1000	450									0.45				
Pinus sylvestris	1	1060	640	100	17	740	130	580	710	240	230	0.60	0.17	0.18	1.22	0.96
Pinus sylvestris	1	790	600	68	33	473	385	796	969	106	140	0.76	0.49	0.81	1.22	1.32
Pinus sylvestris	1	470	400	61	3	300	3	500	600	150	150	0.85	0.05	0.01	1.20	1.00
Podocarpus archboldii	1	1800	2000	110	70	840	1080	1480	1080	220	170	1.11	0.64	1.29	0.73	0.77
Thuyopsis dolobrata	1							706	1330	40	239				1.88	5.98
Tsuga diversifolia	1	750	400									0.53				
Acer rubrum	2	900	400									0.44				
Acer saccharum	2					1260	1502	2874	2812	643	1084			1.19	0.98	1.69
Acer saccharum	2			80	25			8000	1000				0.31		0.13	
Ackama paniculata	2			53	53	1100	210	610	490				1.00	0.19	0.80	
Aesculus turbinata	2					500	1000	1250	3200	500	700			2.00	2.56	1.40
Ardisia sp.	2	1250	1620	90	30	860	130	420	440	160	70	1.30	0.33	0.15	1.05	0.44
Banksia serratifolia	2			58	15	1300	170	580	710				0.26	0.13	1.22	
Betula lenta	2	950	500									0.53				
Carya sp.	2	2500	1500									0.60				
Castanea crenata	2							366	363	210	20.1				0.99	0.10
Castanea crenata	2					1250	560	300	200	300	20			0.45	0.67	0.07
Castanea sativa	2	1588	762	124	6	607	220	377	291	292	115	0.48	0.05	0.36	0.77	0.39
Casuarina cristata	2			70	43	770	1800	8800	8600				0.61	2.34	0.98	
Casuarina torulosa	2			40	10	450	10	630	720	120	140		0.25	0.02	1.14	1.17
Cedrela tonduzii	2	1200	600									0.50				
Ceiba pentendra	2	3900	1100									0.28				
Ceratopetalum apetalum	2			209	113	1940	1695	187	944				0.54	0.87	5.05	
Ceratopetalum apetalum	2	1700	1400	45	40	800	1100	3210	1930	240	370	0.82	0.89	1.38	0.60	1.54
Cornus florida	2	2000	2000									1.00				
Cryptocarya sp.	2	1000	1570	140	120	960	990	700	1200	950	3400	1.57	0.86	1.03	1.71	3.58
Dryadodaphne crassa	2	1370	1030	60	10	2300	540	540	4300	1220	710	0.75	0.17	0.23	7.96	0.58
Elaeocarpus ptilanthus	2	1200	1230	100	40	1180	720	1030	1700	210	1030	1.03	0.40	0.61	1.65	4.90
Eucalyptus cameronii	2			53	3	370	25	240	30				0.06	0.07	0.13	
Eucalyptus campanulata	2			53	3	160	32	60	25				0.06	0.20	0.42	
Eucalyptus dalrympleana	2	2000	1000	615	870	2250	600	580	1430	470	360	0.50	1.41	0.27	2.47	0.77

Eucalyptus dives	2	1200	700	75	10	1050	180	640	180	180	40	0.58	0.13	0.17	0.28	0.22
Eucalyptus grandis	2	3100	1500	130	5	1250	200	650	750	200	230	0.48	0.04	0.16	1.15	1.15
Eucalyptus gummifera	2			60	5	900	50	310	160	110	90		0.08	0.06	0.52	0.82
Eucalyptus laevopinea	2	1900	1100	70	15	650	20	260	240	130	80	0.58	0.21	0.03	0.92	0.62
Eucalyptus maculata	2	1800	1000	50	5	800	220	1240	2370	340	770	0.56	0.10	0.28	1.91	2.26
Eucalyptus oleosa	2			45	3	1600	540	1600	2700				0.07	0.34	1.69	
Eucalyptus saligna	2			110	3	1000	35	500	100				0.03	0.04	0.20	
Fagus sylvatica	2	1500	800	165	70	1100	950	700	850	180	225	0.53	0.42	0.86	1.21	1.25
Flindersia maculosa	2			70	43	900	790	4200	3500				0.61	0.88	0.83	
Flindersia pimenteliana	2	730	1710	60	20	640	20	170	1350	190	170	2.34	0.33	0.03	7.94	0.89
Fraxinus americana	2	1700	900									0.53				
Galbulimima belgraveana	2	1450	1470	50	330	2410	2070	1170	890	830	480	1.01	6.60	0.86	0.76	0.58
Geijera parviflora	2			190	120	900	3200	15000	12000				0.63	3.56	0.80	
Hovenia dulcis	2					2000	2000	1000	1600	450	450			1.00	1.60	1.00
Jacaranda copaia	2	1600	1400									0.88				
Kalopanax pictus	2							1090	2050	241	243				1.88	1.01
Kalopanax pictus	2					1500	1250	1000	1600	250	310			0.83	1.60	1.24
Licaria cayennensis	2	1100	1100									1.00				
Liriodendron tulipifera	2	1500	1000									0.67				
Maclura pomifera	2			390	10			4600	2700	700	300		0.03		0.59	0.43
Magnolia obovata	2					800	125	450	210	80	2			0.16	0.47	0.03
Nothofagus truncata	2	630	375			1200	550	1000	650	200	250	0.60		0.46	0.65	1.25
Ochroma lagopus	2	1800	500									0.28				
Orites excelsa	2			94	27	1300	400	92	270				0.29	0.31	2.93	
Orvenia acidula	2			81	11	1000	290	4900	7000				0.14	0.29	1.43	
Oxydendron arboreum	2	2500	2300									0.92				
Phellodendron amurense	2					1500	300	910	800		200			0.20	0.88	
Planchonella firma	2	1400	2500	100	70	1470	1900	750	1350	400	710	1.79	0.70	1.29	1.80	1.78
Populus robusta	2			390	44	980	1760	1400	4000	240	730		0.11	1.80	2.86	3.04
Populus trichocarpa	2			107	39	970	2800	980	1920	180	400		0.36	2.89	1.96	2.22
Prunus sargentii	2							510	532	233	68.5				1.04	0.29
Prunus avium	2	1100	600	130	10	800	400	1100	1800	230	180	0.55	0.08	0.50	1.64	0.78
Quercus alba	2			115		1311	900	1050	708	92	17		0.00	0.69	0.67	0.18
Quercus alba	2	1530	1880	190	50	1160	730	850	1020	178	113	1.23	0.26	0.63	1.20	0.63
Quercus alba	2			188	12	1609	548	994	713	108	19		0.06	0.34	0.72	0.18
Quercus alba	2	900	550	100	70	1000	700	3300	1000	140	150	0.61	0.70	0.70	0.30	1.07
Quercus alba	2	4000	1500									0.38				
Quercus coccinea	2	1000	1400	27	20	1360	610	520	500	165	56	1.40	0.74	0.45	0.96	0.34
Quercus coccinea	2			162	6.3	1056	485	532	201	140	22		0.04	0.46	0.38	0.16
Quercus coccinea	2	3000	2000									0.67				
Quercus petraea	2					1100	640	3000	2000	140	25			0.58	0.67	0.18
Quercus prinus	2	2000	1000									0.50				
Quercus robur	2	2500	1200	200	20	2200	600	600	400	300	30	0.48	0.10	0.27	0.67	0.10
Quercus robur	2	2150	1450	160	30	1750	900	1250	950	600	165	0.67	0.19	0.51	0.76	0.28
Quercus robur	2	1800	1100	325	52	1750	650	525	395	190	42	0.61	0.16	0.37	0.75	0.22
Quercus robur	2	2750	900	180	10	1500	300	340	220	160	50	0.33	0.06	0.20	0.65	0.31
Quercus rubra	2	3100	800									0.26				
Quercus rubra	2	950	650	100	70	800	650	1250	600	110	80	0.68	0.70	0.81	0.48	0.73
Quercus rubra	2	2300	900									0.39				
Quercus serrata	2					1600	1600	630	450	100	20			1.00	0.71	0.20
Robinia pseudoacacia	2			310	30	1800	1500	1700	1300	190	160		0.10	0.83	0.76	0.84
Sloanea pulleniana	2	830	860	80	150	1650	2460	4040	2700	710	880	1.04	1.88	1.49	0.67	1.24
Sorbus alnifolia	2							1000	1500	300	400				1.50	1.33
Sphenostemon papuanum	2	1560	1610	110	180	3800	4500	1410	1610	1290	2300	1.03	1.64	1.18	1.14	1.78
Symphonia globulifera	2	1900	500									0.26				
Syncarpia glomulifera	2			70	5	950	45	600	130	250	75		0.07	0.05	0.22	0.30
Tarretia actinophylla	2			91	80	2600	900	760	750				0.88	0.35	0.99	
Tristania conferta	2	1800	1700	75	5	1050	1050	800	1750	130	600	0.94	0.07	1.00	2.19	4.62
Vouacapoua americana	2	1300	1200									0.92				
Zelkova serrata	2							1600	1000	560	320				0.63	0.57

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1/2017 Suomen Soodakattilayhdistys ry
Konemestaripäivä 26.1.2017, esitelmät
Scandic hotelli Oulu, Stora Enso Oyj, Oulun tehdas
(16A0913-E0176) 26.1.2017

2/2017 Suomen Soodakattilayhdistys ry
Soodakattila-alan yhteistoiminta
Vuosikertomus 2016
(16A0913-E0177) 27.4.2017

3/2017 Suomen Soodakattilayhdistys ry
Soodakattila-alan yhteistoiminta
Pöytäkirja. Vuosikokous 27.4.2017, Holiday Inn Helsinki City Centre, Helsinki
(16A0913-E0178) 27.4.2017

4/2017 Suomen Soodakattilayhdistys ry
Soodakattilapäivä 2.11.2017
Clarion hotelli, Helsinki, (16A0913-E0179) 2.11.2017

5/2017 Suomen Soodakattilayhdistys ry
Understanding Low Temperature Corrosion in Black Liquor Combustion, Phase 3
Nikolai DeMartini, Emil Vainio, Åbo Akademi
(16A0913-E0180) 22.9.2017

6/2017 Suomen Soodakattilayhdistys ry
Soodakattiloiden käynninaikaiset tiiveydenvalvontajärjestelmät
Timo Karjunen, Varo Oy
(16A0913-E0181) 19.9.2017

7/2017 Suomen Soodakattilayhdistys ry
Hitsauspinnoitettujen putkien käyttö soodakattiloissa OSA 3 - mikrorakennemuutokset vanhennushehkutuksissa
Satu Tuurna, Pertti Auerkari, Sanni Yli-Olli, VTT
(16A0913-E0182) 6.11.2017

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Selvitys sularännien toiminnasta vaihtelevalla kuormalla
Eetu Rantanen, Lappeenrannan teknillinen yliopisto
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SUOMEN SOODAKATTILAYHDISTYS RY, RAPORTTISARJA

1/2018	Suomen Soodakattilayhdistys ry Konemestaripäivä 25.1.2018, esitelmät Park hotel Tornio, Stora Enso Oyj, Veitsiluodon tehdas (16A0913-E0184) 25.1.2018
2/2018	Suomen Soodakattilayhdistys ry Soodakattila-alan yhteistoiminta Vuosikertomus 2017 (16A0913-E0185) 26.4.2018
3/2018	Suomen Soodakattilayhdistys ry Soodakattila-alan yhteistoiminta Pöytäkirja. Vuosikokous 26.4.2018, Helsinki Congress Paasitorni (16A0913-E0186) 26.4.2018
4/2018	Suomen Soodakattilayhdistys ry Soodakattilapäivä 25.10.2018 Sokos hotelli Torni, Tampere, (16A0913-E0187) 25.10.2018
5/2018	Suomen Soodakattilayhdistys ry Black Liquor Evaporation Book Jim Frederick and Niko DeMartini (16A0913-E0188) 25.10.2018
6/2018	Suomen Soodakattilayhdistys ry Sularännisuositus (16A0913-E0189) 10.12.2018
7/2018	Suomen Soodakattilayhdistys ry Soodakattilan päästömittausten menetelmät Paula Juuti, Pöyry Finland Oy (16A0913-E0190) 10.12.2018
8/2018	Suomen Soodakattilayhdistys ry NCG-järjestelmien turvallisuusauditointi, syntyvät hajukaasumäärät ja koostumukset, tyypilliset onnettomuuteen johtavat syyt – prosessikonseptitarkastelut Kirsi S. Hovikorpi, Esa Vakkilainen, Lappeenrannan Teknillinen Yliopisto (16A0913-E0191) 10.12.2018
9/2018	Suomen Soodakattilayhdistys ry Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport Roland Balint, Markus Engblom, Åbo Akademi (16A0913-E0192) 10.12.2018
10/2018	Suomen Soodakattilayhdistys ry Nitrogen in wood and its fate in kraft pulping – a review Klaus Niemelä, VTT (16A0913-E0193) 17.12.2018