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Intra-specific Variation in Cell Wall Constituents of Needle Age Classes of *Pinus sylvestris* in Relation to Soil Fertility Status in Southwest England

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First, second and third year needles were collected from the same branches of young Scots pine trees growing on soils of two different status (high and low fertility sites) that varied in mineral nutrient concentrations and N mineralisation potential. All needle age classes were analysed for total carbon, acid detergent fibre (ADF), lignin, cellulose, phenylpropanoid derivatives (PPD) of lignin, sugar constituents of non-crystalline, hydrated cellulose and hemicellulose, and nutrient concentrations (N, P, K, Ca, Mg and Mn). Significant intra-specific variation in the litter quality variables in relation to soils of high and low fertility was found in the second and third year needles, whereas there were no differences in the other cell wall constituents and mineral elements of the first year needles. The second and third year needles from the low fertility soil contained higher concentrations of ADF, lignin, cellulose, sugar constituents of non-crystalline, hydrated cellulose and hemicellulose, and phenylpropanoid derivatives (PPD) of lignin, but lower concentrations of N, P and Mg than the same needles from the high fertility and fertilised soils. The results in the present study indicate that under different soil fertilities, needle age classes show significant variations in the cell wall constituents and mineral elements, and suggest that this can result in significant variation in litter quality and decomposition rates.

Keywords needle age classes, soil fertility, lignin, phenylpropanoids, hemicellulose, nitrogen, *Pinus sylvestris*
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1 Introduction

Many studies have characterised the initial chemical composition of litters from temperate plant species as a means of predicting their inherent patterns of decomposition (Swift et al. 1979, Heal et al. 1997). In general terms, if the lignin concentrations are below about 20% most of the litter mass comprises structural polysaccharides, which are readily degraded by micro-organisms, and the decomposition rates can be predicted from the initial C : N ratios or simply N concentrations (McClaugherty and Berg 1987). Higher concentrations of lignin increasingly dominate the processes of litter decomposition and mass losses can be related to initial concentrations of lignin (Fogel and Cromack 1977), the lignin:N ratio (Berendse et al. 1987), lignocellulose concentrations (Aber and Melillo 1991) or ratios of structural polysaccharides: lignin (McClaugherty and Berg 1987).

The biochemical composition of forest litter is primarily a function of the tree species (e.g. Berg and Wessen 1984, Johansson 1994) but there is also evidence in the literature that trees can show considerable intra-specific variations in litter constituents in relation to different soil conditions, which variations can affect decomposition rates (Davies et al. 1964, Swift et al. 1979, Lambers 1993). All plants need basically the same resources for growth such as light, water and certain nutrients, and most use similar physiological mechanisms to obtain these resources. When resources are available in abundance, there is generally selection for a suite of characteristic related to rapid growth rate. However, when any one of these environment resources becomes limiting to plant growth, plants have evolved mechanisms to conserve growth-limiting nutrients within their tissues (Birk and Vitousek 1986, Escudero et al. 1992). In deciduous species, there is an annual cycle with rapid accumulation of nutrients in foliage as the leaves flush and expand, followed later in the year with redistribution of some nutrients and finally, abscission with the loss of remaining nutrients. Some deciduous trees are enforced to vary the amounts of primary cell walls constituents in leaves with high and low fertility soil types, which can be related to degree of polymerisation of lignins and hemicellulose according to soil base status as shown by Sariyildiz and Anderson (2003, 2005).

It is, however, well known that evergreen species differ from deciduous species having two or more living needle generations that may be retained for several years before abscission (Chapin 1980, Chapin and Kedrowski 1983, Aber and Melillo 1991). Nutrients stored in the older needles can be used more efficiently in other parts of the plant, such as the young needles in rapid growth and with a high photosynthetic capacity (Mooney and Gulmon 1979) and efficient translocation from older needles may decisively improve the efficiency of the nutrient use. This is more likely to occur in plants, which are less resource-limited. However, plants that occur on infertile soils generally cannot acquire sufficient resources to support rapid growth. Although growth is slow, some coniferous trees can respond to particularly low site quality by carrying needles produced in several different years (Aber and Melillo 1991). The effect of needle age classes on the distribution of mineral nutrients has well been investigated (e.g. Shaver 1981, Chapin et al. 1986). However, variation in cell wall constituent of needles with age has been less documented. It is clear from fertiliser experiments for coniferous trees that the chemical quality of needles can be altered significantly in a single species by increasing nutrient availability (Tamm 1991, Berg and Tamm 1991a,b), though mineral element concentrations, rather than plant structural compounds, has been the main variable in litter affected by these treatments. Under natural soil conditions, Sanger et al. (1996, 1998) showed for Scots pine that, N, lignin, cellulose as well as the chemical characteristics of the lignin polymer and hemicellulose varied significantly either between needles (second year class) and litters or between different soil types in relation to high and low base status.

The present study was firstly carried out to investigate whether there was significant intra-specific variation in nutrients and biochemical constituents of Scots pine trees in relation to different soil fertilities, and to determine whether this intra-specific variation in the biochemical compositions of needles according to different soil fertilities was enhanced with the age of the needles. Secondly, to emphasise the effects of this intra-specific variation in biochemical com-

positions of needles age classes in response to different soil fertilities on needle litter qualities and decomposition rates.

2 Materials and Methods

2.1 Sampling Areas, Sites and Sample Preparation

This study was carried out in two areas, Haldon Forest and Asclyst Forest in Devon, south-west England. The sampling sites (three sites in each area) were young Scots pine plantations growing next to mature Scots pine trees in Haldon Forest and Ashclyst Forest, This region was not glaciated in the last Ice Age, so that within a small geographical area there was a distinct pattern of soils in relation to the main groups of parent materials (Clayden 1971). Ashclyst Forest and Haldon Forest were chosen for the sampling sites since they presented two extremes of soils with high (HF) and low fertility (LF) status respectively. Although the soils in the area were extremely heterogeneous over relatively small distances, the sites from which needles were collected were subject to similar climate conditions (mean annual temperature 10–11 °C, mean annual precipitation 1000–1200 mm). Site characteristics are shown in Table 1.

Approximately 20 years ago, Forest Enterprise of Exeter established Scots pine plantations in each forest. Among these plantation sites, three sites, approximately 500 meters away from each other, were selected to collect the needle samples in each forest. Young Scots pine trees showed three age class needles (first, second and third year) on the same branches. However, some plantation sites in Haldon Forest had been fertilised at planting (Forest Enterprise of Exeter). They applied diammonium phosphate $(NH_4)_2HPO_4$ fertiliser (18–21 percent by weight for N, 20–23 percent by weight for P) as a starter (about 45–50 kg/ha), but no fertiliser was used after that. On these fertilised plantation sites, Scots pine trees had only first and second year age class needles on the same branches. In order to determine the effect of fertiliser on the chemical composition of the needle age classes, the first and second year needles were also sampled from three fertilised plantation sites, which were approximately 800 meters away from each other. Since all plantations were established at the same year, Scots pine trees were the same age (20 years old), approximately the same height (6–7 meters), girth and growth form.

An approximately 150 gram needle for each

Table 1. Site and soil characteristics of the young Scots pine plantations used for samples of needle age classes and for soil samples.

Site	Haldon Forest (plantation sites with low fertility soil characteristics)	Haldon Forest (fertilised sites)	Ashclyst Forest (plantation sites with high fertility soil characteristics)
Altidude (m)	122	122	76
Grid reference	SX 911 825	SX 911 825	SX 999 997
Longitude, latitude	50°39´N, 3°33´W	50°39´N, 3°33´W	50°51´N, 3°25´W
Parent material	Gravel over flinty clay	Gravel over flinty clay	Sand stone
Soil type	Podsol	Podsol	Brown earth
pH (H_2O)	4.3	5.2	6.7
Base saturation (%)	7	15	79
CEC (m-eqiv 100 g^{-1})	5	7	21
Ca (m-eqiv 100 g^{-1})	2.5	3.2	4.6
Mg (m-eqiv 100 g^{-1})	0.1	0.4	0.9
K (m-eqiv 100 g^{-1})	0.02	0.03	0.3
N mineralisation (µg N g $soil^{-1}$ day^{-1})	3	10	22

year class was needed to carry out all chemical analysis in the laboratory. The needles were collected by hand from five trees chosen at random from each site in early October. The needles were sampled from five lower branches of each tree. Approximately 30 gram needles from each lower branch was collected and then bulked to give a single representative sample for each tree. The needle samples were air-dried in the laboratory and then oven-dried at 80 °C for 48 h. The oven-dried material was then ground in a laboratory mill to a mesh fraction less than 1 mm, homogenised and stored at 6 °C in sealed glass vials until required for chemical analyses. Soil samples were also collected under the same trees (2 m from the base of the trunk) from which the year class needles were sampled. The soil samples were taken by using a core (20 cm length, 5 cm diameter), placed in bags and labelled. The moist soils were sieved (< 2 mm), homogenised and bulked to give a single representative sample from each site. Top-soil samples were also collected under the same trees to carry out an assay for anaerobic N mineralisation.

2.2 Chemical Analysis

2.2.1 Soil Analysis

Nitrogen mineralisation potential was determined using anaerobic incubation method as described by Anderson and Ingram (1993). Assays for anaerobic N-mineralisation potential were set up in the laboratory with the fresh top-soils on the same day of sampling. The dry weight of soils was also calculated by weight loss after drying 1 gram of soil for 48 h at 80 °C. Soil pH was measured in a 10:1 v/w mixture of deionized water and soil using a glass calomel electrode, after equilibration for 1 hour. Exchangeable cations were extracted by shaking 5 gram of field moist soil with NH_4Ac (ammonium acetate) adjusted to soil pH 7 and then determined on the NH_4Ac extract using flame atomic absorption spectroscopy (AAS) with $LaCl_3$ as a releasing agent. Extracted soils were subsequently washed with 80% ethanol, filtered and shaken with 1 M NaCl for 1 h. The NH_4^+ concentration in this final extract was determined by a colorimetric automatic-analyser technique. The results obtained from both extracts were used to calculate cation exchange capacity (CEC) and percent base saturation (%BS). All soil sample analyses were carried out in triplicate.

2.2.2 Chemical Analysis of Needles

Organic C was analysed using a Leco HF10 gravimetric carbon analyser (Leco Corporation, St. Joseph, MI, U.S.A.). Total N was determined by Kjeldahl digestion (Allen 1989) followed by analysis of ammonium by the indophenol method using an auto-analyser (Bemas, Burkhard Ltd, Uxbridge, UK).

Acid detergent fibre (ADF), α-cellulose and lignin were determined using the ADF-sulphuric lignin method of Rowland and Roberts (1994). Sugar constituents of labile carbohydrates in samples were hydrolysed by 4 M TFA (trifluoro acetic acid) using a method modified from Guggenberger and Zech (1994). A mild hydrolysing reagent (TFA), which released carbohydrates predominantly from non-crystalline, hydrated cellulose and hemicellulose in plant cell walls, was highly recommended method. The 4 M TFA hydrolysis hydrated cellulose, which was a minor constituent of mature cell walls, but not crystalline cellulose. Hence the sugars in the digest mainly represented hemicelluloses. The sugar concentrations were then determined using a Shimadzu Gas Chromatography (GC) 14-A capillary GC, with a BP5 25m × 0.25 mm i.d. column with standards of xylose, arabinose, fucose, mannose, galactose, glucose, sucrose and maltose (Sanger et al. 1998).

Phenylpropanoid moieties (PPDs) of uncondensed lignins were determined after alkaline CuO oxidation using the modified procedure of Hetherington and Anderson (1998). The concentrations of PPDs were determined using a Shimadzu GC 14-A capillary GC, with a BP5 25m × 0.25 mm i.d. column with standards of *p*-hydroxyl (p-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, *p*-hydroxyacetophenone), vanillyl (vanillin, acetovanillone, vanillic acid), syringyl (syringaldehyde, acetosyringone, syringic acid), coumaric acid and ferulic acid (Sanger et al. 1996).

The sub-samples of litter used for the determi-

nation of total N by Kjeldahl digestion were also used for the determination of mineral elements Ca, Mg, Mn, K and P. Concentrations of Ca, Mg and Mn were determined in the acid digest solution by atomic absorption spectrophotometer (AAS), K by flame emission spectrophotometer (FES) and P by continuous flow colorimetry using the molybdenum blue method (Allen 1989). All analyses were carried out in triplicate.

Variability in litter quality variables between the three soil nutrient status was determined using the Tukey method of multiple pairwise comparisons at alpha = 0.05 using SPSS 9.0 for Windows. Analysis of variance (ANOVA) of the data was made using the computer package MS Excel 2000.

3 Results

3.1 Soil Chemistry

Mean soil characteristics of the plantation sites in Haldon Forest and Ashclyst Forest, and of the fertilised plantation sites in Haldon Forest are shown in Table 1. On the basis of those soil characteristics, soils were categorised into three groups; plantation sites in Haldon Forest with the low fertility soil and with the fertilised soil, and plantation sites in Ashclyst Forest with the high fertility soil (Table 1). Results for pH, %BS, CEC, exchangeable Ca^{2+} and Mg^{2+}, and N mineralisation potential could be ranked with increasing value in the order low fertility soil < fertilised soil < high fertility soil (Table 1).

3.2 Needle Chemistry

Scots pine trees growing on the fertilised soils showed higher nitrogen concentration (2.9%) in the first year needles than the same year needles from the low (2.0%) and high (2.1%) fertility soils, but the other cell wall constituents and mineral elements were approximately the same between three different fertility soils. Hence, only litter quality variables for the second and third year needles are described below.

3.2.1 Carbon, N, ADF, Lignin and Cellulose Concentrations

Carbon, N, ADF, lignin and cellulose concentrations in the second and third year needles for the three soil types are shown in Table 2a. Mean N concentrations in the second year needles were 2.1% for the fertilised soil, 1.8% for the high fertility soil and 1.5% for the low fertility soil. Mean ADF, lignin and cellulose concentrations in the second year needles were highest on the low fertility soil compared to the fertilised and high fertility soils which showed quite similar concentrations for ADF, lignin and cellulose (Table 2a). Carbon-to-N and lignin-to-N ratios in the second year needles were also higher on the low fertility soil than on the fertilised and high fertility soils (Table 2a).

Mean nitrogen concentration in the third year needles was higher on the high fertility soil (0.8%) than on the low fertility soil (0.5%). ADF, lignin and cellulose showed the opposite trend to nitrogen, with higher mean concentrations on the low fertility soil (64, 30 and 34% respectively) than on the high fertility soil (52, 23 and 29% respectively). Similarly, C-to-N and lignin-to-N ratios were also higher on the low fertility soil (90 and 56) than on the high fertility soil (58 and 28).

3.2.2 TFA-hydrolyzable Sugars of Non-Crystalline, Hydrated Cellulose and Hemicellulose

Concentrations of total and individual sugar of non-crystalline, hydrated cellulose and hemicellulose are shown in Table 2b. Mean concentrations in the second year needles were 236 mg g^{-1} for the fertilised soil, 243 mg g^{-1} for the high fertility soil and 280 mg g^{-1} for the low fertility soil. Individual sugar concentrations also showed the same trends as total sugars with the fertilised soil < the high fertility soil < the low fertility soil (Table 2b).

Mean total sugars in the third year needles were also higher on the low fertility soil than on the high fertility soil. This was mostly related to higher concentration of glucose on the low fertility (95 mg g^{-1}) than on the high fertility (72 mg g^{-1}). The other individual sugar concentrations (xylose, arabinose, rhamnose, fucose, man-

Table 2. Litter quality variables in needle age classes of young Scots pine plantations growing on three soils of different status. All ANOVAs were significant at $P < 0.05$. The Tukey method of multiple pairwise comparison at alpha = 0.05 used to determine significantly different means. Means with the different letter are significantly different by lines (n=9).

a) Total C, N, ADF, lignin and cellulose

	Low fertility soil		Fertilised soil		High fertility soil	
	Mean	Range	Mean	Range	Mean	Range
First year needles						
C (%)	43	42–44	45	44–46	44	43–45
N (%)	2.1a	1.8–2.3	2.9b	2.7–3.1	2.0a	1.6–2.4
ADF (%)	44	42–47	44	44–47	44	41–48
Lignin (%)	15	14–16	16	15–17	14	13–15
Cellulose (%)	30	28–33	29	28–32	30	26–33
C-to-N	21 : 1a	19–24	16 : 1b	15–17	23 : 1a	18–28
Lignin-to-N	7.4 : 1a	6.9–9.2	5.5 : 1b	5.6–5.7	7.2 : 1a	6.4–8.2
Lignin-to-Cellulose	0.5 : 1	0.4–0.5	0.5 : 1	0.5–0.6	0.5 : 1	0.4–0.5
Second year needles						
C (%)	46	46–47	46	45–47	45	44–46
N (%)	1.5a	1.5–1.6	2.1b	1.8–2.3	1.8b	1.6–2.1
ADF (%)	60a	56.9–62.5	40b	39–41	44b	43–44
Lignin (%)	28a	25.0–29.2	16b	14–17	14b	14–15
Cellulose (%)	32a	31.9–32.2	25b	24–26	26b	28–30
C-to-N	31 : 1a	29.0–31.2	22 : 1b	21–25	25 : 1b	23–27
Lignin-to-N	18 : 1a	17.1–18.4	7.6 : 1b	7.4–8.1	7.9 : 1b	7.2–8.6
Lignin-to-Cellulose	0.9 : 1	0.78–0.91	0.6 : 1	0.6–0.7	0.5 : 1	0.5–0.6
Third year needles						
C (%)	45	44–46			46	46–47
N (%)	0.5a	0.7–0.8			0.8b	0.7–1.6
ADF (%)	64a	59–69			52b	46–55
Lignin (%)	30a	28–33			23b	18–26
Cellulose (%)	34a	30–37			29b	28–30
C-to-N	90 : 1a	55–66			58 : 1b	46–67
Lignin-to-N	56 : 1a	43–45			28 : 1b	25–26
Lignin-to-Cellulose	0.9 : 1	0.9–1.1			0.8 : 1	0.7–0.9

b) TFA-hydrolyzable sugars of non-crystalline, hydrated cellulose and hemicellulose

	Low fertility soil		Fertilised soil		High fertility soil	
	Mean (mg g^{-1})	Range (mg g^{-1})	Mean (mg g^{-1})	Range (mg g^{-1})	Mean (mg g^{-1})	Range (mg g^{-1})
First year needles						
Xylose	20	19–21	20	19–22	21	19–23
Arabinose	40	38–43	39	37–42	36	31–45
Rhamnose	5.9	5.6–6.7	6	6.1–7.6	5.8	4.9–6.8
Fucose	2.0	1.9–2.1	2	1.9–2.4	1.9	1.5–2.2
Mannose	51	46–54	57	54–61	58	51–65
Galactose	44	40–49	44	42–49	43	39–48
Glucose	71	70–75	70	65–81	78	83–86
Total	235	221–246	240	227–265	244	225–270

Table 2 continued.

	Low fertility soil		Fertilised soil		High fertility soil	
	Mean (mg g^{-1})	Range (mg g^{-1})	Mean (mg g^{-1})	Range (mg g^{-1})	Mean (mg g^{-1})	Range (mg g^{-1})
Second year needles						
Xylose	23	22–24	19	18–19	20	19–20
Arabinose	43a	40–49	37b	33–40	36b	33–40
Rhamnose	8.0a	7.5–8.4	5.9b	5.4–6.7	6.5b	5.6–7.5
Fucose	2.5a	2.3–2.6	1.9b	1.8–2.1	2.0b	1.6–2.3
Mannose	58a	56–63	46b	45–47	48b	43–51
Galactose	50a	45–56	44b	41–47	44b	42–47
Glucose	95a	68–80	85b	75–91	88b	82–95
Total	280a	240–278	236b	228–244	243b	235–255
Third year needles						
Xylose	22	21–22			21	19–23
Arabinose	39	35–41			39	37–40
Rhamnose	8.7	6.7–9.6			8.5	7.4–9.4
Fucose	2.6	2.1–2.9			2.4	2.3–2.5
Mannose	57	53–60			53	52–54
Galactose	50	45–54			48	46–51
Glucose	95a	91–99			72b	70–75
Total	274a	257–290			244b	238–254

c) CuO-hydrolyzed phenlypropanoid derivatives

	Low fertility soil		Fertilised soil		High fertility soil	
	Mean (mg g^{-1})	Range (mg g^{-1})	Mean (mg g^{-1})	Range (mg g^{-1})	Mean (mg g^{-1})	Range (mg g^{-1})
First year needles						
p-hydroxyl	1.5	1.4–1.8	1.6	1.4–1.7	2.2	1.8–2.7
Vanillyl	30	20–39	30	23–34	27	25–35
Syringyl	1.3	1.1–1.4	1.2	1.1–1.3	1.3	1.4–1.7
Coumaric acid	3.5	3.3–3.7	3.5	2.9–4.2	3.5	3.2–3.9
Ferulic acid	1.0	0.8–1.2	1.2	1.0–1.4	1.4	1.2–1.6
Total	37	28–46	38	32–42	36	33–44
Lignin-to-PPD	4.1	3.6–5.7	4.2	4.0–4.8	4.0	3.5–3.9
Second year needles						
p-hydroxyl	1.8	1.6–1.9	1.8	1.5–2.1	2.0	1.8–2.2
Vanillyl	41a	40–42	30b	21–35	30b	27–34
Syringyl	1.9	1.3–2.2	1.5	1.1–1.4	1.8	1.6–1.9
Coumaric acid	3.2	3.1–3.6	2.6	2.1–2.9	3.7	3.3–4.0
Ferulic acid	1.6	1.3–1.8	1.1	1.0–1.2	1.5	1.3–1.9
Total	50a	47–52	37b	28–42	39b	35–43
Lignin-to-PPD	5.5 : 1a	5.3–5.7	4.2 : 1b	3.9–5.8	3.7 : 1b	3.3–4.1
Third year needles						
p-hydroxyl	2.3	1.1–1.7			2.1	2.0–2.3
Vanillyl	43a	25–45			31b	23–35
Syringyl	2.0	1.3–1.6			2.0	1.8–2.0
Coumaric acid	2.5	2.3–3.0			3.3	3.0–3.5
Ferulic acid	1.2	1.0–1.3			1.5	1.2–1.6
Total	51a	38–53			40b	31–44
Lignin-to-PPD	6.0 : 1	5.2–8.4			5.6 : 1	5.0–7.7

Table 2 continued.

d) Mineral elements

	Low fertility soil		Fertilised soil		High fertility soil	
	Mean	Range	Mean	Range	Mean	Range
First year needles						
P (%)	0.2	0.2–0.3	0.2	0.2–0.3	0.1	0.1–0.2
K (%)	0.5	0.4–0.6	0.4	0.3–0.5	0.4	0.3–0.6
Ca (%)	0.1	0.1–0.2	0.1	0.1–0.2	0.1	0.1–0.2
Mg (%)	0.7	0.5–1.0	0.7	0.6–0.8	0.7	0.6–0.8
Mn (%)	0.03	0.03–0.04	0.03	0.02–0.04	0.1	0.1–0.2
Second year needles						
P (%)	0.03a	0.02–0.04	0.2b	0.2–0.3	0.1b	0.1–0.2
K (%)	0.7	0.6–0.9	0.7	0.7–0.9	0.7	0.6–0.8
Ca (%)	0.1	0.1–0.2	0.1	0.1–0.2	0.1	0.1–0.2
Mg (%)	0.1a	0.1–0.2	0.6b	0.5–0.8	0.6b	0.6–0.7
Mn (%)	0.04	0.04–0.06	0.04	0.03–0.05	0.1	0.1–0.3
Third year needles						
P (%)	0.04a	0.02–0.05			0.1b	0.1–0.2
K (%)	0.8	0.7–0.9			0.7	0.6–0.8
Ca (%)	0.1	0.1–0.2			0.1	0.1–0.2
Mg (%)	0.1a	0.1–0.2			0.6b	0.6–0.7
Mn (%)	0.05	0.02–0.06			0.1	0.1–0.3

nose and galactose) were approximately the same in the third year class needles between the low fertility and high fertility soils (Table 2b).

3.2.3 CuO-hydrolyzed PPDs

Concentrations of total and individual CuO-hydrolyzed phenylpropanoid derivatives (PPDs) of lignin are shown in Table 2c. Mean total PPDs in the second year needles were 37 mg g^{-1} for the fertilised soil, 39 mg g^{-1} for the high fertility soil and 50 mg g^{-1} for the low fertility soil. Individual vanillyl concentration showed the same trend as total PPDs with the fertilised soil < the high fertility soil < the low fertility soil. The other individual PPDs were approximately the same in the second year class needles between the three different fertility soils. Lignin-to-PPD ratios in the second year class needles were also higher on the low fertility soil compared to the fertilised soil and the high fertility soil.

Mean total PPDs and individual vanillyl concentrations in the third year class needles were also higher on the low fertility soil (51 mg g^{-1} and 43 mg g^{-1} respectively) than on the high fertility soil (40 mg g^{-1} and 31 mg g^{-1} respectively). The other individual compounds were rather similar between the low fertility and high fertility soils.

3.2.4 Mineral Elements Concentrations

Concentrations of mineral elements are shown in Table 2d. Mean P and Mg concentrations in the second year needles were lower on the low fertility soil (0.03 and 0.1% respectively) than on the fertilised (0.2 and 0.6%) and the high fertility soils (0.1 and 0.6%). Mean P and Mg concentrations in the third year needles were also lower on the low fertility soil (0.04 and 0.1% respectively) than on the high fertility soil (0.1 and 0.6%). The other

nutrients (K, Ca and Mn) were approximately the same in the second and third year needles between the three different fertility soils.

4 Discussion

The present study on variability in the quality of needle age classes from the same branches of Scots pine trees growing on the high and low fertility soils has shown that in addition to intra-specific differences in conventional measures of litter quality there are also significant intra-specific differences in the phenylpropanoid constituents of lignin and in the sugar constituents of non-crystalline, hydrated cellulose and hemicellulose in the second and third year needles. This is the first time these qualitative and quantitative differences in the needle age classes have been demonstrated within species.

A number of studies (e.g. Boerner 1984, Johansson 1994) showed that trees growing on soils of inherent fertility, particularly even-aged plantations with high nutrient demands generally had lower foliar nutrient concentrations than those growing on more fertile soils. The others also found higher concentrations of polyphenols in foliage of trees under nutrient stress (e.g. Davies et al. 1964, Bryant et al. 1983, Lambers 1993). In the present study, the first year needles didn't show any significant differences in the chemical compositions between the low and high nutrient soils. However, the first year needles from the fertilised plantation had higher N concentration compared to the same needles from the low and high nutrient soils, but the other cell wall constituents and mineral elements were approximately the same between three different soil nutrient status. Similar results were also shown in a number of studies where fertilisation resulted in increased uptake by the trees and, consequently in enhanced concentrations of N in the freshly formed foliage (e.g. Berg and Tamm 1991a,b, Berg and Matzner 1997).

Although the composition of the first year needles from Scots pine showed no variation with soil fertility in contrast to deciduous trees (Sariyildiz and Anderson 2003, Sariyildiz et al. 2005), significant intra-specific variation in the litter quality variables in relation to soils of high and low fertility was found in the second and third year needles and certain biochemical characteristics may be related to soil base status and N-mineralisation potential under young Scots pine plantations. The second and third year needles from the low fertility soil showed lower N, P and Mg concentrations and higher concentrations of cell wall constituents (ADF, lignin, cellulose, sugars and PPD). These results were consistent with trends found by other authors who reported that tree species on soils of low inherent fertility generally tend to produce low foliar nitrogen concentrations, high concentrations of polyphenol and greater lignification of leaf tissues (Davies et al. 1964, Sanger et al. 1996, 1998, Tresender and Vitousek 2001 and Hattenschweiler et al. 2003). This trend may be indicative of nutrient stress, which can elicit lignification in plant tissues (Stafford and Ibrahim 1992). Berg et al. (1993) observed that N availability was inversely correlated with total N concentration in *Pinus sylvestris* needles. There was also evidence in this present study that by increasing the availability of soil nutrients using fertiliser altered the carbon/nutrient balance, and mitigated the production of cell wall compounds in the second year class needles from the Scots pine trees. It was noted that the second year class needles from the fertilised soil contained higher nutrient concentrations, but lower cell wall constituents compared with those from the low fertility soil.

An inverse relationship between nutrient concentrations (mainly N, P and Mg) and cell wall constituents in the second and third year needles was also noted. Scots pine trees from the low fertility soil had lower storage of nutrients in the second year needles. This resulted in higher concentrations of lignin, cellulose as well as PPDs and the sugar constituents of non-crystalline, hydrated cellulose and hemicellulose. However, trees from either of the high fertility or fertilised soils stored the same nutrient concentrations in the second year needles and no significant variations in other litter quality variables. The same trend was also observed in the third year needles from the high and low fertility soils, i.e. lower nutrient concentrations in the third year needles from the low fertility soil were correlated with higher concentrations of cell wall constituents compared to the high fertility soil. An inverse

correlation between nitrogen concentrations and the concentrations of lignin and polyphenols is generally shown in deciduous tree leaf litters (Heal et al. 1997). In evergreen conifers, nitrogen limitation is also associated with greater needle retention time on the trees and higher concentrations of lignin, and hence lower litter quality (Flanagan and Van Cleve 1983). The result in this present study, however, indicated the relative importance of nutrient concentrations affecting not only concentrations of lignin but also the other cell wall constituents with needle age.

The differences in nutrients and biochemical constituents of needles in relation to soil fertility status suggest variation in litter qualities and decomposition rates after needle falls. Unfortunately, the variations in the biochemical composition in needle litters between the high and low fertility soils were not determined here because the needle litters were not sampled. But, the results reported by Sanger et al. (1996, 1998) from the same sites for mature trees indicated that variations in the biochemical composition of Scots pine needles (second year class needles) between soils of different soil types showed the same variations in these constituents within their needle litters.

Many researchers have demonstrated the relationships between initial litter quality characteristics and decomposition rates for a large number of plant species (e.g. Fogel and Cromack 1977, Meentemeyer 1978, Melillo et al. 1989 and many others). In general, it would appear that when lignin concentration increases above about 20% it can dominate litter decomposition rates irrespective of other constituents. It has been shown that lignin can physically inhibit the activity of carbohydrates by masking substrate surface of hemicellulose and cellulose from enzyme attack (Lewis and Yamanoto 1990). In the present study, young Scots pine trees on high fertility soils produced needles with low lignin concentrations mainly associated with vascular tissues (Table 2a). The high quality litters can decompose rapidly and support high plant production through fast turnover of the nutrient pools. The same trees on soils of low inherent fertility produce needles that decompose slower, limiting the rates of nutrient turnover, because of greater lignification of needle tissues.

In conclusion, this study has shown significant intra-specific variation in nutrients and biochemical constituents of second and third year needles from the same branches of young Scots pine trees in relation to high and low fertility soils. Trends in the litter quality variables in needle classes appear to be related soil base status and N-mineralisation potential under young *Pinus sylvestris* trees. There is an inverse relationship between nutrient concentrations (mainly N, P and Mg) and cell wall constituents in the second and third year-class needles, but this relationship shows significant differences with soil fertility. These variations in nutrients and biochemical constituents of needles in relation to soil fertility status can results in variation in litter qualities and decomposition rates after needle falls. In turn, this variation affects the structure, function and nutrient cycling processes of natural ecosystems.

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