The effect of aluminum on the growth and mineral composition of Douglas-fir and western hemlock

by

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Abstract

THE EFFECT OF ALUMINUM ON THE GROWTH AND MINERAL COMPOSITION OF DOUGLAS-FIR AND WESTERN HEMLOCK

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Soil properties such as high exchangeable Al, high Al saturation, and low base status are a major deterrent for plant growth in strongly acid soils. Yet these properties are notable features of the coastal forest soils of Oregon and Washington, and there have been suggestions that for these soils Al may be an important contributor to the erratic growth response by the coastal forests from N applications. Consequently, two studies were initiated to determine the potential effect of Al on the growth and nutrient composition of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.), the two most common tree species on these soils. The first study was an *in situ* seedling fertilizer trial designed to investigate the growth response of both species to N, P, and N+P applications, and to examine the fertility status of these soils to determine whether Al had an impact on growth response to fertilizer application. The study revealed that these soils had high P sorption capacity (>93%) and were dominated by Al on the soil exchange sites. For Douglas-fir there was a consistent positive growth response to P application, while for western hemlock growth response was erratic, and high N applications depressed growth, particularly on burnt sites. Foliar analysis revealed that only P was below the reported optimum level for Douglas-fir. For western hemlock, application of N or P had no

significant effect on foliar levels of these elements. Slash burning appeared to reduce dramatically western hemlock's foliar N and Zn to below critical levels and part of this species' erratic response is attributed to a Zn deficiency on burnt sites. Slash burning also appeared to have a marked effect on western hemlock foliar Al and Ca levels - Al levels were higher and Ca levels lower on burnt sites. Two years after planting western hemlock had twice the foliar Al levels of Douglas-fir.

Because of the high P sorption capacity and low base status of these soils a second study was initiated, using solution culture techniques, to determine the effect of pH, and varying Ca:Al, P:Al, and OH:Al mole ratios on Douglas-fir and western hemlock root growth and tissue concentrations. Both species were extremely tolerant of low pH and high levels of Al relative to crop plants; western hemlock was more tolerant of low pH compared with Douglas-fir and there is evidence suggesting that western hemlock seedlings may be more tolerant of Al at low pH and low Ca levels compared with Douglas-fir. Increasing the Ca:Al and OH:Al ratios ameliorated the toxic effects of Al on root growth, especially for Douglas-fir; for Ca this was attributed mainly to its physiological role rather than its effect on Al activity in solution. However, increasing the P:Al ratios depressed root growth due to the decrease in solution pH as P additions increased. Tissue analyses revealed that while Douglas-fir generally had the highest P and Zn levels, western hemlock had the highest Al, Ca, Mg, Mn, and Fe levels.

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CHAPTER I

INTRODUCTION, OBJECTIVES, HYPOTHESES

Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) and western hemlock (*Tsuga heterophylla* (Raf.) Sarg) are the two most commercially important forest species of western Oregon and Washington. Natural stands of these species contain individuals of remarkable size and record stand volumes; longevity of these species commonly exceeds 500 years (Waring and Franklin 1979). Many of the most productive stands, particularly western hemlock, occur along the coastal zone of Oregon and Washington, on soils that are highly weathered, acidic and nutrient depleted relative to soils of the interior valleys and Cascade mountains. Waring and Franklin (1979) and Minore (1979) have pointed to many of the attributes of these species that facilitate such massive biomass accumulations on these soils under "natural" conditions. However, the effects of logging and silvicultural practices, such as slash burning, have broken the "closed nutrient cycling" pattern of these forests, while at the same time shortening rotations and attempting to increase productivity.

Fertilizers are used in many parts of the world to sustain or enhance productivity of natural and plantation forests, and the Pacific Northwest is no exception to this (Bengtson 1979). Over the past three decades, research has shown that for this region plant available nitrogen has been the factor limiting forest productivity (Gessel et al. 1950, 1979, Lavender and Walker 1979, Radwan and Shumway 1984). This in itself is not surprising for, on a world-wide basis, N is the element most commonly deficient and limiting plant (crop) production. While the adequacy of many of the plant essential elements has been examined for the Pacific Northwest (Gessel et al. 1972), the overriding limitation is generally considered to be N. While N, in the form of urea, has been widely applied to young and middle-aged stands of Douglas-fir and, to a lesser extent western hemlock, growth response to such applications have not always been consistent, particularly on coastal hemlock soils and especially by western hemlock (Webster et al. 1976, Radwan and Shumway 1984). Application of N sources other than urea have also proved inconsistent (Radwan et al. 1984), and it has generally been concluded that response by western hemlock to fertilizer applications could not be improved by applying some form of N other than urea.

A number of reasons have been proposed for the variability in response by Douglas-fir and western hemlock to N applications on coastal hemlock soils, including the limited supply of other essential elements, in particular P (Heilman and Eukan 1980a,b, Gill and Lavender 1983, Anderson et al. 1982), and deleterious changes in soil and forest floor chemistry following urea application (Cole et al. 1975, Otchere-Boateng and Ballard 1981, Gill 1981). However, the inter-relationship between western hemlock and (forest) soil acidity can affect many of the reasons proposed for western hemlock's inconsistent response. Acidic soils are typically low in essential nutrients and usually contain an imbalance of both essential and non-essential elements (Rorison 1980). Hewitt (1952) listed the soil chemical factors (Table 1.1) that greatly impacted plant growth on acidic soils. Soil acidity and nutrient leaching are closely related, and as pHs decrease to below 5, Al can dominate soil exchange acidity (McLean 1976, Bache 1980). The lower soil pH, the greater will be the amount of Al in solution and hence its effect on soil fertility and plant growth (Foy 1984).

Table 1.1. Chemical factors associated with acidic soils, and their effect on plant growth. (After Hewitt 1952).

1. Direct effect - injury by hydrogen ions

2. Direct effect due to low pH
   (a) Physiologically impaired absorption of Ca, Mg and P
   (b) Increased solubility and toxicity of Al, Mn, Fe, etc.
   (c) Reduced availability of P - Al x P interaction
   (d) Reduced availability of Mo

3. Low base status
   (a) Ca deficiency
   (b) Deficiencies of Mg, K and possibly Na

4. Abnormal biotic factors
   (a) Impaired nitrogen cycle and fixation
   (b) Impaired mycorrhizal activity
   (c) Increased attack by soil pathogens

5. Accumulation of soil organic acids or other toxic compounds due to unfavorable oxidation - reduction conditions.

Coastal soils of Oregon and Washington are highly acidic (pHs commonly <4.5), with low levels of exchangeable bases and plant available P, and high levels of exchangeable Al (Heilman 1976, Meurisse 1976). Under such conditions Al^{3+} may reach concentrations in the soil solution that could make it a major factor in determining plant growth (Ulrich 1983, Foy 1984). Ryan (1983) found western hemlock to be more tolerant of low pH but less tolerant to elevated solution Al levels compared with Douglas-fir. The two species have been treated similarly in terms of extensive forest fertilization, yet there is evidence indicating that the two species have different nutrient requirements. For example, Douglas-fir is less tolerant of N deficiency (Minore 1979), and can absorb luxury levels of P (Ingestad 1979). While such features help explain the difference between species response to N application, they do not completely explain the inconsistent response to urea-N application, particularly by western hemlock growing in coastal soils.

Because of the nature of the coastal soils of Oregon and Washington, and given the effect that elevated Al levels may have on plant growth, two studies were initiated, using Al as the pivotal factor, with the following objectives: 1) to determine the nutritional status of four coastal soils with respect to Douglas-fir and western hemlock response to P and N applications; and 2) to determine whether varying levels of P and Ca (elements of potential deficiency in these coastal soils) could ameliorate phytotoxic effects of Al.

The following hypotheses were tested:

1. The coastal soils of Oregon and Washington are reported to have "andic" soil properties - high levels of exchangeable Al and sesquioxides, and high levels of P adsorption (Heilman 1976, Meurisse 1976). Under such conditions applications of P, rather than N, will result in significant growth responses.

   While total soil P levels are high, often exceeding 700 ug g^{-1}, plant available levels are generally <10 ug g^{-1} (Heilman 1976). Such low levels of available P are usually considered inadequate under forest plantation conditions in other areas and have been found to lead to P deficiency in plants; depending on the extent of such a deficiency, inconsistent response to N applications can result.

2. Additions of OH, P, or Ca to the growth medium can ameliorate the toxic effects of aluminum in Douglas-fir and western hemlock grown under controlled conditions.

> Symptoms of Al toxicity are reported to resemble P and Ca deficiencies (Foy 1984). The coastal soils under investigation contain low levels of "available" Ca and P. Phosphorus and Ca can ameliorate toxic effects of Al by two different mechanisms: P by complex ligand formation with Al and thereby reduce toxic Al concentrations, and Ca (or other base cations) by reducing the *activity* of toxic Al species. A direct physiological effect may also be achieved by increased Ca additions due to increased interaction with Al at uptake and/or binding sites.

3. Western hemlock has foliar cation concentrations comparable to those of Douglas-fir when grown in the same medium.

> Western hemlock has been reported to be more acid tolerant and have higher root cation exchange capacity under high H^+ conditions (Ryan 1983). Previous reports (Beaton et al. 1965, Krajina 1970) on the chemical composition of the two species have often failed to take account of the difference in chemical composition of the rooting medium. More recent evidence (Van Den Driessche 1976) from nursery grown stock has suggested that western hemlock may have equal or greater foliar cation concentrations when compared with Douglas-fir.

Corollary A: The levels of plant available N and micronutrients are sufficient in the coastal soils to sustain a growth response to P applications.

Site index has been reported to be poorly correlated with growth response to N application (Radwan and Shumway 1984), suggesting that the primary factor limiting productivity on the coastal soils, at least for western hemlock, is not low N. Also, given the low pH of these soils, micronutrient cation deficiencies *per se* are unlikely.

A final corollary, which embraces all three hypotheses is:

Corollary B: Douglas-fir and western hemlock have different mechanisms or abilities of ion uptake under similar environmental conditions.

Douglas-fir has been shown capable of absorbing "luxury" quantities of P, and to be less tolerant of low N levels compared with western hemlock; "optimum" nutrient solutions for the two species are not identical. Species that are efficient P absorbers may be more subject to micronutrient stress, particularly Fe and Zn, unless there is also a complementary mechanism for uptake of such micronutrient ions. While there is no evidence indicating a difference in the requirement or mechanism of uptake of micronutrients, it is highly probable that such differences may extend over a broader range of nutrients than N and P, particularly when the difference in the ecological amplitude of the two species is taken into account.

CHAPTER II

LITERATURE REVIEW

2.1 Nature of Coastal Soils of the Pacific Northwest

2.1.1 Introduction

Studies attempting to elucidate soil-site characteristics and growth of Pacific Northwest conifers have segregated "Coastal" and "Cascade" sites (DeBell et al. 1975, Radwan and DeBell 1980, Gill 1981, Gill and Lavender 1983, Radwan and Shumway 1984). However, when applied on a regional basis, such geographical division fails to distinguish differences between: soils originating from the last continental glaciation and the older, more weathered residual soils; coastal, interior valleys and the Cascade foothills and mountain zones; climatic zones; and different vegetation zones. Such differences will obviously cause a great deal of environmental diversity, confounding attempts to relate forest growth and productivity to soil-site characteristics.

In this study the "coastal" zone is defined as the *Picea sitchensis* (Sitka spruce) zone of Franklin and Dyrness (1973), extending from the southern slopes of the Olympic Range to the Oregon-California border. This definition conforms to zones of climatic similarity (approximately 220 frost free days per annum and the coastal 180 cm rainfall isohyet (Shumway 1981)). Also, such a definition relates strongly to the main state factors of soil formation (Jenny 1941) of importance in this zone, namely parent material, climate, time, and vegetation. These state factors are responsible for the features that distinguish the coastal soils from those of the Cascades.

2.1.2 Vegetation of the Coastal Zone

Figure 2.1 shows the major forested regions of the Pacific Northwest (Franklin and Dyrness 1973). Of importance to this study is the Picea sitchensis zone in which the "climax" species is considered to be P. sitchensis (Sitka spruce). In reality however, the major species in this zone is Tsuga heterophylla (western hemlock) and also common is Pseudotsuga menziesii (Douglas-fir); Thuja plicata (western red cedar) occurs in many of the poorly drained or wetter areas (Franklin 1981). The two species of major interest are western hemlock and Douglas-fir and their ecology and autecology has been extensively reviewed (Fonda and Bliss 1969, Krajina 1970, Franklin and Dyrness 1973, Scott et al. 1976, Packee 1976, Minore 1979, Waring and Franklin 1979, Franklin 1981). The following summarizes some of the more pertinent information.

The late Miocene and early Pliocene saw the emergence of conifers as the dominant species in the Pacific Northwest. The structural characteristics of these forests are described as massive, evergreen with "needle" shaped leaves, and large leaf areas. This, plus the longevity of these species, give them a distinct competitive advantage under the moisture, temperature and nutrient regimes of the region. A number of specific differences are evident between Douglas-fir and western hemlock - the two species of interest in this presentation.

Douglas-fir: This species regenerates well in ash beds under strong light conditions. It prefers more light intense, drier environments and has a high heat and drought tolerance. It is a species tolerant of acid

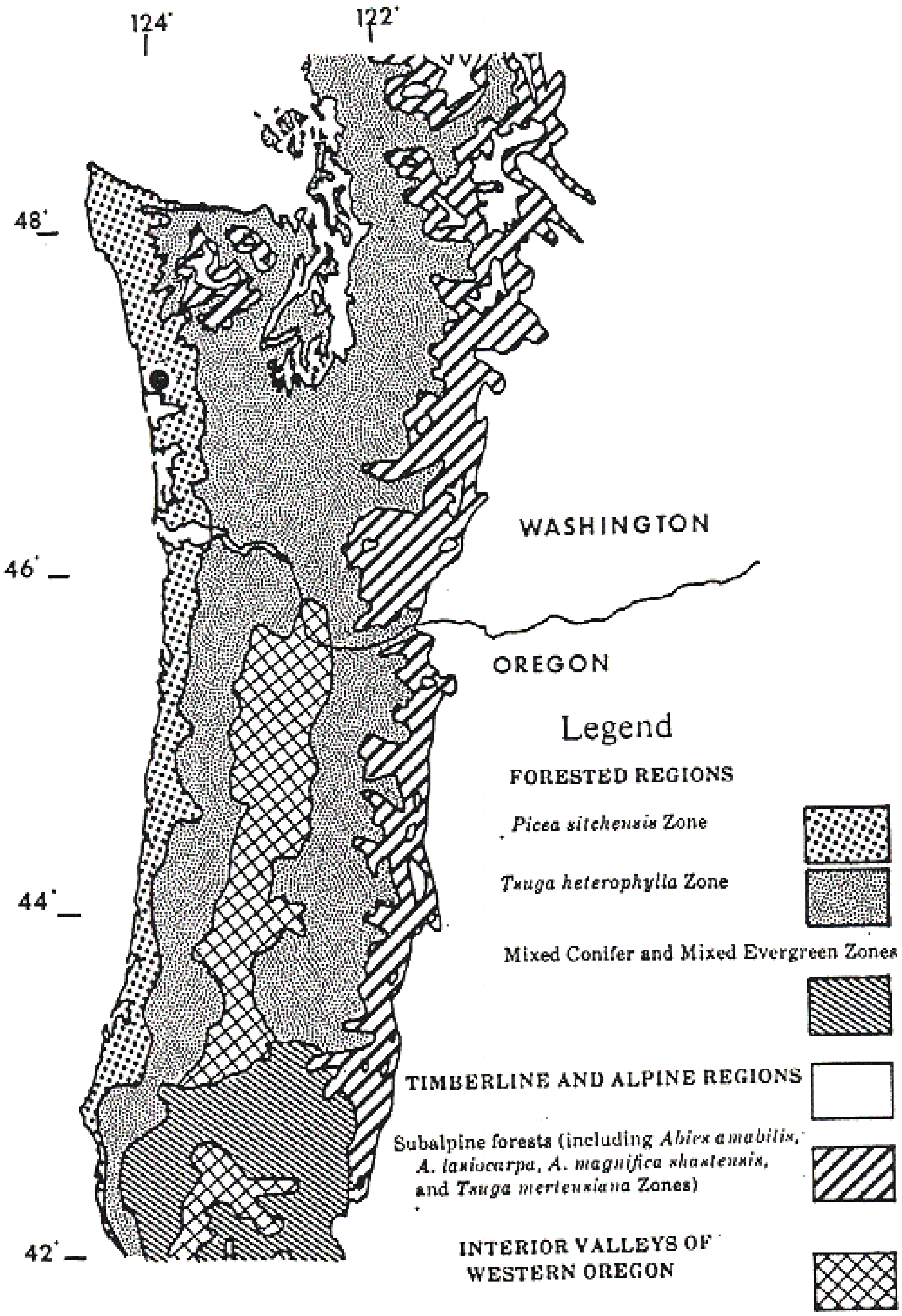


Fig. 2.1 Generalized vegetation map of Oregon and Washington (after Franklin and Dyrness (1973)). ● - Location of the study sites.

soils and high Al levels (Ryan 1983). Ingestad (1979) found that Douglas-fir could absorb luxury amounts of phosphorus, but was relatively intolerant of nitrogen deficiency.

Western hemlock: Regeneration of this species commonly occurs on "rotting" nurse logs and in organic, acid seed beds, often under conditions of low light intensity. Hemlock has a shallow rooting habit, poor stomatal control, and a large total leaf area (25-30 m^2m^{-2} for coastal hemlock) (Grier and Running 1977). These features contribute to hemlock's high shade tolerance, low heat resistance, high water requirements and low drought resistance. The nutrient levels of hemlock biomass were reported to be low relative to other indigenous conifers (Krajina 1970), and it has been hypothesized that this species' total nutrient requirements are low (Krajina 1970, Beaton et al. 1965). This has been suggested as a mechanism explaining hemlock's tolerance and adaptation to acid soils (Heilman and Ekuan 1973), but to date there is no strong evidence to support such ideas.

A major feature of the coastal forests is the high level of accumulated biomass. For example, a 110 year old hemlock-Sitka spruce forest (Oregon coast) had a biomass of 871 ton ha^{-1} (Waring and Franklin 1979) and a 121 year old forest had reported total ecosystem biomass of 1064 ton ha^{-1} (Grier 1976).

2.1.3 Geology and Parent Material

According to Snavely and Macleod (1981), the coast ranges of Oregon and Washington are partly derived from tertiary, eugeosynclinal sediments and from basic andesitic volcanic and volcanic-derived sediments. Parent material of the Oregon-Washington coastal soils frequently contain volcanic ash (Heilman 1981). The most recent advance of the continental ice sheet came as far south as the Soleduc River on the west side of the Olympic Peninsula, but had no direct effect on the lower west coast regions (Heusser 1977). However, glaciofluvial outwash from the Puget Sound Lobe of the Vashon Stade glaciation was responsible for the extensive alluvial plains of the Chehalis River Valley. During the glacial epoch, sea level fluctuations caused terrace formations up to 450m high along the coastal zones of Oregon and Washington. In general the soils of the coastal zone have been formed in situ from volcanically derived material and are considerably older than those in the Puget Sound region (Heusser 1974).

2.1.4 Climate

Since the late Miocene, about 15 million years ago, the climatic pattern of wet, mild winters and warm, dry summers in the region west of the Cascade mountain crest has remained relatively stable (Heusser 1977, Waring and Franklin 1979). This date in fact corresponds with the uplifting of the Coastal, Olympic and Cascade Ranges. Formation of these geographical influences to maritime air masses has been responsible for the climatic patterns of this region, and has exerted a tremendous influence on the indigenous vegetation communities. It was during the late Miocene to early Pliocene that most hardwood extinction occurred in the Pacific Northwest (Waring and Franklin 1979). Shumway (1981) and Waring and Franklin (1979) characterize the present day climate of the coastal zone as having mild temperatures with prolonged cloudiness and a narrow diurnal and seasonal fluctuation (6 to 12 °C) in temperature. Winters are extremely wet with annual precipitation levels ranging from 180 and exceeding 250 cm of regular, low intensity rainfall in many areas; the wettest months are October through to January. Freezing temperatures are unusual. Summers are cool to mild and, without exception, July and August are the two driest months, receiving less than 4% of the annual precipitation. However, the low summer precipitation is offset by extended periods of cloudiness and fog which greatly reduces evaporation. According to Fujimori (1971) and Waring and Franklin (1979) such climatic conditions greatly favors the massiveness and long-lived nature of conifer species in the coastal zone.

In summary, coastal Washington and Oregon have soil parent material, climatic patterns and plant communities which have remained relatively stable since the late Miocene. As such, these factors have resulted in intense weathering and leaching processes, forming fine textured, highly weathered, acid, nutrient poor soils with good moisture holding capacity due to their depth and texture.

2.1.5 Soil Classification

Soils of the coastal zone generally belong to the Inceptisol order, although some Spodosols have been identified in southern coastal Oregon soils (Nettleton et al. 1982). In Grays Harbor County, Washington, a number of soils have been classified as Andic Dystrochrepts, (S.C.S. Staff, 1975) while for coastal Oregon, Andic Haplumbrepts (Astoria series), Umbric Dystrochrepts (Trask series), and Typic Haplumbrepts (Hembre and Klickitat series) have been identified (Meurisse 1972). However, Meurisse (1972), in his study of four "andic" soils of coastal Oregon, concluded that they all had properties which allow their placement into the Dystrandepts under the U.S.D.A. Comprehensive Soil Classification System.

2.1.6 Soil Chemical and Physical Properties

Soil (surface 0-15 cm) and forest floor data from the Regional Forest Nutrition Research Project (RFNRP) were compiled by Ryan (1983) and are summarized in Table 2.1. Both regional ("coast" versus "Cascade") and species (western hemlock versus Douglas-fir) comparisons are shown. From Table 2.1 it is clear that there are a number of surface soil and forest floor properties that differ significantly between species or between regions. Of interest here are the data for the coastal (hemlock) soils. These soils have the lowest pH, exchangeable Ca, base saturation, available P, and C:N ratios. Further, these soils have the highest total N, C, and CEC. Soils of both the coastal and Cascade region had uniformly low pH values in the surface soil horizon

Table 2.1. Comparison of surface soil, and forest floor properties under Douglas-fir and western hemlock stands from coastal (W) versus Cascade (E) sites. (From Ryan 1983).

	REGION	DOUGLAS-FIR	WESTERN HEMLOCK	MAIN EFFECTS	
				Species	Region
SURFACE SOIL (0-15 cm)					
pH	E^+	5.1	4.5	**	*
	W^{++}	4.9	4.4		
Exchangeable Cations ($cmol(p^+)kg^{-1}$)					
Ca	E	3.8	1.7	**	NS#
	W	3.0	1.2		
Mg	E	.80	.36	**	NS
	W	.96	.73		
K	E	.41	.27	NS	NS
	W	.38	.32		
CEC	E	26.0	35.1	**	**
	W	37.1	47.3		
Base saturation (%)	E	20.4	7.2	**	**
	W	11.4	4.8		
Available P($ug\ g^{-1}$)	E	97	44	**	**
	W	51	15		
Total P($ug\ g^{-1}$)	E	1070	809	*	**
	W	1370	954		
Available S($ug\ g^{-1}$)	E	7.7	9.9	NS	NS
	W	9.5	10.2		
Total N($g\ kg^{-1}$)	E	1.6	3.1	**	**
	W	3.1	4.5		
Total C($g\ kg^{-1}$)	E	47	84	**	**
	W	83	109		
C:N Ratio	E	30.3	28.5	NS	*
	W	27.2	24.4		

Table 2.1 continued

	REGION	DOUGLAS-FIR	WESTERN HEMLOCK	MAIN EFFECTS	
				Species	Region
FOREST FLOOR					
Total Weight (kg ha^{-1})	E[+] W[++]	21700 18700	29800 27000	**	NS
Total N (g kg^{-1})	E W	9.5 10.5	10.5 10.2	NS	NS
Total C (g kg^{-1})	E W	391 397	415 434	**	NS
Nitrogen Weight (kg ha^{-1})	E W	200 190	310 260	**	NS
Carbon Weight (kg ha^{-1})	E W	8050 7320	11750 11260	**	NS
C:N Ratio	E W	38.7 39.0	38.0 42.9	NS	NS

[+] E : Puget Sound - Western Washington Cascades Region

[++] W : Western Washington coast - Olympic Peninsula Region

*, ** represent significance levels of a 2-way ANOVA at a=0.01 and a=0.05, respectively.

[#] NS : not significant

(Ryan 1983). Ryan (1983) also showed that variations in surface soil pH was strongly correlated with exchangeable Ca and exchangeable acidity; decreasing exchangeable Ca or increasing exchangeable acidity decrease both Douglas-fir and western hemlock surface soil pH.

Heilman (1976, 1981) and Meurisse (1972, 1976) have summarized the features that distinguish the coastal forest soils from those of the Cascades as being: 1) low pH and base saturation, 2) pH dependent CEC, 3) Al dominated exchange complexes, 4) high soil organic matter content, and 5) presence of sesquioxides and/or "andic" soil properties. While forest floor available P was high (84 ug g^{-1}), levels in the mineral soil were low, usually less <10 ug g^{-1}, and values <5 ug g^{-1} were not uncommon in coastal soils (Heilman 1976, Grier 1976).

Reported "andic" properties of these soils (i.e. high levels of amorphous Al and Fe or organic matter) is of major importance in soil-fertility and plant growth. In particular, it may influence the ability of these soils to supply PO_4^{3-} and MoO_4^{2-}, anions which are readily adsorbed by sesquioxides. While these soils have been found to contain high levels of total P (in the order of 1000 ug g^{-1} (Heilman 1976, 1981; Meurisse 1972, 1976; Grier 1976), it is the (plant) "available" level that is low, indicating the high sorptive capacity of these soils for P.

Another important "andic" aspect of these soils is the high level of exchangeable Al. According to Ulrich's (1983) scheme of soil acid buffering ranges, the coastal soils of Oregon and Washington would fall into the cation-aluminum buffer ranges (pH 5.0 to 2.8). At pHs reported for these soils we can therefore expect exchangeable Al to be high. According to Reuss (1983), soil solutions will be dominated by Ca as long as base saturation exceeds 10 to 20%. The switch to Al dominance is then quite abrupt. At pHs of <4.7 soil acidity can be regarded as largely a function of Al in solution (McLean 1976). At such pHs, Al^{3+} may reach concentrations in the soil solution that make it the most important factor in determining plant growth (Foy et al. 1978, Ulrich 1983).

2.1.7 Soil Mineralogy and Its Significance

Jenne (1961) and Meurisse (1972) investigated the clay mineralogy of some coastal Oregon soils, and reported that montmorillonite is generally the principal smectite in many of these soils. Both authors reported the presence of measurable amounts of chlorite. According to Meurisse (1972) the predominant crystalline phyllosilicate in a number of coastal Oregon soils is one with properties intermediate between smectite and vermiculite on the one hand and chlorite on the other with the chloritic intergrades possibly having Fe or Al interlayers. For the coastal Washington soils, S.C.S. Staff (1964) reported that the main clay minerals were vermiculite and halloysite.

Heilman (1981), in a synthesis of soils of the Douglas-fir region, reported chlorite and chloritic intergrades as common constituents in soils of this region. This author also reported an abundance of sesquioxides (hydrous oxides), in crystalline and amorphous form, of either Fe or Al in coastal zones of Oregon and Washington. The presence of Fe oxides is readily apparent due to the strong colors they impart; striking red colors from hematite of the southwest Washington soils to yellow and yellow-brown colors from limonite along much of the Oregon coastal zone. Also volcanic ash is reported in many of the coastal soils

(Heilman 1981) and so allophane is likely to be present.

Thus the clay fraction of the coastal soils is made up largely of montmorillinite, vermiculite, chlorites (probably with Al interlayers), and halloysite; the first two have permanent charge while the latter two have predominately variable charge. Also present are crystalline and amorphous sesquioxides, and allophane, all of which are variable charge minerals. Under acid conditions vermiculite and montmorillonite can be transformed into a chlorite-like mineral by incorporating Al into the interlayer spaces (Uehara and Gillman 1981), and in this way will lose their permanent charge characteristics. Such aluminum-interlayered chlorites are common in naturally acid soils.

The clay mineralogy will have dramatic effects on the fertility and chemistry of the soils. Firstly, the relative abundance of variably charged minerals and soil constituents will result in high P sorption in these soils. Secondly, at the low pHs found in these soils, montmorillonite is unstable and may release large quantities of Al^{3+} ions into the soil solution (Uehara and Gillman 1981).

2.1.8 Organic Matter Accumulations

Heilman (1981) reported that organic layer depth for a range of coastal Washington soils varied form 6.5 to 22.5 cm, with the thicker layers occurring on less well drained areas. Table 2.1 shows the depths of a number of forest floor horizons, and comparable values have also been reported by Grier (1976, 1978). Unfortunately, the data in Table 2.1 do not list levels of exchangeable bases within the forest floor layers. Heilman (1976) showed an almost 9-fold increase in exchangeable

Ca in the litter layer compared with the A horizon, and similar trends were evident for Mg and K. This increase in the level of available plant nutrients, compared with the mineral soil, may be an important feature in the productivity of these forests.

An aspect often over-looked in relation to the litter layer is its ability to supply P. For example, while levels of available P in the mineral soil were low (<10 ug g^{-1}), forest floor available P levels were commonly >80 ug g^{-1} in many of the coastal soils (Heilman 1976). The release of inorganic P from that organically bound in the soil is fundamental to the maintenance of the phosphorus cycle in natural and semi-natural ecosystems (Harrison 1978, Miller et al. 1979). Only a small portion of soil organic P needs to be mineralized annually to provide sufficient amounts for plant growth.

The forest floor layer also contains a significant amount of both total and available N, as outlined in Table 2.1, although the availability of this N is greatly dependent on the chemical composition of the litter. For example, C:N ratios ranging from 20 to 40 have been reported (Table 2.1), but only C:N ratios of less than about 25 permit a net release (availability) of N from decomposition processes.

It is beyond the scope of this paper to review the role and mechanisms of mineral cycling in forest ecosystems. However, Fig. 2.2 summarizes the major components and processes involved in nutrient cycling, and comprehensive reviews have been prepared by Turner (1975), Cole and Rapp (1981), Miller et al. (1979), Vitousek (1982), Johnson et al. (1982), Van Miegroet (1986), Vogt et al. (1986). Fogel and Kromack (1977) reported limited mineralization of organic matter during the dry summers of the Pacific Northwest on Douglas-fir and western hemlock

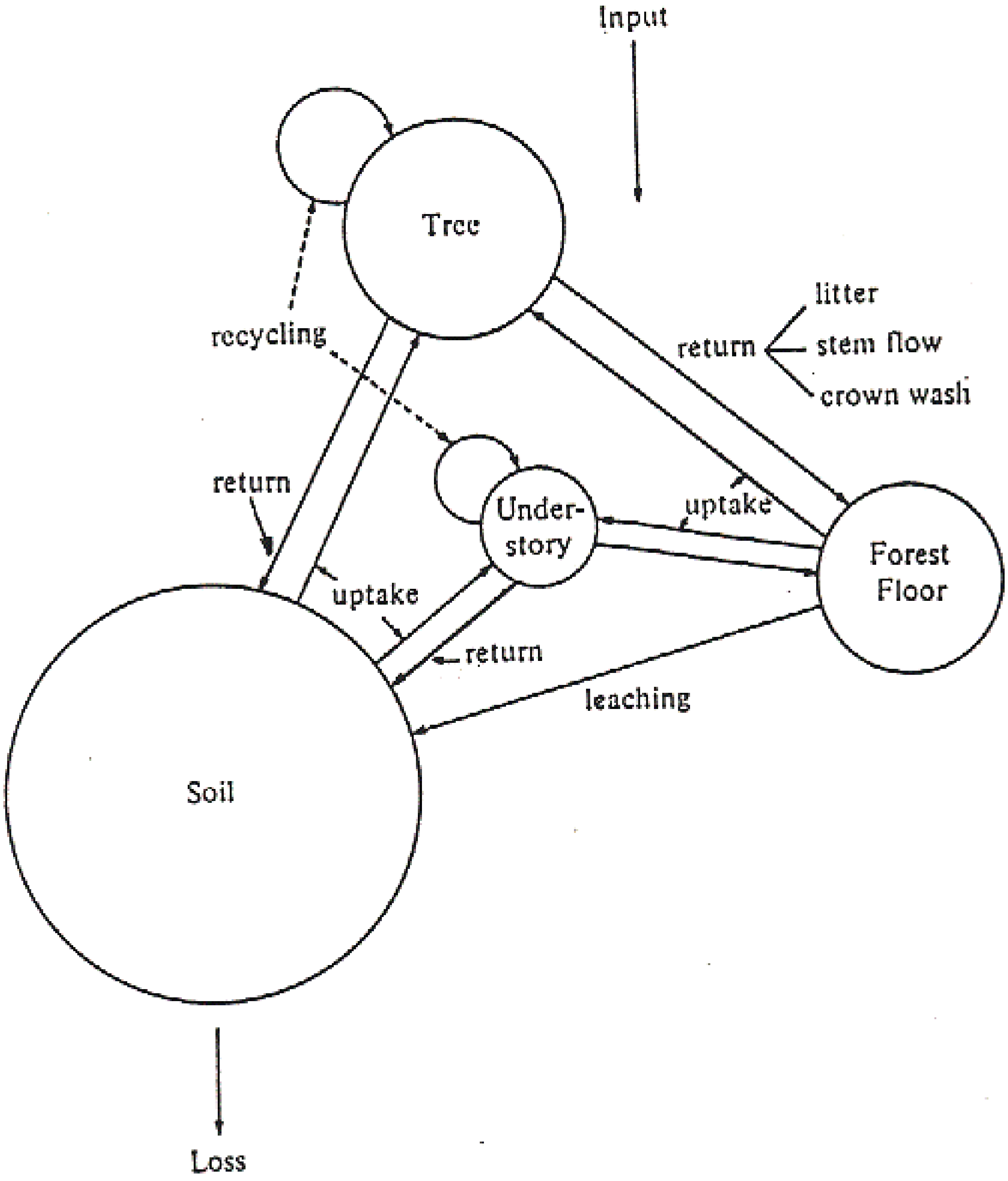


Figure 2.2. Schematic representation of nutrient cycling in forest ecosystems (adapted from Turner, 1975).

sites; most nutrient release was during the wetter months. Waring and Franklin (1979) concluded that, under nutrient release regimes characteristic of Douglas-fir and western hemlock, plants that have low nutrient requirements, can conservatively use acquired nutrients, and can accumulate nutrients during the wet "dormant" season have a great competitive advantage on otherwise nutrient poor sites. For example, Cole et al. (1975) reported that a 20-year-old Douglas-fir stand obtained 55% of its nitrogen from the litter layer while a 100-year-old stand may absorb nearly all its external N from the litter layer. Johnson et al. (1982) present similar supporting evidence for Douglas-fir and western hemlock. Organic phosphorus is also an important P source for plants. This was demonstrated by Harrison (1978), who reported that mineralization of 1% of the P content of organic matter in the surface 5 cm of the soil profile (95 mg m^{-2} $month^{-1}$) could supply the net annual uptake (11 kg P ha^{-1}) of vegetation in a woodland. Such findings underscore the importance of the litter layer and soil organic matter in forests growing on inherently nutrient poor soils. Chapin et al. (1986) have reviewed the nature of nutrient limitation in plant communities growing in infertile soils, and concluded that the concept of "nutrient limitations" defined for agricultural systems could not be simply extrapolated to plant communities on infertile soils.

Not only is the cycling of essential elements important in plants, but also that of non-essential elements. The biogeochemical cycling of Al, especially where it occurs at high concentrations, has important effects on organic matter and soil properties and may also influence plant distribution and regeneration. Webb (1954) reported that in a cool temperate rainforest dominated by coachwood (Ceratopetalum apetalum) the litter layer (2.5 cm in depth) accumulated about 11 kg Al ha^{-1} annually, which counter-balanced Al losses through eluviation. Incorporation and complexing of Al by the litter layer and organic compounds would also be an important mechanism for "detoxifying" Al. The production and turn over of roots in the forest floor and soil has often been ignored in nutrient cycling or productivity studies. Yet this component can represent a major fraction of annual productivity (Vogt et al. 1981) and an important component in nutrient (and Al) cycling. Vogt et al. (1987a, b), in studying the above- and below-ground biocirculation of elements in Abies amabilis and Tsuga mertensiana, reported that fine roots had the highest Al concentrations within the below ground system. In addition, the proportion of the total element pool circulated annually was highest for Al (76%) in this A. amabilis stand; except for Fe (31%), annual circulation of all other elements was <13%.

An ecologically significant finding arising from the study by Vogt et al. (1987a, b) was that Al accumulation in root tissue was closely related to soil horizon (soil depth), that is, Al concentration within root tissue was not uniform for all horizons (depths). For example, the high concentration of Al in roots in the Bhs horizon was retained in that horizon and did not appear to contribute significantly to Al biocirculation. The ability of a plant to retain, by accident or design, phytotoxic ions within the zone (horizon) of greatest availability (e.g., Bhs) may enhance its ability for nutrient uptake from other soil horizons (e.g., the E horizon) where the levels of phytotoxic ions are much less. Such a mechanism may be crucial for a species survival. Vogt et al.

(1981) found 75% of the fine root biomass in an A. amabilis stand restricted to the forest floor and E horizon, and similar observations have been reported for coastal western hemlock stands. However, the ecological significance of this has not yet been fully investigated.

Messenger (1975) and Messenger et al. (1978) proposed that Al content of leaf litter may be important in:

i) retaining Al in surface horizons;

ii) restricting microflora in the forest floor to Al- tolerant species; and

iii) restricting seedling survival and species diversity. That is, plant successional patterns could be altered by the pattern of biogeochemical cycling of phytotoxic elements.

2.1.9 Forest Fertilization in the Pacific Northwest

Within this region the two species of greatest commercial interest are Douglas-fir (in particular) and western hemlock. Early investigation of the nutritional status of these species on coastal and Cascade Mountain soils revealed that moderate to large growth response could be gained from Douglas-fir, and possibly hemlock, by application of nitrogenous fertilizer (Gessel et al. 1950, Gessel and Walker 1956, Heilman and Gessel 1963, Heilman and Ekuan 1973). By 1979 about 480,000 ha had been fertilized in the region, principally with N as urea (Bengtson 1979). Considerable investment has been made in attempting to provide forest managers with reliable data on the effects of fertilizing Douglas-fir and hemlock. However, growth response of hemlock stands to N fertilization has been erratic compared with Douglas-fir (DeBell et al.

1975, Webster et al. 1976, RFNRP Staff 1982), with response ranging from +50% to actual growth depression (-28%). Radwan et al. (1984), investigating growth response of hemlock to different N sources, concluded that the low and inconsistent response of hemlock to N fertilization could not be improved by applying some form of N other than urea. The difference in response to N fertilization between Douglas-fir and hemlock is most pronounced in stands on coastal soils (RFNRP Staff 1982, Webster et al. 1976, DeBell 1975). Proposed reasons for this variability have been: 1) limited supply of other nutrients, especially P (Heilman and Ekuan 1980a, b, Anderson et al. 1982, Gill 1981), 2) geographic and site influence and interactions (RFNRP Staff 1982, Radwan and DeBell 1980, Gill 1981), and 3) deleterious changes in soil or forest floor chemistry following application of N fertilizer (Gill 1981). Ryan (1983) reported that the relationships between forest soil acidity and western hemlock growth can affect all three of the above hypotheses concerning the erratic fertilizer response.

Gill and Lavender (1983) found that while fertilization of young coastal hemlock stands with urea increased foliar N levels, concentrations of P, Ca, Mg, Mn, Fe, Al and B were reduced. They suggested that the low growth response by hemlock on coastal soils following urea application may be due to a further reduction in the availability or uptake of nutrients other than N. However, the authors maintained that the reduced foliar nutrient levels were most probably due to reduced uptake rather than growth dilution effects, supporting earlier findings by Gessel and Heilman (1963), Radwan and DeBell (1980) and by Radwan et al. (1984). This raises two important questions: 1) whether fertilization of coastal western hemlock and Douglas-fir with N, P, or N

+ P can increase foliar nutrient levels and hence potentially increase productivity, and 2) do the two species have similar nutritional requirements on coastal hemlock soils? A corollary to the second question is whether the two species have similar mechanisms of nutrient uptake.

Greenhouse experiments have shown a positive growth response by hemlock to P and N + P additions (Heilman and Ekuan 1980, Heilman 1981, Anderson et al. 1982). Heilman and Ekuan (1980b) reported that Douglas-fir, growing in coastal hemlock soils under greenhouse conditions, displayed a positive response to P amendments, similar to hemlock. However, except for the study by Zasoski and Gessel (1982) field trials with advanced regeneration have not shown the P response suggested by pot studies.

The trend in response to soil P amendments by the two species growing in coastal hemlock soil raises the question of the nutritional status of the coastal hemlock soils in the Pacific Northwest. As indicated in Table 2.1, soil data (surface soil and forest floor) indicate that the coastal hemlock soils have the lowest pH, exchangeable Ca, base saturation, available P and C:N ratios. These soils have the highest CEC, total N and total C. Only a small portion of forest floor organic P needs to be mineralized annually to provide sufficient P for plant growth. Hemlock is known to root preferentially in the forest floor layer (Heilman 1976). Whether this is due to higher levels of available nutrients (particularly P and Ca) or due to lower levels of "toxic" Al or other conditions is currently not known. It is known, however, that these forest floor layers are particularly acidic, with recorded pH levels often below 4.0. Current regeneration practice in the coastal zone is to plant seedlings in the mineral soil at depths where available P levels are usually <10 ug g^{-1} and base saturation and exchangeable Ca are very low. For Pinus radiata, available P levels <9 ug g^{-1} in the topsoil are likely to result in P deficiencies (Will 1983).

A further aspect that must be considered relates to soil chemical reactions as a result of N fertilization. The application of fertilizer to soils can cause short or long term changes in solution pH and Al concentrations. Hydrolysis of urea and subsequent effects on soil pH and leaching have been documented by Cole et al. (1975). Hydrolysis of urea increases pH to alkaline ranges initially. As exchange reactions occur and HCO_3^- leaching begins, pH levels decrease until H_2CO_3 is formed and leaching stops. The effect of urea application on the leaching of trace elements from forest soil columns treated with 448 kg N ha^{-1} was demonstrated by Otchere-Boateng and Ballard (1981). They found large amounts of trace elements leaching from the columns treated with urea. Aluminum leaching was initially probably as mobilized organo-metallic chelates and then probably in monomeric form as nitrification reduced pH to less than four. There was significantly more leaching of Al, Zn and NO_3^--N from columns containing western hemlock seedlings than those with Douglas-fir. Similar changes in pH and nutrients following urea application were demonstrated by Gill (1981).

From the preceding review on the nature of the coastal hemlock soils, there are three aspects of particular relevance. They are the very low soil pH levels and associated low base saturation, the low levels of available P, and the high levels of exchangeable Al.

2.2 Aluminum Chemistry

2.2.1 Aluminum in the Soil

Aluminosilicates comprise a major portion of the mineral fraction of soils. Aluminum occurs most commonly in the primary minerals such as mica and feldspar, and in secondary minerals and ores; it is regarded as especially important in the composition of soil sesquioxides and clays. McLean (1976) indicates that Al makes up 8.1, 8.2, 2.5 and 0.4% of igneous, shale, sandstone and limestone rocks respectively.

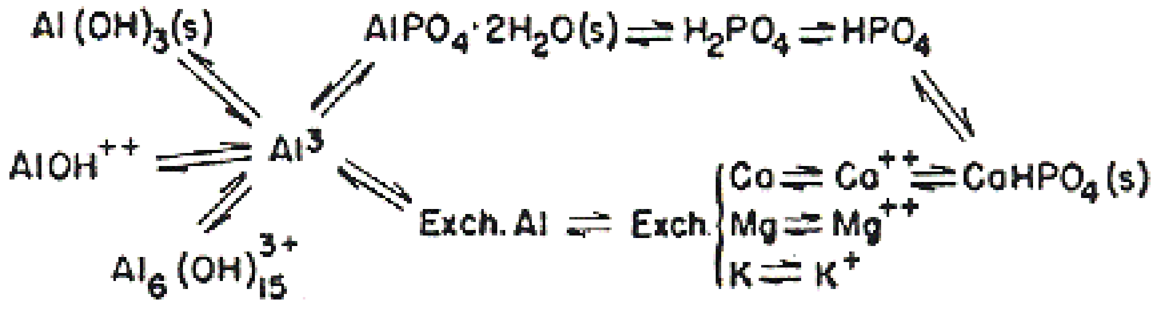
In the aluminosilicates, Al is usually found in an octrahedral coordination with O^{2-} or OH^{-}. Aluminum may also occur in the tetrahedral coordination having been substituted for Si^{4+} (Bohn et al. 1979). A significant role of Al in the various clays is in isomorphous substitution, particularly Al^{3+} for Si^{4+} (tetrahedral coordination) and Mg^{2+}, and Fe^{2+} or Fe^{3+} for Al^{3+} (octrahedral coordination). This substitution of ions with unequal charge generally produces a net negative charge in clays which contributes to the soil cation exchange capacity (Bohn et al. 1979, Lindsay 1979, McLean 1976).

Under conditions of extreme soil weathering (e.g., under high rainfall and moderate to warm climatic conditions) base cations are leached from the soil, leaving behind the less mobile Al^{3+}, which leads to a general dominance of Al (or Fe at extremely low pH) in soil exchange acidity. The lower the pH, the greater will be the amount of Al in solution and hence its potential effect on soil fertility and plant growth. Richburg and Adams (1970) write that the role of soil-solution Al in acid-soil fertility establishes the importance to plant growth of Al-ion equilibria in soils. But, although Al solubility is pH dependent, soil pH per se is a poor measure of Al toxicity or soil solution Al concentration.

At pHs less than about 4.5 significant levels of Al^{3+} will be in solution and will have a strong attraction for anions. In soil fertility this is of particular significance for phosphates, sulfates, and to a much lesser extent nitrate (Hsu, 1977). Richburg and Adams (1970) state that pH, solution Al and exchangeable Al of acid soils are undergoing almost continuous fluctuations and for this reason amorphous forms of $Al(OH)_3$ rather than the crystalline (gibbsite) form will control Al solubility. Hence one must consider three aspects concerning the effect of Al on soil fertility:

- the form of Al in the soil;
- soil-solution pH; and
- the concentration or activity of Al in the soil-solution.

A generalized scheme for aluminum equilibria in a strongly acid soil is outlined below,



(From Adams 1971)

and is an example of simultaneous equilibria in a natural soil system. According to Adams (1971) this scheme shows Al^{3+} in equilibrium simultaneously with $Al(OH)_3(S)$, $AlPO_4$ $2H_2O(S)$, soil-solution $Al(OH)^{2+}$ and $Al_6(OH)_{15}{}^{3+}$, and exchangeable Al. The equilibria are affected by the activities of exchangeable cations and soil-solution ions of Ca^{2+}, $H_2PO_4^-$ and other electrolytes and ions. The precipitation of $CaHPO_4$ at pHs<5 is unlikely due to its high solubility at low pH (Lindsay and Moreno 1960). Also existence of polymeric Al in soil solution is not resolved, due mainly to the reactivity of Al with soil organic compounds, phosphates, and strong exchange reactions with soil colloids (Bohn et al. 1979, Woolhouse 1983, Haug 1986).

2.2.2 Aluminum and Solution Reactions

Weathering of clay minerals can release Al^{3+} from the octahedral layers into solution. Once in solution the Al^{3+} ions hydrolyze (i.e. the acidity of the ion is great enough to break the H-O bonds) to yield hydronium ions (Thomas and Hargrove 1984). This can be represented by the following reaction from Haug (1986):

$$Al^{3+} + 6H_2O == [Al(H_2O)_6]^{3+} + [Al(H_2O)_{6-n}(OH)_n]^{(3-n)+} + nH^+$$

Lindsay (1979) has listed the sequence of hydrolysis for the Al monomers, including their respective activity equilibrium constants. According to Marion et al. (1976) the total soluble Al in solution could be described as follows:

$$Al_T = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^{+}] + [Al(OH)_3^{0}] + [Al(OH)_4^{-}] + [Al(OH)_5^{2-}]$$

With sulfate in solution and over a pH range 4 to 6, Marion et al. (1976) suggested that the stoichiometric concentrations of Al could be described by:

$$Al_T = Al^{3+} + Al(OH)^{2+} + Al(OH)_2{}^{+} + Al(OH)_3{}^{0} + Al(SO_4)^{+}$$

The relative distribution and average charge on the soluble Al species between pH 3 to 10 is shown in Fig. 2.3. The dashed line represents the average charge on the soluble Al species, and the isoelectric pH for soluble Al was 7.3 (Marion et al. 1976). A great deal of controversy exists as to the dominant form of Al in solution. In acid conditions between pH 4 to 6, Al^{3+} and $Al(OH)_2{}^{+}$ are generally considered the dominant Al-monomer forms present (Lindsay 1979, Marion et al. 1976), although Woolhouse (1983) and Haug (1986) consider that $Al(OH)^{2+}$ is also dominant in this pH range. Bertsch et al. (1986), using NMR spectrometry, found that at pH 4, Al^{3+} comprised 70% of total Al while $Al(OH)^{2+}$ and $Al(OH)_2{}^{+}$ about equally made up the balance.

As solution ionic strength increases, polymerization complexes of Al also increase (Stumm and Morgan 1981). But according to Hsu (1977), in dilute soil solutions polymerization is a more common phenomenon for <u>adsorbed</u> Al-hydroxides on exchange surfaces. At concentrations >60 uM, and acid pHs, a significant fraction of Al was found to exist as polymers, with $Al_{13}(OH)_{32}{}^{7+}$ identified with some confidence (Haug 1986, Woolhouse 1983, Nair and Prenzel 1978); the presence of the dimer $Al_2(OH)_2{}^{4+}$ is also commonly reported (Lindsay 1974, Nair and Prenzel 1978, Woolhouse 1983). However, the structure of soluble Al-hydroxy

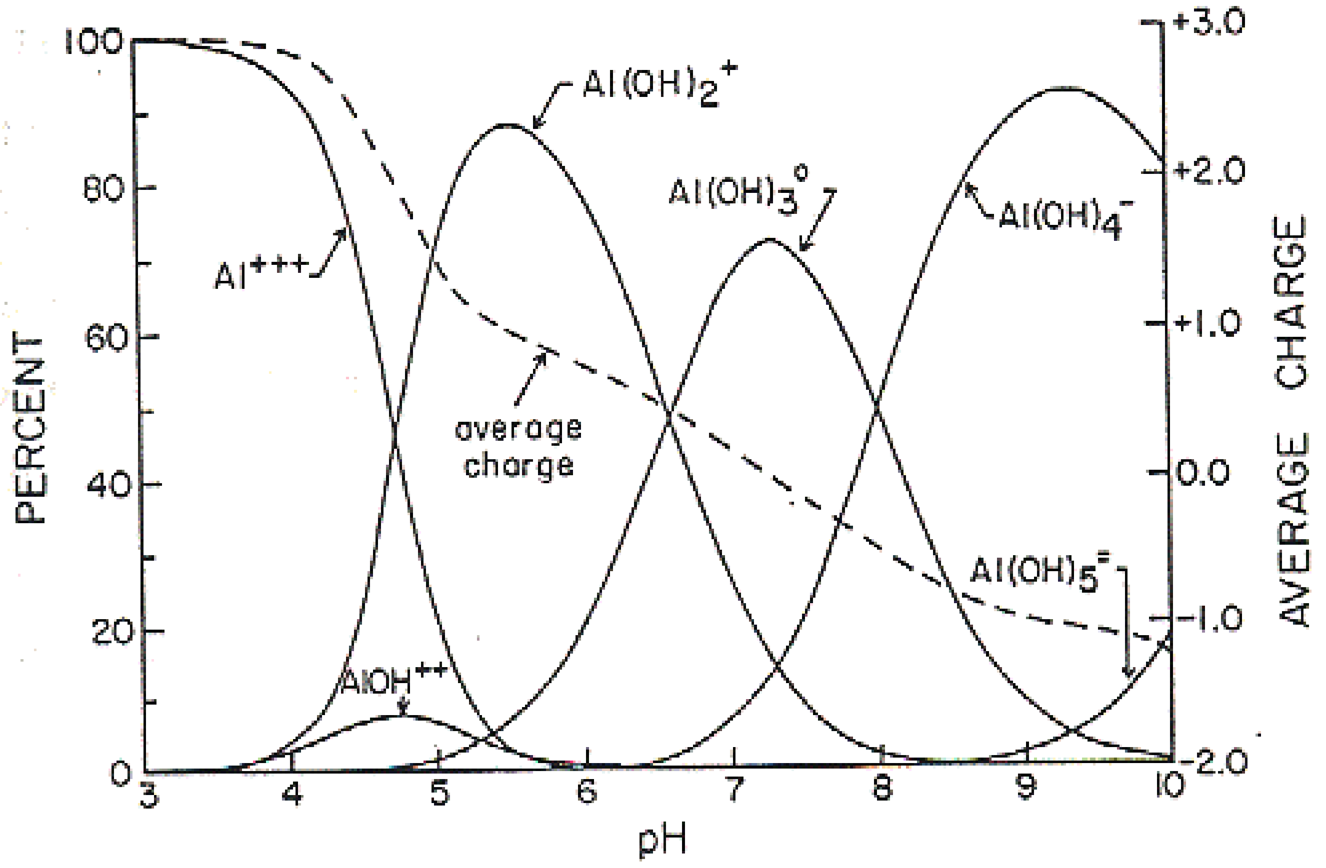


Fig. 2.3. The relative distribution and average charge on the soluble Al species as a function of pH at u=0.1M. (From Marion et al. 1976).

polymers is still highly controversial, and a number of ring-type structures have been proposed (Hem 1968, Baes and Mesmer 1976, Hsu 1977, Woolhouse 1983). As polymerization progresses, Al-hydroxides and oxy-hydroxides will predominate and regulate Al^{3+} activity in solution (Hsu 1977). Intense leaching and weathering of clay minerals can therefore produce Al-rich acid mineral soils. At the extreme end of polymerization, highly stable Al-sesquioxides will form and these will be in equilibrium with low Al^{3+} activities (McLean 1976).

White et al. (1976) reported the presence of soluble uncharged Al-P complexes in dilute solutions. The exact structure of these complexes was unknown, although Parks (1972) considered them to be intermediates in the formation of insoluble $AlPO_4$ and $Al(OH)_3{}^0$.

Aluminum has a propensity to complex with oxygen binding ligands. An important component of soil acidity in organic rich horizons is due to carboxyl (R-COOH), carboxyl and phenolic (R-COH) groups present in complex-humic compounds (Bohn et al. 1979, Schnitzer and Khan 1972). The interaction of Al with such ligands in the soil environment is complex and still not well understood; perhaps the best defined interactions are with humic acid (HA) and fulvic acid (FA) (Woolhouse 1983). The empirical formulae for these acids are:

Humic acid = $C_{76}H_{72}O_{18}N_2(COOH)_3$

Fulvic acid = $C_{20}H_{12}(COOH)_6(OH)_5(CO)_2$

Table 2.2 and 2.3 outline the important features on the composition of these organic fractions. From Table 2.3 it can be seen that the oxygen-containing functional groups make up 23% and 61% of HA and FA respectively (Woolhouse 1983). Hence it would be reasonable to conclude that these acids would be highly reactive with Al in solution. Woolhouse (1983) reports that there is mounting evidence on the importance of FA complexes with Al in acid soils. Ramamoorthy and Manning (1974) showed that for an extremely acid heathland soil (pH <3.5), Al would form mixed two-ligand complexes with phosphate and citrate, while at more usual acid-soil pHs about equal amounts of mixed two- and three-ligand (Al-phosphate-fulvic acid-citric acid) complexs would form. An excellent review by Haug (1986) on the molecular aspects of Al toxicity supports earlier work reporting the high reactivity of Al with organic acids.

The high affinity of humic substances in the soil for polyvalent metal cations has been found to promote clay mineral dissolution, particularly for chlorite, but also for other clay minerals (Schnitzer and Kodama 1977). These authors considered FA and low molecular weight HA, which are soluble at low metal to FA or HA ratios, to play a major role in such dissolution processes. The characteristics of these organo-metal complexes are pivotal in processes such as eluviation--illuviation and the formation of spodic horizons (Ugolini et al. 1977). For soils rich in organic matter, the level of exchangeable Al is low at pH's 3.5 to 6, and solution Al^{3+} activity is a function of complexation reactions with organic matter (McLean 1976, Hargrove and Thomas 1981).

Table 2.2. Characteristic values for the elemental percentage composition of humic and fulvic acid extracted from the organic matter fraction of the soil. (From Woolhouse 1983).

	Humic acid	Fulvic acid
Carbon	56.7	50.9
Hydrogen	5.2	3.3
Oxygen	35.4	44.7
Nitrogen	2.4	0.7
Sulphur	0.4	0.3

Table 2.3. The relative proportions of oxygen-containing functional groups of typical humic acid and fulvic acid fractions. (Values expressed as milli-equivalent per gram ash-free material). (From Woolhouse 1983).

	Humic acid	Fulvic acid
Total acidity	5.7	12.4
Carboxyl	1.5	9.1
Total hydroxyl	6.9	6.9
Phenolic hydroxyl	4.2	3.3
Alcoholic hydroxyl	2.7	3.6
Carbonyl	0.9	3.1

2.2.3 Influence of Aluminum on Macronutrient Anions

Phosphorus deficiency in plants is second only to N as the major soil fertility limitation throughout the world (Lindsay and Vlek 1976, Mengel and Kirkby 1982). Thus an element as abundant as Al in the soil, and one which has a strong affinity for phosphate ions under certain soil conditions, will have a strong influence on plant available P. Not only will Al^{3+} ions influence P availability but also (to a lesser extent) available S. For example, using data from Lindsay (1979) based on the solid phase:

Element	Atomic wt	Content in Lithosphere	Content in Soil (ug g^{-1})	Selected Averages Soil (ug g^{-1})	Selected Averages Molar Conc. 10% mc Log M
Al	26.98	81,000	10,000 - 300,000	71,000	1.42
P	30.97	1,200	200 - 5,000	600	-0.71
S	32.06	600	30 - 10,000	700	-0.66

it can be seen from the molecular ratios of Al:P $(10^{1.42}/10^{-0.71} = 102.13)$ that the solubility of P is controlled by Al. Similarly, Al controls S solubility. Hsu (1977) states that many anions can be retained by aluminum hydroxides and that the strength of their retention is a major factor governing their mobility in soil, and hence soil fertility (Tisdale et al. 1985).

In acid clays, phosphate and other anions are readily adsorbed by hydroxy-Al or -Fe surfaces (Parfitt 1978) with the concurrent release of OH$^-$ ions. This pH increase is probably buffered by further hydrolysis of desorbed Al. Anion adsorption on hydroxy-metal surfaces increases the CEC of those surfaces but adsorption capacity decreases rapidly as pH increases to about 6. Insoluble Al- and Fe- phosphates determine $H_2PO_4^-$

activity in acid soils with the predominant form depending on Al^{3+} and Fe^{3+} activities (Lindsay 1979).

The reaction of P with amorphous Al and Fe will be the major factor governing P availability and may overshadow immobilization due to precipitation reactions. There are two mechanisms of anion adsorption in soils high in amorphous minerals: 1) non-specific, whereby anions are held as counter ions in the diffuse double layer adjacent to a positively charged colloid surface, and 2) specific (or ligand exchange), whereby the anion enters into the coordination shell with metal oxides and may displace another anion. Phosphate and MoO_4^{2-} are strongly adsorbed and hence their availability and mobility in the mineral soil will be very low. Hsu (1977) explains the mobility of different essential plant anions in soils by grouping them into four categories on the basis of their affinity for Al^{3+}:

1) Anions with a weak affinity, such as NO_3^-, and which can thus be easily displaced.

2) Anions with a moderate affinity such as SO_4^{2-} where adsorption can occur only on the acid side of the ZPC (Zero Point of Charge).

3) Anions with a strong affinity, such as phosphates, whereby an edge OH- can be removed from clay colloids.

4) Anions with a very strong affinity, such as F^-, which can remove both edge OH^-s as well as breaking interior Al-OH-Al linkages of clay colloids.

Importantly, phosphates are known to induce breakdown of $Al(OH)_3^0$ to form aluminum phosphate precipitates (Ferguson and King 1977).

As a generalization, it has been assumed that phosphate retained by Al is of low availability to plant growth. Given that P levels in soil solutions are often low while Al levels at low pHs may be relatively high, then Al will have a significant influence on soil fertility, particularly as it relates to P and especially as it applies to the ability of the soil to replenish adequately the P removed by plant uptake from the soil solution.

However, Hsu (1977) states that the distinction must be made between P retention and fixation by Al. If phosphate retained by Al can be slowly released (at a reasonable rate) for plant uptake then this may be advantageous to fertility management. But because of the low solubility of Al-phosphates, release of phosphates into solution is often too slow, especially during periods of high demand by plants (e.g., during periods of vigorous growth, particularly early stages). Hsu (1977) considers that:

1) availability of adsorbed P is related to the degree of surface saturation, i.e. at low surface saturation (common where natural levels of P are low and Al levels high, e.g. pHs of 4) adsorbed P may be unavailable for plant uptake; and

2) the continuous addition of fresh $Al(OH)_3^0$ due to weathering may coat already existing aluminum phosphates with more $Al(OH)_3^0$ layers forming occluded phosphate. This process is slow, and it is reasonable to assume that much of the adsorbed phosphate would be taken up by plants before additional layers of $Al(OH)_3^0$ are added.

Because of the non-specific attraction between Al^{3+} ions and NO_3^- it is unlikely that Al will significantly influence N availability to plants. This may not be the case for SO_4^{2-}. However, phosphates will generally be adsorbed preferentially to SO_4^{2-}; it would only be under extreme conditions of high solution Al, low solution phosphates and SO_4^{2-} that SO_4^{2-} availability may be affected by Al. Where P in solution is high, SO_4^{2-} will move from the exchange sites into solution, thereby making it available for plant growth.

2.2.4 Influence of Soil Aluminum on Fertilizers

Of crucial importance to soil fertility is the influence of Al on applied fertilizer. McLean (1976) writes that when soluble phosphate is added to acid soils, much of the added P will be converted to Al-phosphates. Initially this may be unstable so that the phosphate will slowly move into solution and be available for plants. However, with time this Al-phosphate availability is reduced due to crystallization to $AlPO_4.2H_2O$ (Varisite) or to amorphous $AlPO_4$ forms.

But, as pointed out by McLean (1976), Lindsay (1979), and Tisdale et al. (1985), the common ion effect of Al must be taken into account. For example McLean (1976) shows a considerable reduction in concentration of $AlPO_4$ with the "common ion" being present and concludes that $AlPO_4$ may be a good source of available P in the absence of Al as the common ion. Where high levels of Al exist in solution, additions of phosphate may help to reduce Al toxicity by the formation of Al-phosphates (Tisdale et al. 1985) as well as increasing plant available P.

Reactions of phosphate fertilizer with soils, particularly with concentrated superphosphate, have received considerable attention. The major P compound in this fertilizer is $Ca(H_2PO_4)_2.H_2O$, commonly known as monocalcium phosphate monohydrate (MCP). When MCP is added, the soil solution becomes super saturated with respect to $CaHPO_4.2H_2O$ (dicalcium phosphate dihydrate or DCPD) and $CaHPO_4$ (dicalcium phosphate or DCP), and these minerals precipitate at the granule site (Lindsay, 1979). Such precipitation of DCPD and DCP in acid soils results locally in pHs of 1.48 and 1.01 respectively. These pHs are much lower than pH 4.68 expected from congruent dissolution of MCP. This lower pH is due to the formation of phosphoric acid when DCPD is precipitated (Lindsay 1979).

The dissolution reaction of MCP in soil is important in that the resulting very low pHs around the fertilizer granule causes Fe and Al to come into solution; Lindsay (1979) reported an Al concentration of 0.7M in an acid Hartsell soil following P additions. Neutralization reactions with soil bases eventually cause pH to increase, and the subsequent precipitation reactions decrease Al and Fe in the soil solution. Hence very soluble phosphate fertilizers that greatly reduce soil pH (even if only temporarily) may exacerbate the pH and Al problems in low pH - high Al soils, especially in the vicinity of plant roots. Such reactions would greatly reduce the efficiency of applied P. The inclusion of cations such as NH_4^+, K^+, Ca^{2+}, and Mg^{2+} in fertilizers enables them to be included in the initial reaction products and may reduce the amount of phosphate precipitated by Al, as well as reducing Al-induced deficiencies of the base cations.

Application of lime to acid soils is a long established practice in agronomy. Liming raises soil pH, generally resulting in the release of phosphate and formation and precipitation of $Al(OH)_3$. On soils with very low pH and significant buffering capacity, for instance forest soils where pHs may range from 4.0 - 4.5, additions of lime may be impractical if the pH is to be raised any appreciable amount, as the lime required would be in quantities too high to be feasible. In such cases more Al and acid tolerant plant species, or spot application of fertilizer to the plant rooting zone to reduce the potential for Al adsorption, may be necessary. As well, application of less soluble and less acid forming fertilizers may be more beneficial (e.g., rock phosphate).

2.3 Aluminum-Acidity and Plant Growth

2.3.1 Introduction

Aluminum: Group III element, most plentiful of all metallic cations, second most plentiful oxide, third most plentiful element, and exhibiting both ionic and covalent bonding (McLean 1976, Lindsay 1979). Together with silica and oxygen, aluminum forms the structural basis for a major portion of rock and soil forming minerals and is released into the soil as a result of weathering (Bohn et al. 1979). However, despite its abundance Al has not yet been found essential for higher plant growth according to the criteria of what constitutes an essential element (Mengel and Kirkby 1982). While low concentrations of Al have been shown to have a beneficial effect on plant growth (Foy 1974, 1984, Ryan 1986 a, b, Konishi et al. 1985) it is generally accepted that Al at such concentrations is synergistic rather than essential.

Extreme weathering will leach base cations from soils leaving behind less mobile cations such as Al^{3+}, leading to a general dominance of Al in soil exchange acidity. Under such conditions soil pH will be <5.0 and, according to McLean (1976), at pHs <4.7 soil acidity can be regarded largely as a function of soil Al chemistry: the lower the soil pH the greater the amount of Al in solution. At such elevated concentrations Al toxicity is probably the most important growth limiting factor in most strongly acid soils (Foy 1974, 1984, McLean 1976, Messenger et al. 1978, Ulrich 1983).

According to Foy (1984) the poor root development observed in acid soils can often be attributed primarily to Al toxicity. This limits root elongation and branching, hence exploration/utilization of the soil, and thus leads to drought susceptibility. Aluminum toxicity also is first expressed at the roots (Foy 1974, 1984, Foy et al. 1978, McCormick and Steiner 1978, Steiner et al. 1980, Ryan 1986 a, b, Hecht-Buchholz 1983, Schier 1985, Horst et al. 1982, Bennet et al. 1985a, b). This is due to the high sensitivity of roots to deleterious changes in the growth medium. Roots are the primary organ for water and nutrient uptake and, therefore, factors that inhibit normal root growth and function will sooner or later be manifested in reduced above ground plant development.

Alexander (1980) presented evidence suggesting that elevated soil Al levels, or high foliar Al levels may limit microbial breakdown of organic matter under strongly acidic conditions. Mutatkar and Pritchett (1966, 1967) found that while Al had little effect on organic matter decomposition at pHs >4.5, at pHs <4.5 a marked reduction in CO_2 evolution occurred. Matsuda and Nagata (1957) and Yoshida and Sakai

(1964) reported reduced numbers of fungi, bacteria, and actinomycetes as Al concentrations approached 10 ug g^{-1}; fungi were usually more tolerant of Al than bacteria. Zwarun et al. (1971) found that survival of a _Bacillus_ sp. was much more reduced in an Al-clay treatment relative to a Ca-clay treatment. Although there is disagreement in the literature on the overall effect of Al on soil micro-organism survival (Mutatkar and Pritchett 1967, Zwarun et al. 1971) there is nevertheless sufficient evidence indicating that the decomposition of organic matter is reduced with increasing levels of Al at pH's <4.5. Because most of the N, P and S, plus other nutrient elements are bound in organic matter, a reduction in heterotrophic activity, and hence organic matter decomposition, due to "toxic" concentrations of Al will have an adverse effect on nutrient cycling rates, availability of nutrients for plant growth, and accumulation of organic matter.

Blamey et al. (1983) state that the interaction of many factors affecting Al toxicity in plants are still not clearly understood due largely to: a) the many variables involved in acid soil fertility problems, and b) the complex and interactive behavior of Al in soils. The critical pH at which Al becomes soluble or exchangeable in toxic concentrations depends on soil factors such as the predominant clay mineral, the amount of organic matter, concentrations and availability of other nutrient elements (cations and anions), and plant species or cultivar (Foy 1974, 1984, Haug 1986).

A further complication in Al-plant interaction is identification of the toxic Al species/form. This remains an issue because commonly used analytical procedures cannot differentiate between Al in monomeric dissolved form and polymeric, colloidal, or crystalline forms in natural waters or artificial solutions. According to Smith (1971) only monomeric Al ions, free or complexed, can be considered equilibrium species. Below about pH 4, Al^{3+} dominates (Hem 1968, Smith 1971, Cambell et al. 1983), while above pH 7 the $Al(OH)_4^-$ ion is the predominant species (Hem 1968, Smith 1971, Campbell et al. 1983, Blamey et al. 1983). However, between approximately pH 4 to pH 7 little agreement exists as to what Al species are present, or dominant. Many researchers investigating the effects Al on plant growth have attributed toxicity to Al^{3+} (Pavan and Bingham 1982, Pavan et al. 1982), but more recent investigations have also implicated monomeric aluminum hydroxides (Blamey et al. 1983, Alva et al. 1986 a, b) as well as polymeric Al forms (Bartlett and Riego 1972, Wagatsuma and Ezoe 1985). While it is likely that plant species differences exist as to the degree of toxicity of different forms of Al, the interaction of Al, solution pH and elemental composition will confound research on this toxicity.

2.3.2 Plant Symptoms of Aluminum Toxicity

The suite of symptoms commonly associated with Al toxicity is not easily identified, and may be confused with symptoms brought about by other injurious or environmentally detrimental factors (Foy et al. 1978, Foy 1984, Adam and Adams 1979). For example, in some plants the foliar Al toxicity symptoms resemble those of P deficiency: overall stunting; small, dark green-blue leaves; late maturity and depression of fruit and seeds; purpling of leaf veins, leaves and stems due to increasing levels of anthocyanins; and chlorosis and necrosis of leaf tips and margins (Foy

1984, Taylor and Foy 1985, Mengel and Kirkby 1982). Aluminum toxicity may also appear as induced Ca deficiency or a reduced Ca transportation: curling or rolling of young leaves; chlorosis and necrosis of leaf tips and margins; and collapse of growing points or petioles (Foy 1984, Mengel and Kirkby 1982). Aluminum induced Fe deficiency symptoms (inter-veinal to complete chlorosis of the newest foliage) have also been reported (Foy 1974, Pegtel 1986, Taylor and Foy 1985). However, some of these symptoms were also reported by Moore (1974) for H^+ ion toxicity, and hence care must be taken to separate the effects of excess Al and excess H^+ ions in solution.

Because Al toxicity is first expressed in the roots (Foy 1984, Foy et al. 1978, McCormick and Steiner 1978, Steiner et al. 1980, Ryan 1983, Clark 1977, Hecht-Buchholz and Foy 1981, Schier 1985, Rorison 1960, Clarkson 1965, Horst et al. 1982) most symptoms ascribed to plant Al toxicity are related to root morphology. Foy (1984) has summarized these symptoms, for crop and tree species, as follows:

> "...Aluminum injured roots are characteristically stubby and brittle. Root tips and lateral roots become thickened and may turn brown. The root system as a whole appears collaroid, with many stubby lateral roots but no fine branching. Such roots are inefficient in absorbing nutrients and water..."

Young seedlings have been reported to be more susceptible to effects of Al than older plants (Thaworuwong and Van Diest 1974).

2.3.3 Physiological and Biochemical Effects of Aluminum Toxicity

As plant species and varieties vary widely in their tolerance to excess Al (Foy 1974, 1984, Taylor and Foy 1985, Ohki 1986, Pegtel 1986, Woolhouse 1983), the exact physiological/biochemical mechanisms of Al toxicity (or tolerance) are still debated. Obviously, Al tolerant plants must have the capability of restricting Al absorption at uptake sites, detoxifying Al at the root surface (rhizoplane), apoplast or symplast, or sequestering Al into areas of low physiological activity. Some of the physiological and biochemical mechanisms are reviewed below.

The plant root tip, which includes the root cap, meristematic zone and zone of elongation, is one of the most active physiological and biochemical regions of plants (Foster 1986). Investigations of Al effects have thus centered on this region and have shown it to be the zone of Al entry and its subsequent accumulation in cortical cell walls and nuclei (Wright and Donnan 1953, Rorison 1958, Clarkson 1965, McCormick and Borden 1974, Henning 1975, Matsumoto et al. 1976a, Hecht-Buchholz and Foy 1981, Bennet et al. 1985a, b). Several authors have reported that most of the Al absorbed by roots was subsequently adsorbed onto exchange sites of the apoplast cell walls (Rorison 1958, Clarkson 1966, Clarkson and Sanders 1971, Foy and Fleming 1978). This adsorbed Al reduced cell wall plasticity and extendibility by cross linking pectins in the middle lamella. However, Matsumoto et al. (1976b) found no evidence of Al-pectin interaction in Al-stressed pea roots.

Clarkson (1965), investigating the effects of Al on onion plants, concluded that depression of root elongation as a result of reduced mitotic activity was the main effect of Al toxicity. Dysfunction of cell division in the root meristmatic tissue due to penetration of Al into the root protoplasm is one of the most commonly reported major effects of Al toxicity in roots (Foy 1974, 1984, Foy et al. 1978, Henning 1975, Hecht-Buchholz and Foy 1981, Rios and Pearson 1964). Hecht-Buchholz and Foy (1981) observed rapid autolysis of Al affected barley root cells, beginning with the disorganization of the plasmalemma and breakdown of the ultrastructure of the cytoplasm. This eventually led to the disintegration of the root tip and mucigel cover, supporting earlier findings by Henning (1975) who showed that Al could enter the wheat root stelar tissue at the root meristem. Henning (1975) suggested that this was the pathway by which Al toxicity caused destruction of the root cap cells and disintegration of the outer root. The association of Al with root meristematic tissue led Matsumoto et al. (1976b) and Morimura and Matsumoto (1978) to conclude that Al binds to P in nucleic acids of DNA where it interferes with cell division processes, thereby preventing primary root elongation and causing abnormal root morphology.

However, Bennet et al. (1985a, b) questioned the concept of Al acting directly on cell division, and considered such effects as secondary. They found that the peripheral cells of the root cap were the primary uptake sites of Al; the root cap initials were the last root cap cells penetrated and further, there was little evidence of Al reaching the proximal meristem in the first 20 hours of exposure to Al. Bennet et al. showed further that the first observable effects of Al toxicity were Al-induced changes in root metabolism and the structure of cytoplasmic organelles of the root cap. From this they hypothesized that Al-induced changes in the root cap influenced control of the root meristem and hence must be regarded as the primary site of Al toxicity. They argued that the reported effects of Al toxicity on cell division could not be reconciled with the low mobility of Al in plant tissue, unless sites of uptake and action were co-incidental. However, the suggestions of Bennet et al. (1985a,b) conflict with reports by Clarkson (1965), Hecht-Buchholz (1983) and Horst et al. (1982) who reported changes in root meristem cell structure after only a few hours of root exposure to Al.

An interesting aspect of the work by Bennet et al. (1985a, b) was that decapped roots were slower in developing Al toxicity symptoms than intact roots, even though entry of Al into the proximal meristem and stelar region was enhanced in decapped roots. These authors cite earlier work by Barlow (1974) who found that removal of the cap stimulated cell division in the proximal meristem toward the formation of a new cap. Similar results have been reported by Hecht-Buchholz (1983) and Horst et al. (1982). In fact, Horst et al. (1982) suggested that increased mitotic activity in the proximal meristem, and the subsequent recovery from Al toxicity, may be due to an increase in root organic exudates which detoxify Al in the outer mucigel cover by forming stable Al-organic complexes. Complexing of Al and its detoxification by plant roots had earlier been reported by Bartlett and Riego (1972) and more recently by Aniol (1984) and Suhayda and Haug (1986).

Aluminum toxicity has been reported to affect photosynthesis, chlorophyll, and transpiration responses. Ohki (1986) found that for wheat, Al decreased photosynthesis, chlorophyll concentration, and transpiration; however in sorghum photosynthesis and chlorophyll concentration were increased but transpiration rates decreased. Bollard

(1983) reported Al-induced stomatal closure for broad bean, and suggested that this may be a factor in reducing transpiration.

Aluminum has been found to accumulate in the roots of many plants (Foy 1974, Foy et al. 1978, Matsumoto et al. 1976b, Ryan 1983, McCormick and Borden 1974), and therefore Al tolerance has often been related to a plant's ability to absorb and translocate P. Al-hydroxide is present at the root and cell wall surfaces, thus such areas are a potential site for P fixation, leading to a reduction in available P for active uptake (Clarkson 1966, Rorison 1958). In sugar beet, Foy and Fleming (1978) reported insoluble Al-P in the cortical region of roots rendering the plant P deficient, it was shown that plants grown with Al had very little P in their conductive tissue. Barley plants grown in solutions with high Al levels had higher P levels in their roots, but lower levels in their tops compared with plants grown in the absence of Al.

James et al. (1978) attributed reduced growth of Sitka spruce to Al-induced P deficiency. Foy (1974) reported that removal of soluble Al from solution culture increased recovery of P by pine trees. Increased root P levels in the presence of Al has commonly been reported (White 1976, Wallace and Romney 1977, Mullette 1975, Humphreys and Truman 1964, Prichard et al. 1984, Cummings et al. 1986). However, as suggested by Black (1968), this higher apparent P status probably has little nutritional value and is likely the result of an Al-P fixation/precipitation reaction at the cell wall. This is supported by the results of Vickers and Zak (1978) and Cummings et al. (1986) who reported that although Al apparently enhanced root P levels, translocation of P to plant tops was reduced. For example, Cummings et al. (1986) found that translocation of P to the apical buds and mature primary needles of red spruce was reduced by 20% and 9% respectively compared with controls, while root Al concentrations increased greatly. Cummings et al. (1986) showed that in the absence of Al, P uptake was active and followed the Michaelis-Menten model of ion uptake. However, the presence of Al in the solution culture changed the pattern of P uptake and reduced P translocation from roots to shoot, probably due to fixation of P as $Al(OH)HPO_4$ on cell wall surfaces. Pritchett et al. (1984) examined the effect of Al, Fe and Al+Fe on P sorption (adsorption and/or absorption) in clover; they found increased P sorption from solution in the presence of Al, Fe and Al+Fe and attributed this to physico-chemical sorption processes involving the root surface.

Aluminum has been found to have a major effect on uptake of Ca. Foy et al. (1969) suggested that lower Ca levels in soybean plants resulted from interference of Al in the uptake and transport of Ca within the plant, rather than from low Ca levels in the growth medium. Long and Foy (1970) reported that where high levels of Al occur in the growth medium a Ca deficiency is likely to occur. Huttermann (1983) reported that the toxic effect of Al on tree roots may be attributed to the inhibition of Ca uptake. Foy (1974) and Foy et al. (1978) attribute Al tolerance among plant species to their ability to resist Al induced Ca deficiency. Such deficiency could be overcome by increased availability of Ca in the growth medium (Hecht-Buchholz 1983). Ulrich (1980, 1983) states that mole ratios of Ca^{2+} to Al^{3+} below one in the soil solution will result in Al toxicity within roots, and that this ratio becomes critical below 0.2. Bauch (1983) investigated the effects of acid deposition and resulting soil reactions on cellular concentrations of Al, Ca and Mg in stressed and healthy fir and spruce trees. He found that while Al concentrations were similar in the root cortex of healthy and stressed trees, levels of Ca and Mg were significantly lower in stressed trees. The importance of Ca in maintaining cell membrane integrity is well documented (Clarkson 1977, Mengel and Kirkby 1982). Membrane permeability to inorganic compounds depends greatly on Ca^{2+} and H^+ concentrations in the growing medium. Biological membranes consist of protein and lipid molecules in approximately equal proportions. One role of Ca is to bind the protein and phospholipid molecules; if Ca^{2+} is replaced (e.g. by H^+ or Al^{3+}) membrane permeability is greatly increased. Epstein (1961) and Rains et al. (1964) had earlier demonstrated the requirement of Ca in maintaining ion uptake selectivity and in reducing deleterious effects of low pH. However, cytoplasmic Ca concentration is very low, and is maintained against a higher extracellular concentration by Ca efflux pumps (Kinzel 1983).

One of the major regulative functions of Ca occurs at the interface between the apoplastic fluid (soil surface) and the cell wall/plasmalemma surface. Under conditions of low Ca in the growth medium, membrane permeability breaks down due to root Ca-deficiency. However, the exact mechanism of Al inhibition on Ca uptake is not yet clear. At high Al concentrations exchange of Ca for Al can occur at the plasmalemma and may structurally alter the membrane. This replacement of Ca by Al has been suggested to occur as a result of adsorption of Al on cell walls and membrane components (Lance and Pearson 1969). Johnson and Jackson (1964) found that Al reduced the accumulation of Ca in roots, and that this could not be overcome completely by supplying additional Ca, suggesting that part of the Ca accumulating mechanism was depressed. Clarkson and Sanderson (1971) concluded that the role of Al was relatively non-specific, involving surface reactions rather than the disruption of metabolically dependent transport processes. The trivalent state of Al decreased the activity of Ca in the water- and Donnan-free spaces, and affected plasmalemma permeability to the uptake and efflux of Ca.

According to Clarkson and Hanson (1980) soil concentrations of 1 to 5 mM Ca are required to screen roots against the deleterious effects of low pH, toxic ions and ion imbalance. Huett and Menary (1980) reported that 12.5 mM Ca in nutrient solution completely removed the toxic effects of Al on root yields of cabbage and lettuce. However, this conflicts with the earlier findings of Johnson and Jackson (1964), and Clarkson and Sanderson (1971) who found that increasing Ca concentrations could not entirely overcome the toxic effects of Al.

Aluminum induced deficiencies in Mg, K and Fe have also been reported. Grimme (1982) found that under conditions of low Mg supply, high Al levels reduced yield of roots due to induced Mg deficiency. At sufficiently high Mg supply Al toxicity could be overcome, suggesting that Al tolerance in plants may be related to supply and uptake of Mg (Clark 1977, Grimme 1982). Wallace and Romney (1977), Clark (1977), and Pegtel (1986) reported Al-induced Fe deficiency. According to Marschner (1986), Al can interfere with the reduction of FeIII to FeII in the plant, thereby causing Al-induced Fe deficiency. Matsumoto and Yamaya (1986) found that Al reduced uptake of K to about 58% of the control; however, this was alleviated when 10 mM Ca was added to solution.

2.3.4 Mechanisms of Aluminum Tolerance by Plants

From the literature dealing with plant tolerance to metal toxicities, it becomes obvious that tolerance by different species, and varieties within species, to particular metals can be due to numerous mechanisms, even for a single metal (e.g. Al). Detailed reviews dealing with processes by which plants tolerate elevated levels of metal ions in the rooting mediums (Foy 1974, 1984, Foy and Fleming 1978, Foy et al. 1978, Woolhouse 1983, Rorison 1980) point to the following mechanisms which may lead to a greater tolerance by plants to increasing levels of Al in the root zone.

1. pH changes in the rhizosphere: tolerance to high Al levels by agronomic species and cultivars have been related to their ability to increase pH in the root zone, thereby reducing the solubility of Al. Such pH changes are brought about by increased uptake of anions (mainly NO_3^-) over cations. However, Bartlett and Riego (1972) found that even up to pH 6.8, as long as Al remained soluble it was toxic to corn plants. Magistad (1925), Rees and Sidrak (1956), and Jones (1961) have also reported toxic effects of Al at alkaline pHs. Hence a species' ability to simply raise rhizosphere pH independent of other factors may not necessarily be a mechanism for Al tolerance.

2. Aluminum uptake and distribution: Acid (Al) tolerant plants have been categorized according to whether they:

a) accumulate Al in the shoots, and probably the roots as well (e.g. tea plants; Matsumoto et al. (1976a, b))

b) accumulate Al in root tissues but do not transport it to the shoots (e.g. for cranberry; Medappa and Dana (1970))

c) exclude Al from plant (root) tissue (e.g. wheat and barley cultivars; Foy (1974)).

3. Preferential absorption of N anions over cations, that is, the ability to take up NO_3^- preferentially to NH_4^+ when both are present, resulting in an increase in rhizosphere pH.

4. Lower root CEC and thus lower Al adsorption in the root apoplast.

5. Preferential or efficient absorption of Ca (and other nutrient cations) in the presence of elevated Al levels, or else tolerate/require lower levels of cations, especially Ca in the presence of Al.

6. Preferential and efficient absorption and translocation of P, S, and Mo in the presence of elevated Al levels, or else a reduced overall requirement of these nutrients.

7. The ability to complex Al with organic compounds either in the rhizosphere (and apoplast) and/or in the symplast.

a) Within the rhizosphere: Bartlett and Riego (1972) suggested that organic compounds might be responsible for complexing Al and thereby altering its toxicity. Tan and Binger (1986) showed that the addition of humic acid (HA) to nutrient solutions containing Al reduced the effects of Al toxicity in corn and also increased P content of leaves. Such detoxification of Al by HA is probably related to the formation of organo-aluminum complexes (Tan 1978). Horst et al. (1982) showed that the mucilage covering of cowpea roots provided a protective function against Al injury; they considered this to be due to the high and specific binding capacity of mucilage for Al. According to Horst et al. (1982), the favorable effect of mucilage on Al tolerance can only be explained if the dynamics of root growth, mucilage production and Al migration into the rhizosphere are considered. Foster (1986) considers the thickness of the rhizosphere to range from 1000 to 3000 um, from the root surface (based on increased concentrations of root exudates and nutrient ions, detectability of gaseous diffusates, and microbial populations) and may present a considerable barrier to deleterious agents. Horst et al. (1982) reported that mucilage made up 20% of the dry weight of the meristematic zone of the primary root tip. Grime and Hodgson (1969) hypothesized the existence of a constitutive (chelating) binding system for Al in plants tolerant of acid soils; such a system could bind toxic forms of Al. The role of mycorrhizal fungi in detoxifying Al also cannot be overlooked as they are a potentially important source in providing organic ligands capable of binding, and thereby detoxifying Al.

b) Biochemical complexation within the symplast: An often hypothesized mechanism of Al tolerance in plants is the ability to chelate Al ions by organic acids. Such a method should be effective since plants can accumulate Al chelates without apparent toxic effects (Foy et al. 1978, Bartlett and Reigo 1972, Haug 1986). Indeed this has been proposed as the mechanism for detoxification of Al in the mature leaves of tea plants (Sivasubramanian and Talibudeen 1972). The existence of such a mechanism received further support by findings of Suhayda and Haug (1986); they showed that both malic and citric acids in corn roots could greatly reduce the impact of toxic Al ions on important cellular components and hence on physiological processes. Based on their results Suhayda and Haug (1986) hypothesized that citric and malic acid, because of their large stability constants with Al, plus their relatively high concentration, could reduce Al toxicity in corn root tissue, particularly in the Al tolerant variety.

2.3.5 Aluminum Accumulation by Plants

Numerous authors have compiled lists of Al accumulating plants (Hutchinson 1943, Chenery 1948, 1949, 1951, Webb 1954, Moomaw et al. 1959, Chenery and Sporne 1976). In their review Chenery and Sporne (1976) used the earlier criteria proposed by Chenery (1949) to distinguish an Al accumulator; that is, an accumulator has a biomass Al concentration exceeding 1000 ug g^{-1} (dry weight). Of the 259 families of dicotyledons represented, 37 had species with Al concentrations in excess of 1000 ug g^{-1}. Table 2.4, from Ryan (1983) displays comparative aluminum concentrations of North American tree species and some known Al accumulators.

The evolutionary significance of Al accumulation has been widely discussed (Chenery 1949, Webb 1954). Chenery and Sporne (1976) correlated this trait with a number of "primitive" characteristics of the dicotyledonous families. According to Webb (1954) such a trait would be an obvious competitive adaptation by plants to nutritionally poor, acidic soils of mesic environments.

Because of the great variation in Al concentration of accumulator species due to plant (and tissue) age and habitat type, Moomaw et al. (1959) classified acid tolerant plants based on the following criteria:

i) Those that exclude Al to some extent.

ii) Those that take up Al as: a) obligate accumulators, or

b) facultative accumulators.

iii) Those indifferent to Al in the growth medium.

Fig. 2.4 (from Rorison 1980) is a simple graphical representation of the types of plant response commonly found to increasing soil Al concentrations, and is basically identical to the criteria proposed by Moomaw et al. (1959) for Al accumulators.

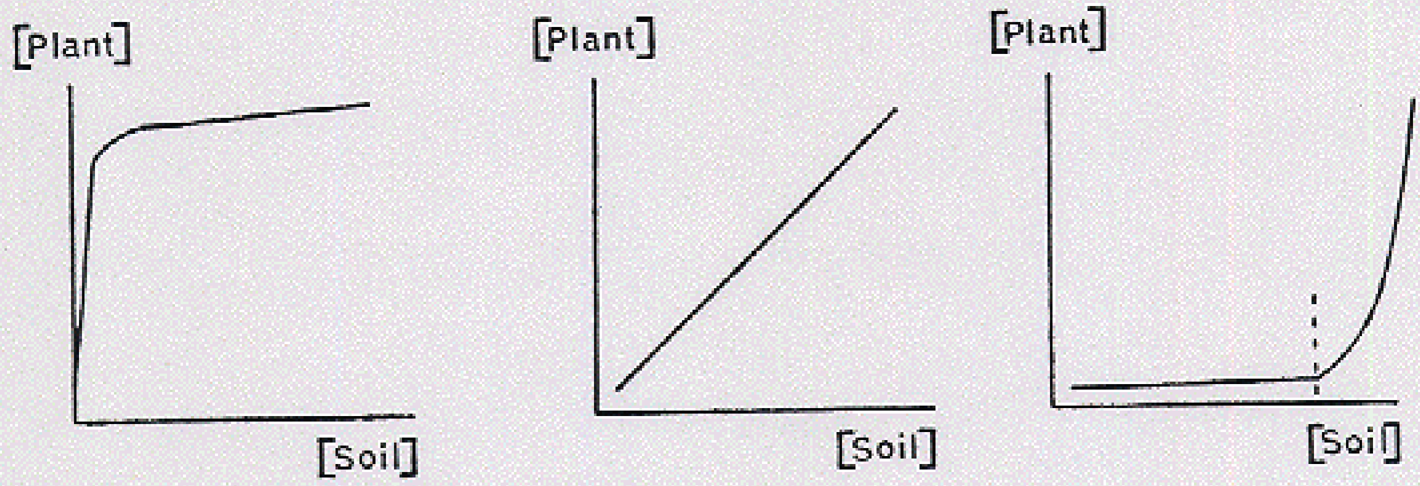
Within the literature there exists a paucity of data on how Al accumulating species survive such high concentrations in their biomass. Webb (1953) reported that Al-succinate was concentrated in heartwood cavities of Cardwellia sublinis , and related the latter finding to "alumina bodies" in ray parenchyma of C. sublinis and Orites excelsa. Matsumoto et al. (1976a,b) reported Al accumulations exceeding 30,000 ug g^{-1} in the epidermal cells of older tea leaves. Previously Sivasubramanian and Talibudeen (1972) had proposed that Al was chelated by citric, malic or other organic compounds and in this form was sequestered in older tea leaves. The existence of such a mechanism capable of detoxifying Al is supported by the recent findings of Suhayda and Haug (1986).

Table 2.4. Comparative foliar Al concentrations in North American forest trees and some known Al accumulators. (From Ryan 1983).

Plant Species	+Foliage (ug g^{-1}) (dry wt. basis)	Reference
1. Pteridophytes:		
Gleichenia linearis	3490-6300	Moomaw et al. (1959)
2. Gymnosperms:		
Pseudotsuga menziesii	175-458	Beaton et al. (1965)
Tsuga heterophylla	465-797	Beaton et al. (1965)
Pinus contorta	494-627	Beaton et al. (1965)
Pinus strobus	155	Messenger (1975)
	*164-428	Messenger (1975)
Tsuga canadensis	266	Messenger (1975)
	*408-463	Messenger (1975)
Abies balsamina	79	Messenger (1975)
	*114	Messenger (1975)
Picea glauca	29	Messenger (1975)
	*88	Messenger (1975)
Pinus resinosa	*141	Messenger (1975)
Pinus banksiana	*604±142	Messenger et al. (1978)
P. strobus	*417±20	Messenger et al. (1978)
P. resinosa	*343±94	Messenger et al. (1978)
3. Angiosperms: Dicots		
Betula nigra	211.5±18.6	Bartuska & Ungar (1980)
	*432.0±211.5	Bartuska & Ungar (1980)
Acer saccharum	*120.9±35.7	Bartuska & Ungar (1980)
Ulmus americana	*160.5±29.1	Bartuska & Ungar (1980)
Quercus alba	*91±12	Messenger et al. (1978)
Quercus rubra	*85	Messenger (1975)
Betula allegnaiensis	*63-71	Messenger (1975)
Acer saccharum	*58-80	Messenger (1975)
A. rubrum	*40-43	Messenger (1975)
Fagus grandifolia	39-63	Messenger (1975)
Camellia sinensis	600	Matsumoto et al.(1976b)
	*30,690	Matsumoto et al.(1976b)
Rhizophora harrisonii	5000	Hesse (1963)
Oryza sativa	500-800	Hesse (1963)
Ceratopetalum apetalum	11,000	Webb (1954)
Monocots		
Paspalum orbiculare	1400-2525	Moomaw et al. (1959)
Setaria geniculata	1540	Moomaw et al. (1959)
Sporobolus capensis	5475	Moomaw et al. (1959)
Spathoglottis plicata	3550	Moomaw et al. (1959)

* old foliage

\+ mean ± standard error



Accumulator Indicator Excluder

Fig. 2.4. Three ways in which the response of plants to increasing soil concentration is reflected in their internal plant concentration. (From Rorison 1980).

2.3.6 Toxic Form of Aluminum

Considerable uncertainty exists in the literature as to the toxic form of Al in the root zone. It has generally been assumed that Al^{3+} was the main toxic species, and the activity of Al^{3+} has been reported to be highly correlated with root elongation (Adams and Lund 1966, Ryan 1983). Pavan and Bingham (1982) showed that root growth of coffee in nutrient solution at pH 4.0 had a correlation coefficient of r^2=0.99 when associated with Al^{3+} activity. Blamey et al. (1983) suggested Al^{3+} or $Al(OH)_2^+$ as the major toxic form of Al responsible for decreased root growth in soybean. Alva et al. (1986a), also using soybean, found that relative root length was closely correlated with the sum of monomeric Al in solution, with the degree of correlation for individual Al monomers in the order $Al(OH)_2^+$ (r^2=0.87), $AlSO_4^+$ (r^2=0.67), Al^{3+} (r^2=0.59). According to Alva et al. (1986) reinterpretation of data on Al toxicity from previous Al-soybean studies showed root growth to be highly correlated with either $Al(OH)_2^+$ or $Al(OH)^{2+}$, and poorly correlated with Al^{3+}. Moore (1974) associated poor root growth of wheat seedlings in solution culture (pH 4.2, 2-6 ug ml^{-1} Al) to increased $Al(OH)^{2+}$ concentrations. Kinraide and Parker (1986) suggested that root elongation of wheat and red clover seedlings was inhibited by Al^{3+} (or mono-nuclear hydroxy Al forms) but not by $Al(SO_4)^+$. Addition of P to nutrient solutions containing Al have shown a "detoxifying" effect on Al (Rorison 1958, Barttlet and Riego 1972, Blamey et al. 1983). Given the high affinity of Al for complexing with phosphate, it is unlikely that $AlPO_4$ in solution would be toxic.

From the previous section dealing with Al chemistry, it was reported that controversy existed as to whether Al in solution between pH 4 to 6 was in monomeric or polymeric form. On this basis it could be expected that evidence of toxicity to Al polymers would be available. However, there is little conclusive evidence on this. Jones (1961), and Rees and Sidrak (1956) found increased concentrations of Al in plants grown in the presence of pulverized coal (fly) ash at pHs above neutrality. This would implicate the aluminate ion $Al(OH)_4^-$ as a potentially toxic form; in fact this ion is responsible for the solubility of Al at pHs >7 (Haug 1986, Lindsay 1979). However, unless the root surface pH is >7, it is unlikely that plants could take up the Al anion as it would be precipitated in the rhizosphere, probably as a hydroxide or phosphate. Jones (1961) suggested that the high Al levels in plants grown in fly ash was probably due to its absorption as a chelated complex with organic acids produced in the rhizosphere. Such a suggestion is supported by the findings of Tan and Binger (1986) and Haug (1986). Indeed, recent evidence suggests that organically bound Al is non-toxic to plant growth. Tan and Binger (1986) added humic acid to solutions containing Al and found that this greatly alleviated Al toxicity.

Wagatsuma and Ezoe (1985) reported toxicity of Al to a host of agronomic plants; at pH <4.7 monomer Al ions predominated, while at higher pHs hydroxy-Al polymers were dominant. These authors concluded that the hydroxy-Al polymers were more toxic to plant growth than Al in the monomer form.

The form of Al in solution will depend on solution composition (particularly Al and P levels), pH, temperature and "aging" of the solution (Haug 1986). Also included should be the presence of solids or amorphous material. Little attention has been given to the rhizosphere and its influence on phytotoxic forms of Al. Plants can depress the acidity of the rhizosphere by as much as 1 pH unit (Mengel and Kirkby 1982, Marschner 1986). A pH decrease of this nature, under already acid conditions could cause most hydroxy-Al crossing this zone to be converted into the monomer form. Further, in soil solutions, Al concentrations rarely exceed 4 ug ml^{-1} (160 uM) (Haug 1986). As the organic fraction of soil contains metal chelators this will further diminish the activity of free Al. Organic phosphates, which can make up between 30% and 75% of the total soil phosphorus, also form strong complexes with Al (Haug 1986), and hence in a soil environment it is unlikely that significant levels of hydroxy-Al polymers will exist given the reactive nature of Al. Therefore the main toxic forms of Al, in the absence of further evidence, can be considered as Al^{3+} and the hydroxy-Al monomers.

CHAPTER III

MATERIALS AND METHODS

3.1 Introduction

To evaluate the proposed hypotheses, two experimental approaches were taken. The first was an in situ fertilizer trial on coastal hemlock soils using N and P as fertilizers. Because N and P can greatly influence uptake and translocation of other elements, including Al, this would provide insight, at the plant level, into the fertility of the coastal soils, differences between the two species under investigation, and the potential role of Al in governing fertilizer response. Dimensional growth and foliar analyses were used in this assessment.

The second approach was to use hydroponic, or nutrient solution culture techniques. By eliminating the solid soil phases greater control could be maintained over various factors in order to investigate the ameliorative effect of OH, P and Ca on Al toxicity. Hewitt (1966) and Asher and Edwards (1983) reviewed the use of solution culture techniques and their basic methods were used in this work. Specific details for each of the two types of experiments are presented below.

3.2 Seedling Fertilization Study

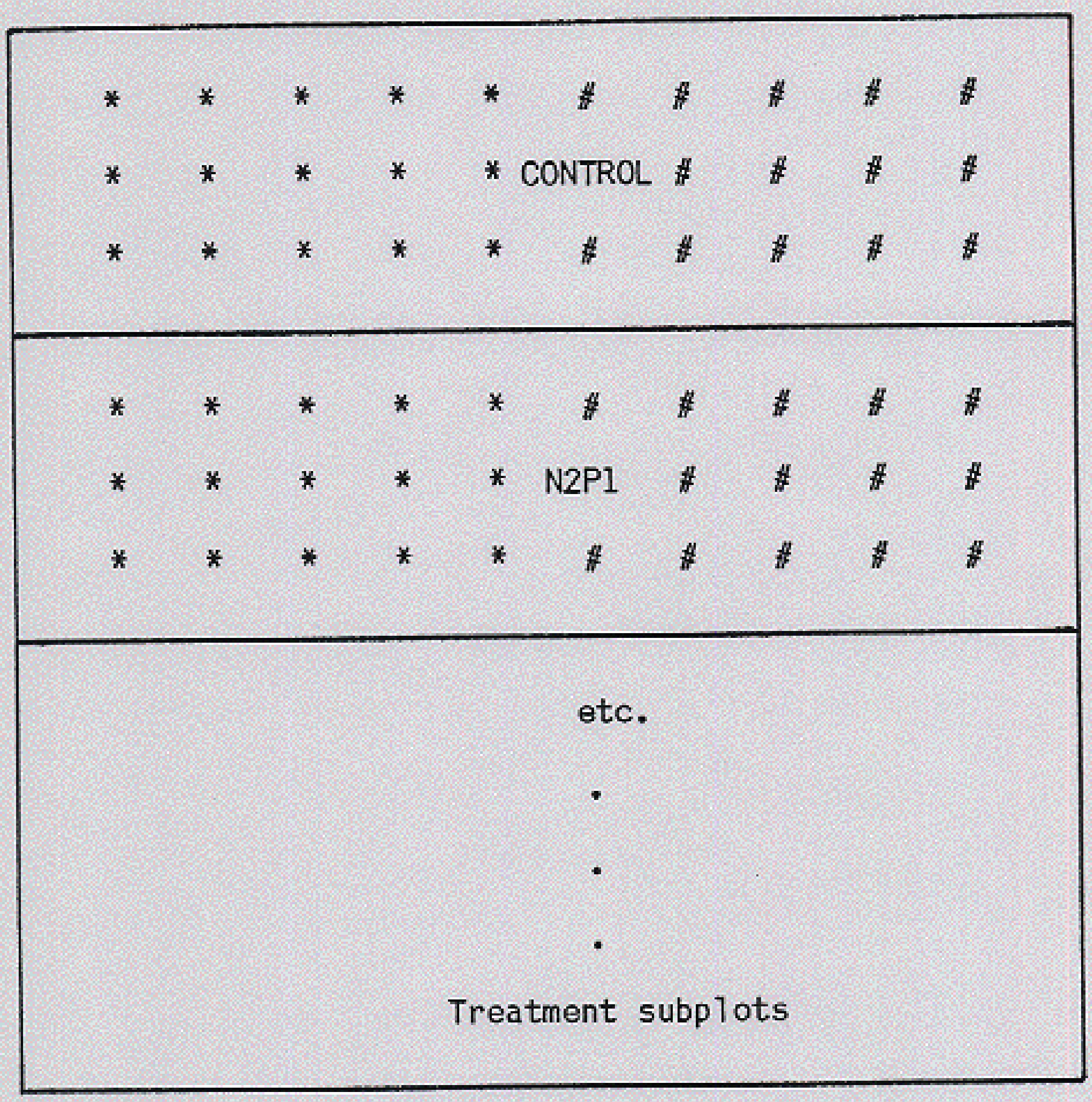
3.2.1 Location, Field Layout and Treatments

The study was located at four sites, two burnt and two unburnt, on the coastal plain of west, central Washington, south of the Olympic Peninsula, the nearest town being Hoquiam, Washington. At each site (location) the entire experiment was replicated. Each site was selected so that, within reason, it would conform as closely as possible to other sites in terms of slope, drainage and logging disturbance. Elevation was in the range 20-50 m above sea level. Land upon which the study was located was owned by the ITT Rayonier and Boise Cascade corporations. Logging had occurred in the twelve months prior to the study, while slash burning occurred in the Fall following logging.

The experimental layout is shown in Fig. 3.1; statistical analysis was carried out based on a nested (split block) experimental design as outlined in Steel and Torrey (1980). Fifteen seedlings of one species (Douglas-fir or western hemlock) comprised a single experimental unit. Within each main plot (replication) fertilizer treatments were randomly located. Seedlings were planted in Spring 1984 on a 1.8 m spacing as shown in Fig. 3.1. Fertilizer was applied four weeks following planting in a slit trench about 10 cm deep and 15 cm from the base of the seedling and on the slope contour.

Plug-1 Douglas-fir and western hemlock seedlings, i.e., container seedlings that spent one year in the greenhouse and one year in transplant beds were used. Seed source for the seedlings was the coastal lowland plain of Washington. All seedlings were obtained from the Toledo Nursery, Washington, and lifted from the nursery beds in late Fall 1983; seedlings were stored in a cold room at 4 ^{o}C until planting in April 1984. Healthy seedlings of average height were selected for planting; mean height of outplanted seedlings was 42 cm for Douglas-fir and 60 cm for western hemlock.

Main Plot Layout



* western hemlock seedling # Douglas-fir seedling
Nine fertilizer treatments per replication. Each treatment randomly located within each main plot. See text on following page for details on treatment types.

Fig. 3.1. Field layout of a main plot (replication). There were four main plots per site preparation.

Fertilizer treatments were based on a 3^2 factorial design using N and P at three equally spaced levels as shown in Fig. 3.2 below.

		Level of P		
		0	1	2
	0	Ctrl	P1	P2
Level of N	1	N1	N1P1	N1P2
	2	N2	N2P1	N2P2

Fig. 3.2. Factorial 3^2 fertilizer trial with N and P at 3 equally spaced levels.

The following fertilizers and amounts, at level 1, were applied:

P as 55 g of triple superphosphate (about 10 g elemental).

N as 30 g of ammonium nitrate (about 10 g elemental).

Level 0 represents no fertilizer for that element, while level 2 rates are double level 1 rates for each element. All fertilizers used were commercial grade products.

3.2.2 Data Collection

Height and root collar (soil surface) diameter measurements were taken immediately following planting, and at the end of each growing season. Foliar samples were collected in Spring and Fall each year except in Fall 1984 (end of first growing season) since it was considered that: a) nursery carry over would still be evident; and b) Spring samples for 1985 would be a good indicator of Fall 1984 levels. A subsample of seedlings of each species was retained from the planting stock for foliar analyses.

Ten surface soil core samples (0-15 cm depth) were collected using a 2.5 cm diameter soil corer at equally spaced intervals along the diagonal of each main plot. For each main plot diagonal, core samples were combined into a single analytical sample (i.e. there were two analytical samples per main plot), and analyzed for pH, exchangeable bases and Al, CEC, percent C and N, total and available P, and total Cu, Zn, Mg, Ca, K and Al. Because of logging disturbance, all soil classification, and horizon designation and description was based on soil classification by the S.C.S.(1964) of a nearby area.

3.2.3 Chemical Analyses

Foliar tissue samples were dried at 70° C for 24 hours and then ground in a Wiley Mill to pass through a 20 mesh screen. Ground samples of about 0.5 g were digested using H_2O_2 - H_2SO_4 - $LiSO_4$ (Parkinson and Allen 1975). Total N was measured colorimetrically on a Technicon Autoanalyzer II. All other elements (P, Ca, K, Mg, Mn, Fe, Zn, Cu, Na, and Al) were analyzed by emission spectroscopy on a Jarrel-Ash 955 Atomcomp Inductively Coupled Plasma Spectrometer. Percent element recovery was determined from analysis of NBS standard reference material 1572 (citrus leaves) and 1575 (pine needles). Average percent recovery of elements from foliar samples was 71% for Al, 76% for Fe, 87% for K, and for the remaining elements between 92 and 105%, based on element recovery from the NBS standards.

Total elemental composition of soil samples was determined using the digest method of Parkison and Allen (1975) and analyzed as outlined above. Cation exchange capacity was determined by the method of Chapman (1965), except that unbuffered ammonium chloride was substituted for ammonium acetate. Soil pH was determined in a 1:1 soil to water and 1:1 soil to $CaCl_2$ suspension using glass electrodes. Exchangeable Al was determined using 2M KCl extraction while total C was determined by LECO combustion furnace.

Determination of the phosphate retention capacity of the soils from the study sites was by the method of Blakemore et al. (1981), and is summarized below.

P- Retention Solution (1 mg P ml^{-1}): 8.80 g of potassium dihydrogen phosphate (KH_2PO_4) and 54.9 g of trihydrate sodium acetate ($NaC_2H_3O_2.3H_2O$) were dissolved in distilled water; 23 ml of glacial acetic acid were then added and the mixture diluted to two liters in a volumetric flask. The pH of the solution was in the range 4.55 to 4.65. All chemicals were reagent grade.

Procedure: 5.00 g of air dried soil (<2mm fraction) were weighed into a stoppered 50 ml polypropylene centrifuge tube. To this 25 ml of the P-retention solution was added. The soil plus solution mixture was shaken for 24 hours at about 20 ^{o}C and then centrifuged at about 12000 rpm for approximately 15 minutes. The supernatant was filtered using No. 1 Whatman filter paper and analyzed colormetrically for residual P on a Technicon Autoanalyzer II.

3.2.4 Statistical Analysis

Statistical analysis of growth response and foliar data was by Multivariate Analysis of Variance (MANOVA) using SPSS (Version 7-9) (Nie et al. 1975, Hull and Nie 1981). The *a priori* level of significance was set at a=0.10. The specific form of the MANOVA used is outlined in Table 3.1. In the case of significant main treatment effects, treatment means were ranked by Duncan's Multiple Range Test using SPSS and a=0.10. Breakdown of treatment N, P, and NP components and linear and quadratic response was by the method outlined in Federer (1955). To examine the effect of site preparation (burning) on the foliar composition of Douglas-fir and western hemlock, the average main plot concentrations (over all nine treatments) of each element on burnt and unburnt sites for Spring 1985, 1986 and Fall 1985 were ranked by Duncan's Multiple Range Test (a=0.10) using SPSS.

In the statistical analyses, site preparation has been used to block the four sites (locations) into more homogeneous units to help explain site variability. However, because the differences between burnt and unburnt sites are considered to be due primarily to the effect of burning, in the statistical analyses site preparation is presented as an "experimental" factor rather than location effect. But, it must be emphasized that the study was not designed specifically to test the effects of site preparation (ie. burning vs not burning) as there were no "control" plots for a given site preparation. Instead, the study was balanced by having an equal number of burnt and unburnt sites.

Table 3.1. Form of the MANOVA for analysis of growth response and foliar data.

Source of Variation	DF
*Site Preparation (Sprep)	1
Plots within Sprep	6
Species	1
Species by Sprep	1
Plots within Sprep by Species	6
Treatment (Treat)	8
Treat by Sprep	8
Plots within Sprep by Treat	48
Treat by Species	8
Treat by Species by Sprep	8
Plots within Sprep by Treat by Specie	48
Total DF	143

Total number of observations = 2 Site preparations x 2 Species x 9 Treatments x 4 Plots per Sprep = 144

* Site preparation was used to block the four sites (locations) into more homogeneous units as differences between burnt and unburnt sites were considered to be primarily due to the effects of burning.

3.3 Solution Culture Experiments

3.3.1 Introduction

A series of nutrient solution culture experiments were carried out based on the design of Blamey et al. (1983). The purpose of the study was to determine the effects of varying Al concentrations, OH:Al, P:Al and Ca:Al ratios, and to examine the effect of pH in the absence of Al. Four week old Douglas-fir and western hemlock seedlings were used and elemental tissue concentrations and root growth were determined.

3.3.2 Seedling Preparation

Douglas-fir and western hemlock seed from the coastal Washington lowlands was obtained from ITT Rayonier Corporation. Douglas-fir seed was soaked for 36 hours in a 1% solution of H_2O_2 (Ching 1959) (approximately 1 ml solution per seed) to stimulate germination; western hemlock seed did not require pre-treatment. Seeds were well washed prior to planting, and were germinated and grown in 15 cm deep boxes containing coarse grade (20 mesh), clear, washed, silica sand. Boxes were placed under an automatic mist spray irrigation system and watered with tap water; no fertilizers were added. Seedlings were grown for four weeks in the greenhouse with day temperatures maintained at 22 to 27° C and night temperatures 16 to 20° C; day length was extended to 16 hours using high pressure sodium vapor lights regulated to give an average intensity of 600 to 700 uEi. At this point seedling root length was 5 to 7 cm for Douglas-fir and 2.5 to 4 cm for western hemlock; roots were relatively free from branching. Seedlings were removed from the germination boxes by gently submerging the boxes in tap water to a depth of 0.5 cm over the sand surface. By gentle teasing, seedlings with branched roots up to 15 cm long could be removed without root breakage; adhering sand grains were carefully washed off and seedlings placed in cool distilled water in the shade prior to pre-treatment initiation.

3.3.3 Hydroponic Solution Culture

Three experiments were planned, each using factorial combinations of five concentrations of Al (10, 25, 50, 75 and 100 ug ml^{-1}) with three ratios of OH:Al, P:Al and Ca:Al. A fourth experiment investigated the effect of pH on seedling growth and chemical composition. Ingestad (1979) reported relative "optimum" levels of essential elements for Douglas-fir and western hemlock growing in solution culture. In this study the nutrient solution used was that of Ingestad (1979) as modified by Ryan (1983). According to Ryan (1983) the differences in the ratios used compared with those from Ingestad (1979) are due to:

> "...parsimonious use of chemicals, simplification of the averaged concentration values in terms of mM L^{-1}, and allowing near equivalence between Ca and Mg concentrations..."

Total N in solution was set at 102 mg L^{-1} and from this the elemental ratios in Table 3.2 were developed. Nitrogen was added at a ratio of 2.5 mEq NH_4^+ to 4.8 mEq NO_3^- to minimize solution pH change due to N uptake, as well as providing a dual N source. Iron was added as $FeSO_4$ in 0.01 M HCl to minimize precipitation in stock solutions. A one third strength optimum solution was used with adjusted P and Ca levels for the P:Al and Ca:Al experiments. Aluminum was added as $AlCl_3.6H_2O$, P as $NaH_2PO_4.2H_2O$, OH as NaOH, and Ca as $CaSO_4.2H_2O$. Appendix 3.1 has the full chemical recipe of the stock nutrient solutions used.

Tanks (treatment solution cultures) were made up about 24 hours before seedlings were added. This was to allow solution equilibration. Additions of the required volumes of $AlCl_3$ solutions to the tanks were made next to last, while the required volumes of OH, P, or Ca solutions were added last. The Al, OH, P, and Ca solutions were all added slowly with continuous stirring of the bulk solution; stirring was continued for about 10 seconds after all solution had been added. Distilled water was used throughout the entire experiment, including all stock solutions. The following specific changes were made to the nutrient solution:

OH:Al Study: Ratios of 0, 0.5, and 1.0 were used. Stock solutions of 185.3 mM NaOH were made up. No other changes were made to the nutrient solution.

P:Al Study: Ratios of 0.0065, 0.025, and 0.1 were used. Stock solutions of 18.53 mM NaH_2PO_4 were made up and no P was added to the stock nutrient solution.

Ca:Al Study: Ratios of 0.03, 0.15, and 0.75 were used. Stock solutions of 11.12 mM Ca SO_4 were made up. No Ca was added to the stock nutrient solution. Instead, $NaNO_3$ added to the stock nutrient solution to maintain the NH_4^+:NO_3^- ratio of 2.5:4.8.

Table 3.2. Comparison of the relative optimum nutrient levels of Ingestad (1979) with those of the nutrient solution formulated for this study.

Element	Relative Optimum Nutrient Levels+		Experimental Ratio	Weight ($mg\ L^{-1}$)
	Douglas-fir	Western hemlock		
N	100	100	100	102
K	50	70	57.5	58.7
P	30	16	19.7	20.1
Ca	4	8	15.7	16.0
Mg	5	5	9.5	9.7
S	9		12.8	13.1
Fe	0.7		0.5	0.503
Mn	0.4		0.4	0.385
B	0.2		0.2	0.216
Cu	0.03		0.03	0.032
Zn	0.03		0.03	0.033
Cl	0.03		4.03	4.1
Mo	0.007		0.007	0.007
Na	0.003		16.9	17.2

+Ingestad (1979)

Optimum levels were determined by initially setting N at 100.

The high Na ratios are due to the use of NaH_2PO_4.

3.3.4 Experimental Equipment

For the solution culture experiments, 20 L stainless steel tanks were used. The interior of the tanks were painted with an epoxy based metal free paint to prevent contamination. Because of the small seedling size the standard lids for the tanks could not be used. Instead, closed-cell styrofoam lids were made to float on top of the solution; a wide black plastic skirt was attached to the lids such that the skirt could drape over the edge of the tank thereby preventing any dust contamination of the nutrient solution. For each styrofoam lid fifty 0.8 cm holes on a 3.0 cm grid spacing were made (using a #4 cork borer of about 8 mm diameter) to hold the seedlings. A #5 cork borer (about 9 mm diameter) was used to cut plugs from waste styrofoam; these plugs were cut about half-way through with a razor and attached to the seedling root collar to anchor the seedling in the styrofoam lid, and also to plug the hole once the seedling root had been inserted into the solution. Ribs were glued to the bottom of the styrofoam lids so that a 0.5 cm gap existed between the top of the solution and the bottom of the lid. Two additional holes at either end of the lids allowed insertion of glass capillary tubes; ground to an acute angle at one end and connected to a compressed air supply at the other via rubber tubing. Main-line air pressure was adjusted to about 3 psi to ensure minimal root agitation. The experimental equipment is shown in Fig. 3.3 below.

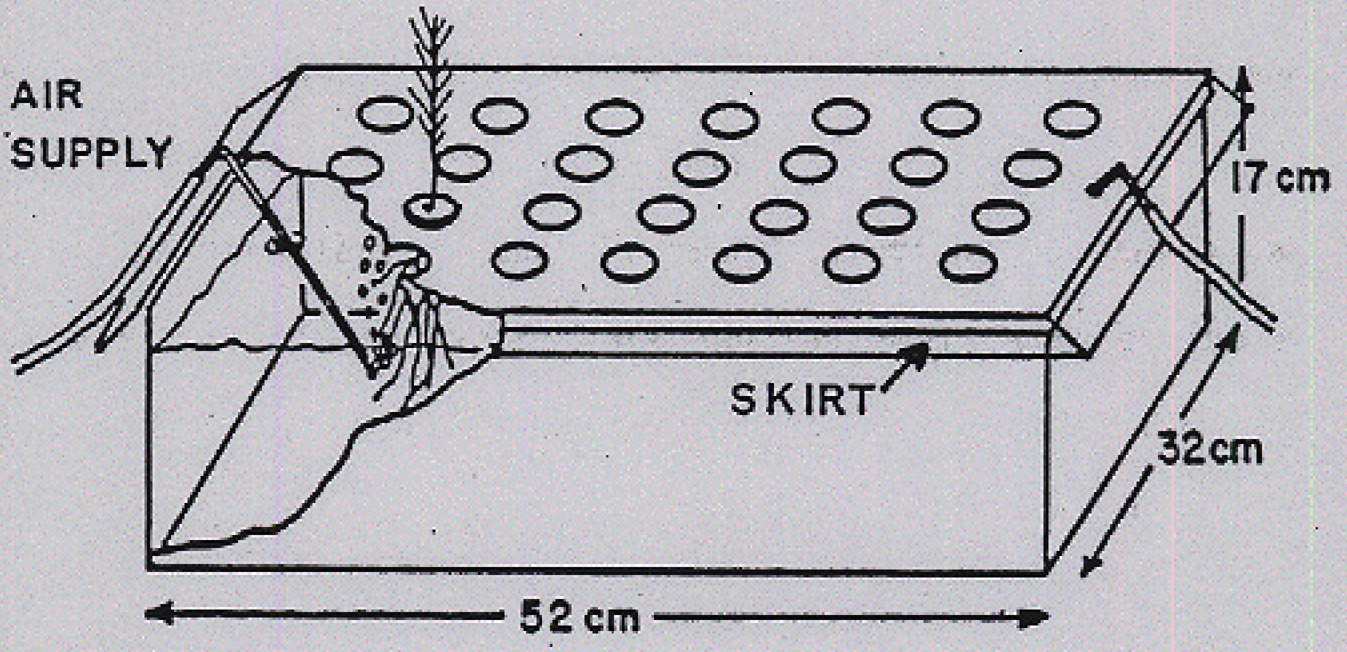


Fig. 3.3. Diagrammatic representation of the nutrient culture equipment.

3.3.5 Experimental Methods and Data Collection

Prior to beginning each experiment, seedlings were placed in a pre-treatment solution of 0.1 mM $CaSO_4$ for three days. At the end of this time 25 seedlings of each species were transferred to the treatment tanks which were randomly located on the greenhouse bench. For each species and treatment, seedlings were randomly located within the tank lid and 10 seedlings were then randomly selected to measure root length and to assess root morphology. Grid position of the measured seedlings was recorded so that the same seedlings were again measured at the end of each experiment. Initial and final "root length" included primary root plus hypocotyl; this ensured a fixed, easily identifiable point (the base of the cotyledons) from which to begin measurements. A preliminary experiment had shown that there was no discernable extension of the hypocotyl about three weeks after germination. Root lengths were taken by placing the seedling on a damp, waterproof sheet of graph paper and lengths were recorded to the nearest millimeter; all measurements were made rapidly to prevent root desiccation.

Seedlings were left in the treatment solutions for seven days. The short term nature of the experiments and the small size of the seedlings ensured minimal change of the nutrient solution. Before placing seedlings into the treatment solution, and again at the end of the experiment, solution samples were collected for chemical analysis.

At the end of each experiment final root length and the number of branch roots were recorded. Seedlings were then partitioned into roots and hypocotyl plus foliage components so as to form composite samples of plant component by species by treatment. All tissue was dried at 70° C for 24 hours and then ground with a mortar and pestle (there was insufficient sample to use a Wiley Mill); chemical digests and analyses were by the method of Parkinson and Allan (1975) and using ICP emission spectroscopy as detailed in section 3.2.3 above. Each experiment was replicated.

For the nutrient solution samples collected at the beginning and end of each experiment, pH was determined using a glass electrode and solution composition checked using ICP emission spectroscopy. Solution Al was speciated using the 8-hydroxyquinoline method of Barnes (1975) but as modified by Bloom et al. (1978) and James et al. (1983). To reduce foaming after the addition of n-butyl acetate and to help separate the aqueous phase, the culture tubes were centrifuged for about 20 seconds at approximately 1000 rpm (this was to help separate the aqueous phase and did not require exact timing or rotor speed). After settling, about 2 ml of the butyl acetate phase was placed into a 1-cm borosilicate glass cuvette using a Pasteur pipet and suction bulb. Absorbance was measured at 395 nm using a digital readout Perkin Elmer 55E Spectrophotometer.

The GEOCHEM Program (Sposito and Mattigod 1980) was used to determine nutrient solution ionic strength and free cation concentrations. Activities were calculated using the data from GEOCHEM and the activity coefficient equation of Guntelberg (Stumm and Morgan 1981).

3.3.6 Statistical Analysis

Experimental data were subject to multivariate analysis of variance (MANOVA) using SPSS (version 7-9) (Nie et al. 1975, Hull and Nie 1981). The *a priori* level of significance was set at a=0.05. Unlike the coastal study, the level of control over this series of experiments was much greater and resulting in lower variances, therefore a lower significance level was used to examine the data. Where treatment main effects were significant, means (or subsets of means) were ranked for significant difference by Duncan's Multiple Range Test using SPSS (a=0.05). Table 3.3 outlines the form of the MANOVA used. The experiment was based on a randomized block design involving complete factorial combinations of three ratios and five Al levels.

Table 3.3. Form of the MANOVA for analysis of seedling root growth response and foliar composition from the solution culture experiments.

Source of Variation		DF
Blocks (reps)		1
Treatments (Treat)		14
Aluminum levels	4	
Ratios	2	
Aluminum by Ratios	8	
Species		1
Treat by Species		14
Error		29
Total		59

Total observation = 2 blocks x 2 species x 15 treatments = 60

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Coastal Study

Plot locations for the coastal study were within a radius of about 15 km to each other and were considered to be "similar" in terms of soils, slope, logging disturbance, and previous vegetation for both burnt and unburnt sites. From the soils data presented Table 4.1 it is apparent that the soils of the four sites are not identical, though it was felt that this difference was no more than could be reasonably expected due to natural variability for the area, or else due to the effect of burning (site preparation). It must be emphasized however, that the study was not designed to test specifically for a site preparation effect, i.e., there were no site preparation "control plots" for a given site preparation. Instead the study was balanced by using an equal number of burnt and unburnt plots.

Site preparation was used as a factor to identify (block) various locations into more homogeneous units, and to help explain the variability of the locations. Through the following chapter, in reference to the coastal study, the results and discussion have been based on the site preparation effect per se, even though in the strictest sense site preparation should be viewed as a "location" (or block) effect. However, because the differences between burnt and unburnt locations are considered to be real, the data and discussion have been presented on the basis that site preparation was a real "treatment" effect, rather than a location (or blocking) effect. This is justified for several reasons: 1) all sites (locations) were within a 15 Km radius to each other and to the coast; 2) surface soil parent material was similar and appeared to be mainly marine sediments; 3) prelogging differences were small and the sites generally appeared to have been dominated by western hemlock; and 4) soil analyses between burnt and unburnt sites revealed that burned sites were more homogeneous than unburned sites.

4.1.1 Soil Analysis - Results and Discussion

Chemical properties of the soils from the four study sites are summarized in Table 4.1. Both unburnt and burnt sites show a striking similarity for a number of important soil properties, and these are discussed below.

For all sites the levels of exchangeable bases are very low, reflecting the highly leached condition of these soils. Thus it is not surprising that soil pH is low; infact the more recent soil pH (H_2O) and pH ($CaCl_2$) analyses indicate the extremely acid nature of these soils and explain the very high levels of KCl-exchangeable Al. Although soil pH was consistently lower on unburnt sites, nevertheless the levels of exchangeable bases were similar.

Except for Site 3 (burnt site), cation exchange capacity (CEC) of the remaining sites was high, and ranged from 35 to 45 cmol(p+) kg^{-1}. However this high CEC was due predominantly to exchange acidity. This is clearly obvious when the level of KCl-exchangeable Al is compared with the base saturation. Although Site 3 had the lowest CEC (25 cmol(p+) kg^{-1}), it also had the lowest level of exchangeable Al. Hence, for the soils of the study sites any differences in CEC are more a reflection of differences in exchangeable acidity rather than in levels of exchangeable bases.

Calculation of percent Al saturation using the method employed by Shoji et al. (1985), namely:

$$\frac{\text{Exchangeable Al} \times 100}{\text{Sum of exchangeable bases + exchangeable Al}}$$

revealed that Al saturation exceeded 93% for <u>all sites</u>. Reuss (1980) stated that soil solutions would be dominated by Ca as long as base saturation exceeded 20%, and in many cases this dominance could extend to 10%; the switch to Al dominance is then quite abrupt. Again, for <u>all sites</u>, base saturation was less than 2.5% (while exchangeable Na was not determined it is unlikely that Na would be present in levels that would change appreciably the base saturation). Based on the level of KCl-exchangeable Al, percent Al saturation, and the extremely low level of base saturation, Al is almost certainly dominating the soil solution. According to Shoji et al. (1980) these are some of the important properties of the nonallophanic Andisols which were a major deterrent for plant growth in strongly acid soils of Japan. Ulrich (1983) maintained that mole ratios of $Ca^{2+}:Al^{3+}$ less than 0.2 in the soil solution were critical in regard to Al toxicity and root growth. While no soil solution analyses were carried out for this study, the exchangeable Ca:Al mole ratios were less than 0.06 for <u>all sites</u> and this further supports the dominance of Al in the soil solution and its potential effect on plant growth.

Soils from all four sites show a high degree of P retention (>93%). Although no oxalate and pyrophosphate extractable Fe and Al analyses were carried out to determine the allophanic nature of these soils, all four soils show almost the same important chemical properties reported by Shoji et al. (1985) for nonallophanic Andisols in Japan. Based on the level of exchangeable and total Al, and the dominance of Al in the soil solution, it is highly likely that Al, due to its reactive nature, is largely responsible for the high degree of P retention in these soils. Indeed, the high P retention of these soils is reflected in the universally low levels of extractable (Bray's #2) P, even though total soil P levels were high (>600 ug g^{-1}). While some of the adsorbed P would become available for plant uptake, it is unlikely that the effect of P application to forest stands on these soils will show the same longevity as that reported by Gentle et al. (1986) for soils inherently low in P. For the soils of the study sites greatest efficiency from applied P (in terms of a growth response) will come from spot application or else by using slow release (rock) phosphate fertilizers.

The C:N ratio of the soils for all four sites was surprisingly uniform, ranging from 18 to 21. While total N was lower on Sites 3 and 4, which is attributed to the effect of slash burning, the level of total N was still reasonably high (3.4 and 2.8 g kg^{-1}). Given the low C:N ratios and the levels of total soil N, plant available N appears adequate on all four sites. However, total soil Cu, and particularly total soil Zn levels are low, and these levels must be viewed with some concern in regard to the capacity of these soils to replenish adequately soil solution Zn removed by plant uptake.

Table 4.1. Chemical properties of soils (0-15 cm depth) from the four study sites. Values represent the mean of a minimum of four observations.

Soil Variable	Site Preparation			
	Unburnt		Burnt	
	Site 1	Site 2	Site 3	Site 4
pH(H_2O)	4.4	4.6	5.0	4.9
pH(H_2O)*	3.8	4.0	4.7	4.7
pH($CaCl_2$)*	3.7	3.9	4.3	4.2
CEC (cmol(p+) kg^{-1})	41	45	25	35
Exchangeable (cmol(p+) kg^{-1})				
Ca	0.20	0.37	0.26	0.30
Mg	0.23	0.24	0.14	0.19
K	0.08	0.04	0.07	0.08
Al	17.7	9.8	6.6	10.2
C:N Ratio	18	21	18	20
Extractable P (ug g^{-1}) (Bray's #2)	3.6	2.2	6.0	3.2
P retention (%)	93	98	98	97
Total (g kg^{-1})				
C	78	78	61	56
N	4.3	3.8	3.4	2.8
Total (ug g^{-1}) ($LiSO_4$-H_2SO_4 extractable)				
P	730	610	900	860
Cu	2.6	6.4	6.8	10.1
Zn	8.6	10.2	13.5	13.1
Al	4200	4100	6200	6500

* Analyses carried out 24 months after all other analyses, but on the same bulk air dry samples as all previous analyses. Samples were stored in sealed Whirl Pak bags at room temperature.

Exclusion of outlying values of extractable P for Sites 1 and 3 reduces the level of extractable P for these sites to 2.1 and 4.1 ug g^{-1} respectively.

There were a number of consistent differences between sites on unburnt and burnt areas. Burnt sites always had higher pHs (H_2O and $CaCl_2$), and higher total P, Cu, Zn, and Al. Further, when two outlying extractable P levels are excluded (one each on Sites 1 and 3), extractable (Bray's #2) P was also consistently higher on burnt sites. As well, burnt sites had consistently lower total soil N and C, and this trend appeared to carry over for CEC.

The differences between unburnt and burnt sites are attributed primarily to the effect of slash burning, rather than to a location effect. This seems reasonable as the differences were in the surface (0-15 cm) horizon, the zone most likely to be impacted from surface perturbations. It could be logically expected that the effect of slash burning (including the organic layer) would increase measurably the surface soil levels of elements found in plant tissue, eg. P, Cu, Zn, and Al (provided of course that variability between measurements was low). As well, there is a strong relationship between total soil C, and CEC and C:N ratio; removal of the organic layer from the soil surface would affect all three soil parameters.

The chemical properties of the soils from the four study sites agree closely with analyses reported by the S.C.S. (1975) for a site in the general area of the study. Their results, including a full description of the soil, is given in Appendix 2.

4.1.2 Growth Results

Height Growth

Analyses for height response, that is the height attributed to a defined treatment period, were carried out for the first and second growing season following planting, and for the total two year period. This permitted the determination of duration of treatment effects as well as the growth effect. Appendix 3A is a summary of the MANOVA statistics for each period while Appendix 4A contains tables summarizing height growth data.

Examination of the MANOVA table for first year height response shows significant main effects for site preparation, species and treatment at a=0.10. There was also a strong interaction between species and site preparation. The effect of site preparation (i.e., burning or not burning logging slash) was significant in the first year (p=0.03) and results are summarized in Table 4.2.

Table 4.2. Effect of site preparation on first year height growth response of Douglas-fir and western hemlock. Values represent the sum of means (cm) for each experimental unit over all treatments.

Site Preparation	Species		Total
	Douglas-fir	Western hemlock	
Unburnt	103.4	107.4	210.8
Burnt	117.6	141.0	258.5
Total	221.0	248.4	469.4

Burning had a positive effect on height growth response of 13%, 31%, and 23% for Douglas-fir, western hemlock, and for both species combined. The value of 141.0 (which represents a 31% response) for hemlock clearly stands out from Table 4.2 and is responsible for the highly significant ($p=0.01$) species effect. This is most apparent for burnt sites where the difference in response between the two species is almost 20%. Treatment main effects were significant ($p=0.01$). While there was no significant interaction between treatment, species and site preparation, examination of the data in Appendix 4A does suggest some interesting trends. For instance, the greatest response in hemlock was for treatments N1P1, N2P1, and N2P2 while for Douglas-fir the greatest response was for treatments involving high levels of phosphorus (P2, N1P2, and N2P2). The effects of N, P, and N+P were separated from the overall treatment effects and the results, for all periods, are presented in Table 4.3. For first year height growth both P and N effects were significant ($p<0.01$ and $p<0.05$ respectively); the NP interaction was non-significant. The shape of the response surface was linear and highly significant ($p<0.01$) for both elements. While N and P effects were significant, it is clear from the slope coefficients (53.5 and 39.2 for P and N respectively) that P contributed more to treatment response.

Table 4.3. Breakdown of treatment main effects into N, P, and NP effects for the combined height response of Douglas-fir and western hemlock.

Response Period	Factor	Value and Significance of F			Regression Coefficients		
		Factor	Linear	Quadratic	Slope	Intercept	r
First Year	P	6.68^{**}	12.50^{**}	NS	53.5	569.3	.995
	N	3.39^{*}	6.73^{*}	NS	39.2	583.5	.996
	NP	NS					
Second Year	P	6.12^{**}	8.92^{**}	3.30^{*}	114.7	1679.1	.854
	N	NS	4.07^{*}	NS	77.5	1716.3	.919
	NP	NS					
Two Year	P	7.34^{**}	12.62^{**}	NS	168.1	2244.2	.927
	N	3.24^{*}	6.09^{*}	NS	116.8	2295.6	.970
	NP	NS					

Regression equation $y = a + bx$

** significant at a = 0.01, * significant at a = 0.05, NS - not significant at a = 0.10

For second year height response the species by site preparation interaction and treatment effects are still significant (p=0.07 and 0.03 respectively). Also significant now is the treatment by species interaction (p=0.07). Examining the species by site preparation interaction, the value of 308.2 for hemlock clearly stands out (Table 4.4 and Appendix 4A). Burning reduced second year height growth response to treatment in hemlock, while site preparation had no effect on Douglas-fir. The species by site preparation interaction is summarized in Table 4.4 below.

Table 4.4. Effect of site preparation on second year height growth response for Douglas-fir and western hemlock. Values represent the sum of means (cm) for each experimental unit over all nine treatments.

Site Preparation	Species		Total
	Douglas-fir	Western hemlock	
Unburnt	342.2	348.3	690.5
Burnt	345.1	308.2	653.3
Total	687.3	656.5	1343.8

As with first year height response, the effects of N and P on second year height growth were separated from the treatment main effect and results are presented in Table 4.3. The effect of P was still highly significant (p<.01) while N and NP were non-significant. The P response curve was still linear. Comparison of values for slope from the linear regressions for N and P clearly shows that P was still the major element contributing to second year height growth response (i.e., 114.7% vs.

77.5% for P and N respectively). However, because of the species by treatment interaction, the main treatment effects must be viewed cautiously. For instance, Fig. 4.1 clearly demonstrates the very strong species by treatment interaction, the most striking detail being the negative effect of the N2 treatment compared with that of N1 for western hemlock. For Douglas-fir there was still a positive response at both these levels, although the slope of the response curves for N and P varied.

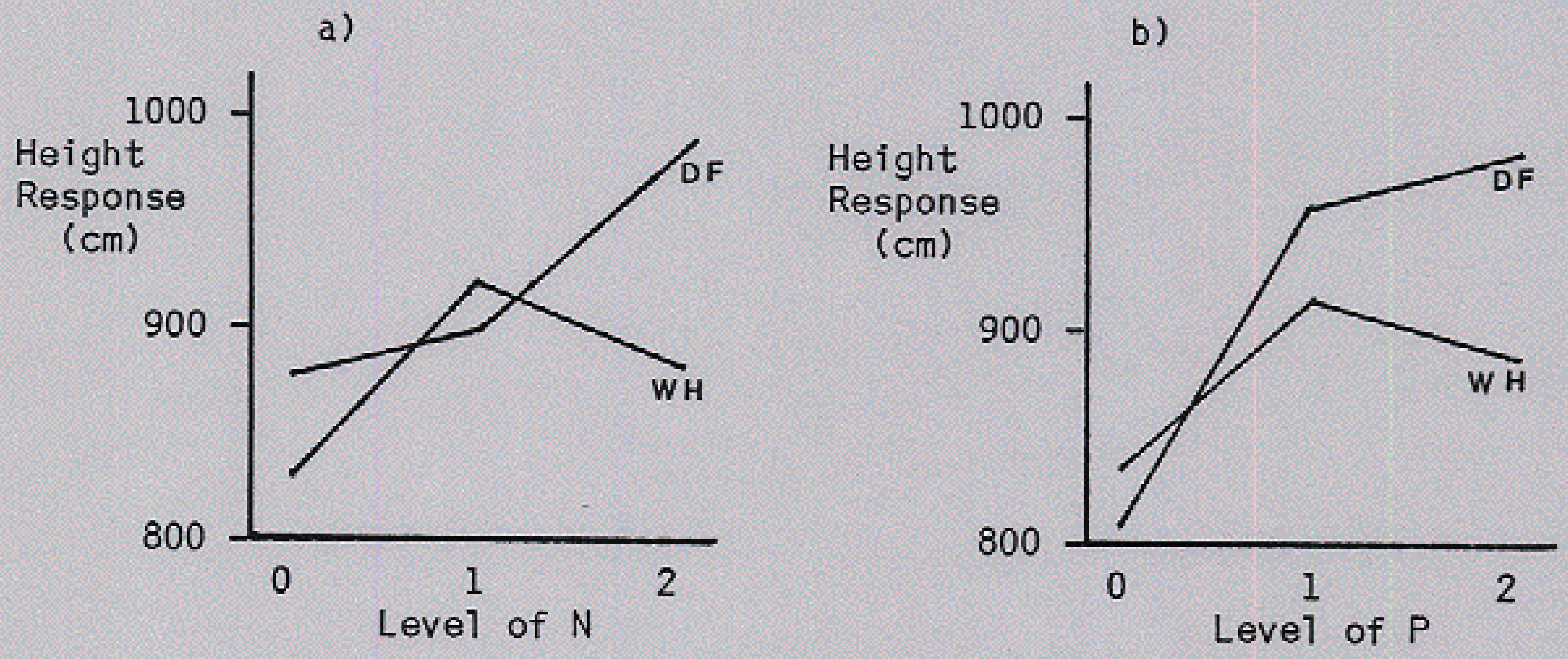


Fig. 4.1. Second year height response for Douglas-fir (DF) and western hemlock (WH) showing the interaction between species and treatment for (a) nitrogen and (b) phosphorus. Y axis represents the sum of mean values (cm) for each experimental unit for the relevant treatments.

Breakdown of sums of squares for the species by treatment interaction are summarized in Table 4.5. The two most striking features in the table are:

1. The strong positive and linear response by Douglas-fir to P; the response to N was non-significant at a=0.05 (but was significant at a=0.10).
2. A significant and quadratic N effect ($p<0.05$) for hemlock, and the absence of a P effect. The N effect was significant due to the strong quadratic (negative) effect at N2 levels.

Examination of the summary MANOVA table in Appendix 3A shows that only treatment effects were significant ($p=0.01$) for two year height response. From Table 4.3 it is clear that the P response is highly significant ($p<0.01$) and linear. There is also a significant ($p<0.05$) linear N response. Comparison of the slopes of the linear regressions for N and P for the two year period reveals that the slope for P is 44% greater than for N. This can be viewed as follows: the overall response to treatment was largest in the presence of P and this response was consistent and highly significant ($p<0.01$) for the first, second and two year response periods. The non-significance of N in the second year is attributed to the species by treatment interaction outlined in Fig. 4.1.

Table 4.5. Breakdown of the species by treatment interaction for Douglas-fir and western hemlock second year height response into species, N, P, and NP effects. response.

MANOVA Terms	Factor	Value and Significance of F			Regression Coefficients		
		Factor	Linear	Quadratic	Slope	Intercept	r
Species by Treatment							
Douglas-fir	P	11.44^{**}	19.90^{**}	2.98^{*}	91.5	823.4	.933
	N	3.34^{*}	6.28^{*}	NS	50.6	864.3	.955
	NP	NS					
Western hemlock	P	NS	NS	2.84^{*}	23.25	855.8	.558
	N	3.73^{*}	NS	5.71^{*}	27.0	852.0	.480
	NP	NS					
Treatment Only	P	6.12^{**}	8.92^{**}	3.30^{*}	114.7	1679.1	.854
	N	2.41^{+}	4.07^{*}	NS	77.5	1716.3	.919
	NP	NS					

Regression equation $y = a + bx$

** significant at a = 0.01, * significant at a = 0.05, $^{+}$ significant at a = 0.10
NS - not significant at a = 0.10

The overall N and P effects are summarized in Table 4.6. Values for the regression coefficients were obtained by plotting the slope values of the linear regressions for P and N respectively, for the treatment main effects of each period. Both slopes are highly linear (r=1.0); however, the slope for the P line is 58% greater than for N, and at the end of two years the two lines are still diverging. However, the results for the two year period must be kept in perspective as they are <u>averages</u> over two years. The second year results (Appendix 4A and Tables 4.3 and 4.5) clearly indicate that the two species are no longer responding similarly, as they appeared to in year 1.

Table 4.6. Linear regression coefficients from plotting slope values for for combined Douglas-fir and western hemlock height response to N and P (Table 4.3) for the first, second, and two year periods.

Factor	Regression Coefficients		
	Intercept	Slope	r
P	53.5	61.2	1
N	39.1	38.8	1

Diameter Growth

In general, diameter growth was a more sensitive parameter than height growth. The reason for this is that diameter growth is not affected to the same degree as height growth by damage, death or browsing of the main leader or apical bud. Appendix 3B outlines the results of the MANOVA analyses for diameter response for each period.

For first year diameter response, both species and treatment main effects were highly significant ($p<0.01$) and examination of Appendix 4B reveals that Douglas-fir diameter response for all treatments and site preparations was about 28% greater than for western hemlock. Treatment main effects were examined to determine the contribution of N and P, and results are presented in Table 4.7. Both N and P effects were highly significant ($p<0.01$) and the response curves for both elements were linear with almost equal slope, indicating that N and P contributed equally to first year diameter response. The NP interaction was non-significant.

Second year diameter response analyses revealed significant interactions (Appendix 3B). Burning reduced Douglas-fir diameter response much more than for western hemlock. Because of the interaction between species and site preparation, the simple effects were examined and the results are shown in Table 4.8.

Table 4.7. Breakdown of treatment main effects into N, P, and NP effects for the combined diameter response of Douglas-fir and western hemlock.

Response Period	Factor	Response Curve			Slope	Intercept	r
		Factor	Linear F	Quadratic F			
First Year Diameter	P	12.25^{**}	24.46^{**}	NS	1.6	11.17	.999
	N	11.77^{**}	21.50^{**}	NS	1.5	11.27	.956
	NP	NS					
Second Year Diameter	P	10.66^{**}	16.91^{**}	4.41^{*}	2.6	35.97	.891
	N	NS	2.50^{+}	NS	1.0	37.57	.908
	NP	NS					
Two Year Diameter	P	19.10^{**}	34.74^{**}	3.24^{*}	4.2	47.01	.950
	N	7.10^{**}	12.31^{**}	NS	2.5	48.77	.930
	NP	NS					

Regression equation $y = a + bx$

** significant at $a = 0.01$, * significant at $a = 0.05$, $^{+}$ significant at $a = 0.10$
NS - not significant at $a = 0.10$

Table 4.8. Analysis of the simple effects for species and site preparation for second year diameter response.

Treatment Comparisons	DF	MS	$F_{(1,6,0.05)}$
Species on unburnt sites	1	1.253	38**
Species on burnt sites	1	.151	4.50
Site preparation and Douglas-fir	1	1.253	38**
Site preparation and western hemlock	1	.151	4.50

** Significant at a = 0.01

Analysis of second year diameter response separately for each species revealed that site preparation was significant for Douglas-fir (p=0.0) but not for western hemlock (p=0.331). Examination of the response data in Appendix 4B clearly reveals that diameter response by Douglas-fir on unburnt sites contributed most to the species by site preparation interaction.

Because of the significant species by treatment interaction, examination of treatment main effects only would be misleading, so the interaction term was partitioned into sums of squares components for N,P and NP for each species, and presented along with treatment main effects in Table 4.9. For Douglas-fir, P is the significant component for treatment effects, and the response curve has a significant quadratic component, indicating that diameter response was not constant for each unit increase in P. However, for western hemlock both N and P contributed significantly to diameter response when measured over all site preparations, and the response curve for each element had a significant quadratic component; N and P appeared to contribute equally

Table 4.9. Breakdown of the species by treatment interaction for Douglas-fir and western hemlock second year diameter response into species, N, P, and NP effects. Treatment main effects are included for comparison.

Species by Treatment Interaction	Factor	Value and Significance of F			Regression Coefficients		
		Factor	Linear	Quadratic	Slope	Intercept	r
	P	21.48**	31.08**	11.65**	1.7	19.7	0.853
Douglas-fir	N	NS	NS	NS	0.2	21.23	0.503
	NP	NS					
	P	5.63*	9.74**	4.56*	0.95	16.22	0.934
Western hemlock	N	6.71*	7.80*	5.62*	0.85	16.30	0.762
	NP	NS					
	P	10.66**	16.91**	4.41*	2.60	35.97	0.891
Treatment Main Effects	N	NS	2.50^{+}	NS	1.00	37.57	0.908
	NP	NS					

Regression equation $y = a + bx$

** significant at a = 0.01, * significant at a = 0.05, $^{+}$ significant at a = 0.10

NS - not significant

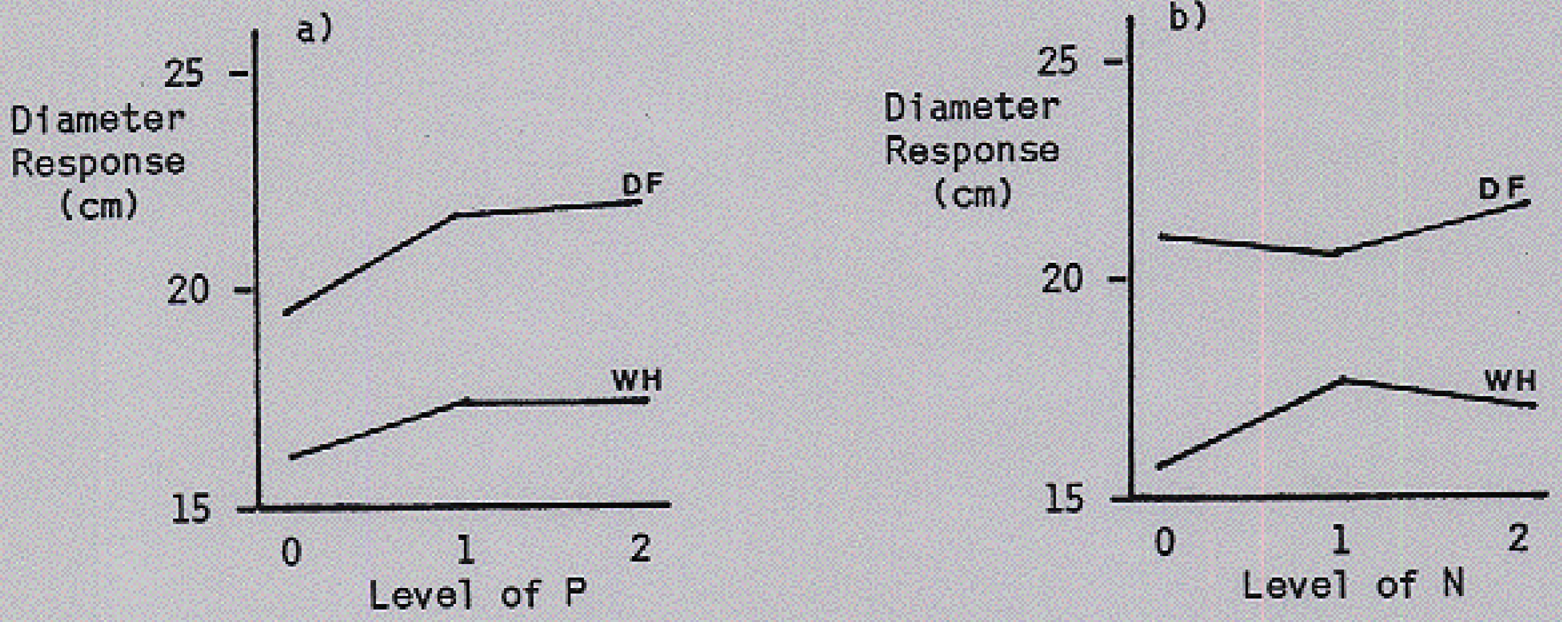


Fig. 4.2. Species by treatment interaction for Douglas-fir (DF) and western hemlock (WH) for second year diameter response to (a) phosphorus and (b) nitrogen. Y axis represents the sum of mean values (cm) for each experimental unit for the relevant treatments.

to diameter response when the slopes from the linear regressions are compared. The species by treatment interaction are shown in Fig. 4.2.

The significant three-way interaction (Appendix 3B) implies that the treatment by species interaction varies according to site preparation. This appears valid given the significant species by site preparation interaction. Separate ANOVAs for Douglas-fir and western hemlock showed no significant treatment by site preparation interaction for either species, although for western hemlock, results from the ANOVA suggested that site preparation may have been influencing treatment response ($p=0.14$). A breakdown of the three-way interaction into species, site preparation, and N and P effects, revealed the following:

1. For Douglas-fir the P effect was significant ($p<0.05$) on burnt and unburnt sites; the response to P was greatest on unburnt sites and was always greater than for western hemlock.

2. For western hemlock, the species by treatment interaction revealed a significant effect of both N and P ($p<0.05$) but when the effect of site preparation was included, only the effect of N was significant ($p<0.05$) and only on unburnt sites.

Analysis of the two year diameter response data revealed that species, species by site preparation, and treatment effects were significant at a = 0.10 (Appendix 3B). The effect of the species by site preparation interaction is shown in Table 4.10 below. Because of the significant interaction, the simple effects of species and site preparation were examined and the results are presented in Table 4.11. The four comparisons are not orthogonal and are "results guided". However, they demonstrate the heterogeneous nature of the species by site preparation interaction for two year diameter response.

As there were no significant interactions involving treatment in the overall MANOVA (Appendix 3B) for two year diameter response, the treatment main effects were analyzed and sums of squares partitioned into N, P, and NP components. The results are shown in Table 4.7. Both N and P effects were significant and linear. Comparison of the slopes from the N and P linear regressions shows that the response per unit of P was much greater than for N (4.2 vs. 2.5 respectively, or 68%), supporting the results from height growth analyses where P was found to be the main contributor.

Although the main emphasis of the coastal study was to determine whether N, P, or N+P would influence growth response and hence provide an insight into the effect of Al and Al-interactions, there was also interest in determining whether the response for any one treatment differed significantly from another. On this basis mean growth response

Table 4.10. The effect of site preparation on two year diameter response of Douglas-fir and western hemlock. Values represent the sum of the means (cm) from each experimental unit for all treatments.

Site Preparation	Species		Total
	Douglas-fir	Western hemlock	
Unburnt	48.3	36.1	84.4
Burnt	37.3	32.2	69.5
Total	85.6	68.2	153.9

Table 4.11. Comparison of simple effects for the species by site preparation interaction for two year diameter response.

Treatment Comparisons	DF	MS	$F_{(1,6,0.05)}$
Species on unburnt sites	1	2.067	73**
Species on burnt sites	1	.361	12.7*
Site preparation and Douglas-fir	1	1.681	59**
Site preparation and western hemlock	1	.211	7.45*

** significant at a = 0.01, * significant at a = 0.05

for each treatment was ranked using Duncan's Multiple Range test (a=0.10) and the results presented in Appendix 5A and B.

For Douglas-fir, except for first year height response on unburnt sites and second and two year diameter response on burnt sites, there was a significant difference between treatment means for height and diameter response. This difference followed the pattern shown earlier, that is, treatments involving P had greater mean response than those without. For both burnt and unburnt sites, the "best" treatment for Douglas-fir was N2P2. Also, the N1 treatment was often ranked equal to the control and again this supports the earlier findings that P, and not N, was the major element limiting growth.

For western hemlock there is a noticeable reversal of trends in the ranking of treatment means for growth response on burnt and unburnt sites (Appendix 5). On unburnt sites there was no significant difference between treatment means for first year height and diameter response. However, on burnt sites the <u>only</u> significant difference between treatment means was for first year growth response for both height and diameter, with the best treatment being the N2P2 treatment. In other words, when western hemlock treatment means were ranked for burnt and unburnt sites, the duration or effectiveness of treatment on burnt sites was no longer evident after the first year, while on unburnt sites growth response to treatment was still evident at the end of two years. However, unlike Douglas-fir, the "best" treatment for western hemlock on unburnt sites was N2P1 for both height and diameter response; the N2 treatment was the "worst" and ranked lower than the control, supporting the overall effect of N on western hemlock height response shown in Fig. 4.1.

4.1.3 Foliar Analyses

Analysis of variance was run for all elements analyzed for Fall 1985 and results are presented in Table 4.12. From the growth analyses it became apparent that the two species were behaving differently, so all statistical comparisons for foliar analyses were made within species rather than between species. Appendix 6A and B contain the foliar data for Douglas-fir and western hemlock respectively for Fall 1985.

From Table 4.12 a number of important differences between the two species stand out. For Douglas-fir, treatment main effects were significant at $a=0.10$ for N (also a significant treatment by site preparation interaction), P, K and Zn, while site preparation main effects were significant for N, Fe, Zn and Cu. For western hemlock treatment main effects were only significant for K and Mg; application of N or P fertilizer had no significant effect on foliar N and P levels in western hemlock. However, for this species site preparation main effects were highly significant for N and Zn ($p<0.01$), and were significant ($p<0.10$) for K, Ca, and Cu. There were significant treatment by site preparation interactions for Al, Ca, and Fe for western hemlock, even though neither Al nor Fe were significant at the main effect level, indicating that for these elements treatment effects varied with site preparation.

Slash burning depressed foliar N levels from 2.23% to 1.88% for Douglas-fir and from 1.80% to 1.10% for western hemlock when averaged over all treatments. The effect of slash burning was most apparent for western hemlock; foliar N levels as low as 0.6% were recorded on some sites regardless of fertilizer treatment. Slash burning also significantly depressed K and Ca in western hemlock and Fe, Zn, and Cu in both species. Again, the effect of burning was most obvious for foliar Ca and Zn levels in western hemlock which fell from 2088 to 1680 ug g^{-1} and 17.4 to 11.8 ug g^{-1} respectively; Zn levels < 10 ug g^{-1} were not unusual for western hemlock on burnt sites.

Since one of the main objectives of the study was to determine if Al could be responsible for limiting seedling response to fertilizer applications on these soils, ANOVAs were run to determine whether treatment, site preparation, or their interaction significantly influenced foliar Al levels. For Douglas-fir in the Spring of 1985, site preparation significantly ($p<0.01$) increased tissue Al on burnt sites compared to unburnt sites (451 and 317 ug g^{-1} respectively). Similar trends occurred in Spring 1986 where there was a significant ($p=0.08$) treatment by site preparation interaction. While a trend to increasing levels of Al on burnt sites was evident for the Fall 1985 (Appendix 6A and B), this was not significant at $a=0.10$.

The effects of various treatments on tissue Al levels in Douglas-fir were also apparent in western hemlock, but there was a significant species difference in the level of tissue Al; western hemlock had higher foliar Al levels than Douglas-fir, regardless of treatment or site preparation. Whereas there was no significant species difference ($p=0.23$) in tissue Al levels for Spring 1985, for Fall 1985 and Spring 1986 this species difference was significant ($p<0.05$).

Table 4.12. Results from the MANOVA for treatment and site preparation on elemental composition of Fall 1985 foliage for Douglas-fir and western hemlock.

Source of Variation		Significance of F									
		N	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu
Douglas-fir	Site Preparation	.019	NS	NS	.086	NS	NS	NS	.087	.099	.004
	Treatment	.004	NS	.001	.067	NS	NS	NS	NS	.010	NS
	Treatment By Site Preparation	.060	NS	NS	NS	NS	NS	NS	NS	NS	NS
Western hemlock	Site Preparation	.001	NS	NS	.084	.050	NS	NS	NS	.001	.042
	Treatment	NS	NS	NS	.004	NS	.003	NS	NS	NS	NS
	Treatment By Site Preparation	NS	.025	NS	NS	.094	NS	NS	.043	NS	NS

NS - not significant at a=0.10

For western hemlock, neither treatment nor site preparation significantly altered tissue Al levels in Spring 1985, and there was no significant interaction between treatment and site preparation. However, by Fall 1985 a significant (p=0.02) treatment by site preparation interaction occurred (Table 4.13) whereby N appeared to decrease tissue Al levels on burnt sites (Figure 4.3), while on unburnt sites there were no significant effects.

By Spring 1986 there was both a significant site preparation (p=0.00) and treatment effect (p=0.01) on the tissue Al levels of western hemlock. Burning greatly increased Al compared with unburnt sites (960 ug g^{-1} and 655 ug g^{-1} respectively). The overall treatment effects are shown in Fig. 4.3. Increasing P levels caused an increase in tissue Al levels of western hemlock, and the more P applied the more N was required to cause a decrease in tissue Al. Even in the absence of P applications, the general influence of N was one of reducing tissue Al levels, similar to Fall of 1985.

Table 4.13. Breakdown of Douglas-fir and western hemlock treatment effects and treatment by site preparation interaction for elements from Fall 1985 sampling where a significant effect (a=0.10) was found (Table 4.12).

Element in Tissue	Significance of F								
	Treatment Main Effects			Treatment by Site Preparation Interaction					
				Unburnt			Burnt		
	P	N	NP	P	N	NP	P	N	NP
Douglas-fir									
N	--	--	--	**	NS	NS	NS	NS	NS
P	***	***	NS	--	--	--	--	--	--
K	NS	NS	**	--	--	--	--	--	--
Zn	***	*	NS	--	--	--	--	--	--
Western hemlock									
Al	--	--	--	NS	NS	NS	NS	***	NS
K	**	***	NS	--	--	--	--	--	--
Ca	--	--	--	NS	*	*	NS	NS	NS
Mg	***	NS	NS	--	--	--	--	--	--
Fe	--	--	--	NS	NS	NS	NS	**	NS

***significant at a=0.01, **significant at a=0.05, *significant at a=0.10, NS non significant at a>0.10.

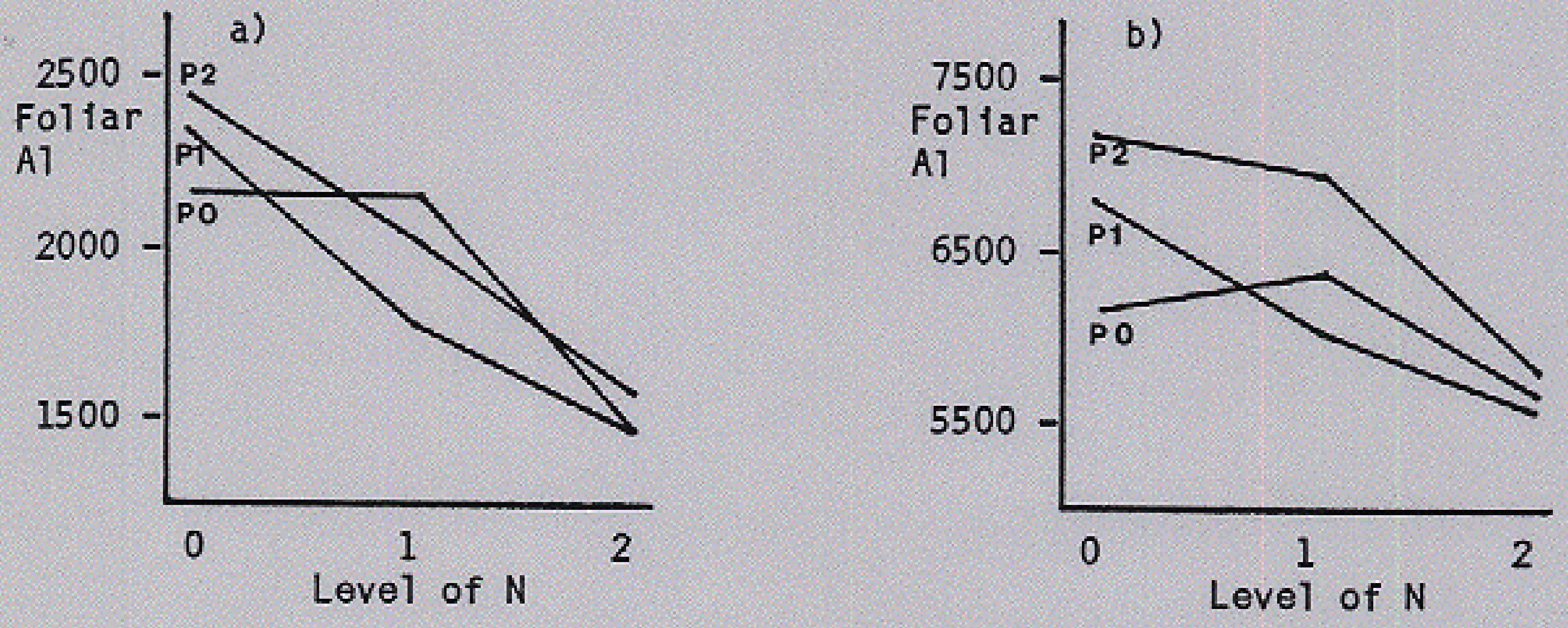


Fig. 4.3. Effect of N and P on mean tissue Al levels (ug g^{-1} dry weight) in western hemlock a) burnt sites Fall 1985, b) all sites Spring 1986.

The breakdown of treatment and treatment by site preparation interaction for elements where significance was found (Table 4.12) is presented in Table 4.13. For Douglas-fir, tissue N levels were reduced by P application on unburnt sites (Fig. 4.4a), probably as a consequence of a growth dilution effect, while on burnt sites treatment had no effect on tissue N levels. Although tissue P levels were significantly affected by N and P treatment, there was no significant NP interaction. The unusual effect of P was to raise tissue P levels (even though there was a significant increase in growth), but at higher levels of applied N, P levels declined as is shown graphically in Fig. 4.4b. For tissue K levels in Douglas-fir a significant NP interaction was evident. This interaction was strongly related to the P1 treatment, although such an interaction is difficult to explain. The general effect of N and P was to depress tissue Zn levels in Douglas-fir (Fig. 4.4c); although the N2P0 treatment resulted in a rise in foliar Zn levels compared to N1P0, they were still less than the control. There was no significant NP interaction on foliar Zn levels in Douglas-fir.

For western hemlock both N and P caused a significant ($p<0.05$) decrease in tissue K levels. Unlike K, tissue Mg levels were increased by treatment, and this was due to the effect of P. Nitrogen ($p<0.10$) and in particular the NP interaction ($p<0.05$), raised tissue Ca levels significantly in western hemlock though there was no significant treatment effect in Douglas-fir. However, the N and NP effect was apparent only on unburnt sites which had the highest foliar Ca levels, although when mean Ca levels were compared for unburnt and burnt sites there was no significant difference at $a=0.05$. The effect of slash burning plus N applications resulted in significantly lower ($p=0.04$) tissue Fe levels in western hemlock. This effect was very pronounced at the N2 application level, regardless of the level of P, as shown in Fig. 4.4d.

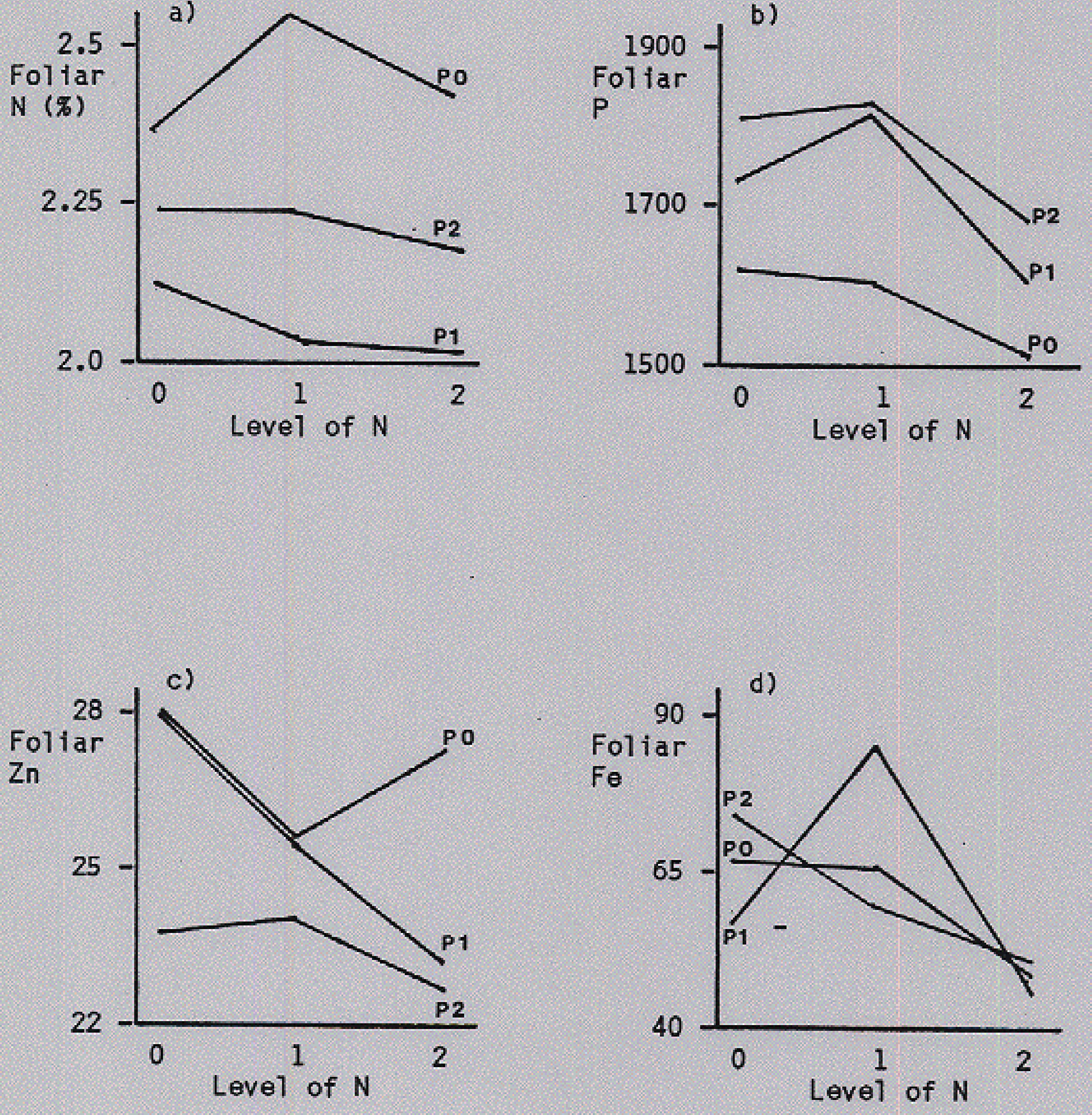


Fig. 4.4. The effect of N and P applications on the mean foliar concentrations (ug g^{-1} dry weight) for: a) N in Douglas-fir (DF) on burnt sites; b) P in Douglas-fir on all sites; c) Zn in Douglas-fir on all sites; and d) Fe in western hemlock (WH) on burnt sites.

Table 4.14. Foliar concentrations of elements for Douglas-fir as influenced by site preparation. Spring 1985 involved samples from the 1984 increment, while Fall 1985 and Spring 1986 both involved samples from the 1985 increment.

Period Site Preparation		ug g^{-1} dry wt. basis								
	N%	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu
Spring 1985										
Unburnt	2.21b	317a	1959b	5531a	2373b	1062c	787b	72.2a	35.0c	4.53b
Burnt	1.88a	451c	2253c	5801ab	2523bc	1005bc	979cd	102.8b	34.9c	5.07c
Fall 1985										
Unburnt	2.23b	337a	1669a	7343d	1883a	857a	518a	117.7b	28.2b	5.16c
Burnt	1.88a	324a	1700a	6676c	1690a	833a	496a	76.4a	22.7a	3.90a
Spring 1986										
Unburnt	2.39c	384b	1886b	5540a	3305d	995b	1145d	63.7a	43.0d	5.23c
Burnt	1.95a	417bc	1915b	5992b	2599c	947b	919bc	55.3a	32.1c	4.56b

Vertical columns with the same letter indicate no significant difference at a=0.05 using Duncan's Multiple Range Test.

&Table 4.15. Foliar concentrations of elements for western hemlock as influenced by site preparation. Spring 1985 involved samples from the 1984 increment, while Fall 1985 and Spring 1986 both involved samples from the 1985 increment.

Period Site Preparation		ug g^{-1} dry wt. basis								
	N%	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu
Spring 1985										
Unburnt	1.54b	387a	1697a	4831a	2543c	1353c	829bc	55.3bc	16.2bc	3.17ab
Burnt	1.47b	452ab	1702a	5185b	2566c	1234b	839bc	35.2a	18.6c	3.48b
Fall 1985										
Unburnt	1.80c	389a	2027c	8476c	2088b	1108a	764ab	65.1c	17.4c	4.16c
Burnt	1.10a	491b	1692a	7701c	1680a	1046a	600a	54.0bc	11.8b	3.02ab
Spring 1986										
Unburnt	1.96d	655c	1883bc	4711a	2984d	1243b	1409d	62.0c	23.0d	3.36ab
Burnt	1.46b	960d	1843ab	5490b	2409c	1221b	998c	46.3ab	14.6b	2.89a

Vertical columns with the same letter indicate no significant difference at a=0.05 using Duncan's Multiple Range Test.

&Table 4.15. Foliar concentrations of elements for western hemlock as influenced by site preparation. Spring 1985 involved samples from the 1984 increment, while Fall 1985 and Spring 1986 both involved samples from the 1985 increment.

Period Site Preparation		ug g^{-1} dry wt. basis								
	N%	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu
Spring 1985										
Unburnt	1.54b	387a	1697a	4831a	2543c	1353c	829bc	55.3bc	16.2bc	3.17ab
Burnt	1.47b	452ab	1702a	5185b	2566c	1234b	839bc	35.2a	18.6c	3.48b
Fall 1985										
Unburnt	1.80c	389a	2027c	8476c	2088b	1108a	764ab	65.1c	17.4c	4.16c
Burnt	1.10a	491b	1692a	7701c	1680a	1046a	600a	54.0bc	11.8b	3.02ab
Spring 1986										
Unburnt	1.96d	655c	1883bc	4711a	2984d	1243b	1409d	62.0c	23.0d	3.36ab
Burnt	1.46b	960d	1843ab	5490b	2409c	1221b	998c	46.3ab	14.6b	2.89a

Vertical columns with the same letter indicate no significant difference at a=0.05 using Duncan's Multiple Range Test.

4.1.4. Discussion - Coastal Study

Douglas Fir

From the growth results and foliar analyses it is clear that response by Douglas-fir and western hemlock to fertilizer application varied both in magnitude and in the elements causing response. Also, for both species response was greatly influenced by slash burning.

However, for Douglas-fir the null hypothesis that P is the element most limiting to growth on coastal hemlock soils is accepted unequivocally; P always gave a consistent positive growth response. When the slopes of the linear regressions were compared for N and P, the response was always greatest for P, both in height and diameter growth. This response pattern by Douglas-fir to P is consistent with results of previous pot studies using coastal soils (Heilman and Eukan 1980, Black 1986), and with results reported by Zasoski and Gessel (1982).

Height response data from Table 4.3 and 4.5 clearly demonstrate the highly significant effect of P on Douglas-fir. An important feature of the data is that the P response curves were linear. Even with the higher P application (P2=110 g triple superphosphate), height response increased linearly, indicating that the amount applied was well short of that required for maximum response. However, given the high P sorption capacity of the soils from all four sites, a considerable amount of the applied P may also have been adsorbed onto soil adsorption sites even though fertilizer had been spot applied to reduce the magnitude of such an effect. Although the greatest response to fertilizer application was for the higher N+P treatment (N2P2), no significant NP interaction was found for height or diameter response.

Although comparison of Douglas-fir foliar P concentrations does not reveal a consistent response to treatment (Appendix 6A), this is due in part to a growth dilution effect from P application, as well as to an antagonistic effect from application of high N levels. However, when the overall effects of N and P are determined separately, the effect of P was to raise foliar P levels (Fig. 4.4b). Also evident in Fig. 4.4b is the antagonistic effect of N2, which cannot be attributed to a simple dilution effect, since growth response in the absence of P additions was minimal, yet an antagonistic effect was still apparent. What is more likely is that high levels of applied N had either a depressive effect on the ability of Douglas-fir roots to absorb P (e.g., physiological impairment), or else resulted in an immobilization of P due to stimulation of microbial activity. Such a depression of P by N application has been reported by Gill and Lavender (1983) for western hemlock stands growing in these coastal soils, while Kumar et al. (1986) reported that application of N had an antagonistic effect on the concentration of P in the leaves, stems, and roots of pearl millet. In this study, maximum recorded foliar P concentrations were about 1800 ug g^{-1}, well below the level of 2500 ug g^{-1} considered adequate for Douglas-fir seedlings by Van Den Driessche (1979) and Flinn and Hopmans (1976). Such an antagonistic effect could help explain the reported inconsistent response to N application by Douglas-fir growing on coastal soils (RFNRP Staff 1982, Webster et al. 1976).

While slash burning reduced growth response to fertilizer treatments by Douglas-fir, this is not synonymous to a reduction in growth. Instead, it appears that burning resulted in a release of P from organic matter, and an increase in the level of available P. This was suggested in Section 4.1.1 when soil chemical properties between unburnt and burnt sites were compared, and is further supported by the data in Table 4.14 which shows that for each of the three sampling periods mean foliar P concentrations were higher on burnt sites. This increase in available P most likely stimulated growth on burnt sites; mean two year seedling heights (over all fertilizer treatments) were similar for both unburnt and burnt sites (91.8 and 95.0 cm respectively), but the mean heights of the control seedlings varied. Mean seedling heights for the control treatments on unburnt and burnt sites were 78.5 and 89.3 cm respectively, and it was this difference in height of the control treatments on burnt sites that was responsible for the lower height response (relative to the control treatments) to slash burning by Douglas-fir.

Foliar data for Douglas-fir shows that N levels are in the range considered adequate for Douglas-fir seedlings (Van Den Driessche 1976, 1979, Flinn and Hopmans 1976). In fact on unburnt sites mean foliar N concentrations after two years growth was virtually identical with that at time of planting (i.e., 2.2%) and the minimum concentration was 2.0%. Although mean foliar N levels for Fall 1985 were about 0.4% lower on burnt sites (1.8%) compared to unburnt sites (2.2%), this difference is unlikely to limit growth response. While the addition of P resulted in a decrease in foliar N this was most likely due to a growth dilution effect attributed to P applications. In no treatment was the concentration of N reduced to a level considered response limiting and, further, additions of N had no significant effect on foliar N levels. Although there was a reduction in the levels of total soil N on burnt sites, nevertheless these levels were still reasonably high (3.4 and 2.8 g kg^{-1}).

The lack of a significant growth response by Douglas-fir to N additions, the high foliar N concentrations, and the lack of a significant increase in foliar N due to N additions supports Corollary A, that is, lack of N is not presently limiting growth response, at least for Douglas-fir under current conditions. This is further supported by the N data from the soil chemical analyses (Table 4.1). The C:N ratios for all sites were well within the range where a net release of N from decomposition processes could be expected.

However, the situation is not quite so clear for a number of other nutrients. Evaluation of the Douglas-fir foliar and growth data by the Diagnosis and Recommendation Integrated System (DRIS) (Beaufils 1973) revealed that in addition to P, Ca, Mg and Zn may also be response limiting, particularly on unburnt sites (Zasoski and Porada 1986). This comes as no surprise as the soil chemical analyses indicated very low levels of exchangeable bases, and also low levels of total soil Zn. Both Ca and Mg foliar concentrations were well below those considered adequate by Lavender and Walker (1979) and Van Den Driessche (1976, 1979,1981), which supports the DRIS results.

Although micronutrient requirements by conifers in the Pacific Northwest are not known with any certainty, Boehle and Lindsay (1969) reported for a range of plant species that foliar Zn concentrations in excess of 20 ug g^{-1} were probably adequate. Lower concentrations are probably approaching critical levels. This is supported by the more recent review of Marschner (1986). While Douglas-fir foliar Zn levels were approaching the critical level on burnt sites, foliar Zn levels on unburnt sites were mostly in excess of 25 ug g^{-1}. The question of Zn levels in Douglas-fir requires a further comment. Treatment effects were highly significant ($p<0.01$), and this was due to P depressing foliar Zn levels (Fig. 4.4c). Such an effect by P on Zn has been widely reported (Ruiter 1972, Lindsay 1972, Olsen 1972, Woods 1983, Robson and Pitman 1983, Marschner 1986) and is attributed to the effect of P on Zn uptake and translocation. Whether the effect of P on Douglas-fir foliar Zn levels affected growth response is uncertain, but is considered unlikely. What is important is that large applications of P to sites where foliar Zn levels are bordering on critical (e.g., on some burnt sites) may result in a depression of Zn to levels that could limit growth response.

Neither treatment nor site preparation had a significant effect on Fall 1985 Douglas-fir foliar Al concentrations. However, when Spring 1985 and 1986 foliar data are examined along with Fall 1985 data (Table 4.14), it appears that slash burning caused an increase in foliar Al levels. This trend was both surprising and unexpected. Firstly, if slash burning increased available P levels, this should have reduced available Al. Secondly, surface soil pH (0-15 cm depth) on burnt sites was in the range 4.8 to 5.1, whereas for unburnt sites pH ranged from 4.3 to 4.5. Assuming Al^{3+} is in equilibrium with gibbsite, only a change in pH will affect the activity of soil Al^{3+}. From Lindsay (1979),

$$\log Al^{3+} = 8.04 - 3pH$$

and therefore an increase in soil pH by about 0.5 should reduce Al^{3+} activity by about 30 (all other factors remaining unchanged). Previous studies have suggested that aluminum-hydrogen ion exchange on organic matter controls Al^{3+} activity in acidic surface soils (Bloom et al.

1979), and more recently it was proposed that the variability of aqueous Al in soils and surface waters involved a solid humic phase absorbent and an $Al(OH)_3$ mineral phase. Hence the assumption that pH (and gibbsite) is controlling Al^{3+} activity may not always be valid. While simple Al-pH relationships indicate the theoretical effects, Al solubility, Al toxicity to plants , and percent exchangeable Al in soils cannot always be predicted from pH alone (Lindsay, 1979).

The reason for the increase in Douglas-fir foliar Al levels on burnt sites is unknown. However, the following scenario is suggested. The effect of slash burning resulted in a release of cations from the litter layer. Because the sum of the concentrations of Ca, Mg, K and Mn in the litter layer would have exceeded greatly that of Al, they would have outcompeted the released Al for reaction sites, as well as removing soil Al from exchange sites due to cation displacement (Bache 1980, Thomas and Hargrove 1984). By removing the litter layer, burning would also have reduced the level of organic compounds in the surface soil, thereby increasing the level of inorganic (or available) Al. Instead of reducing plant available Al levels, burning may in fact have raised such levels (total soil Al levels were higher on burnt sites - Table 4.1). This is further substantiated by foliar chemical analyses. When one-year old Douglas-fir foliage (Fall 1985) was analyzed, mean foliar Al levels on burnt sites had increased to 710 ug g^{-1} from those recorded in Spring 1985 (450 ug g^{-1}), whereas for unburnt sites one-year old foliar Al levels increased from 310 to 510 ug g^{-1}. These higher Al levels in one-year old foliage on burnt sites lends support to the suggestion that burning increased available Al levels.

From the data there is no obvious evidence indicating that Al may have directly influenced Douglas-fir growth. In fact foliar Al levels prior to planting (1590 ug g^{-1}) greatly exceeded any levels recorded subsequently (the reason for the initially high Al levels is unknown, but is most probably due to highly acidic nursery beds as a result of large applications of ammonium-N and P fertilizer). However, because of the significant response to P application, it is highly likely that Al may have an indirect effect by governing soil P availability, especially in light of the soil chemical analyses. Such an Al-P-plant interaction was reported by James et al. (1978) for Sitka spruce growing in acid soils in Scotland, and by Shoji et al. (1980) for a number of species growing in acid soils (Andosols) in Japan. Because Al can form a number of insoluble phosphates, it may control phosphate solubility, particularly where Al is a major constituent in the soil solution, and thereby influence plant growth.

Western hemlock

Unlike Douglas-fir, response of western hemlock to fertilizer treatment and site preparation varied greatly. This is most apparent when its height and diameter response data as a percent of control treatments are compared (Appendix 5A and B). When growth response and foliar data are examined it is clear that no definitive statement can be made with regard to hypothesis 1 or corollary A.

The best indication of what may be occurring in western hemlock lies in the second year growth data and Fall 1985 foliar analyses. Second year growth response data completely masks that of the first year because greater absolute growth occurred once the seedlings became established.

Consequently, little emphasis has been placed on first year growth response.

A significant species difference always was observed, indicating a major difference between Douglas-fir and western hemlock growing under similar conditions. Hence ecological or silvicultural management of the two species should not be based on "generalized" prescriptions; rather, more specific management regimes are required.

Western hemlock growth response to treatment was particularly erratic on burnt sites, even though the P status of these sites appeared slightly better due to the effect of burning (Table 4.1). Although first year growth data indicates better height growth on burnt sites (Table 4.2), this trend was dramatically reversed in the second year (Table 4.4). First year height and diameter response to N and P application by western hemlock and Douglas-fir combined were significant. However, when second year growth data are examined only the N effect was significant for hemlock height growth response (Table 4.5), although for diameter both N and P were found to be about equally significant (Table 4.9). The importance of N in western hemlock response can be seen by examining data in Appendix 5B; greatest response was always associated with high N levels <u>in association with P</u>, though there was no significant NP interaction. This contrasts with Douglas-fir where growth response was associated with P. The overall erratic response by western hemlock to fertilizer treatment was consistent with reports from earlier fertilizer studies (Heilman and Eukan 1973, 1980a, DeBell et al. 1975, Radwan and DeBell 1980).

When examining foliar data for western hemlock (Appendix 6B), low concentrations of a number of elements, particularly N, Zn, and perhaps Fe, make it clear that the inconsistent response is most likely related to nutrient imbalances, especially on burnt sites. For instance, Van Den Driessche (1979), pooling data from a number of sources, reported that adequate nutrient levels for seedlings were: N=2.2 to 1.8%, P=0.33 to 0.25%, K=1.4 to 1.1%, Ca=0.2%, and Mg=0.14%. When these levels are compared with data from this study (Appendix 6B) it is immediately apparent that foliar N levels on burnt sites are extremely low, even below the critical level. In fact, on certain burnt sites, western hemlock foliar N levels as low as 0.6% were recorded. Yet, fertilizer treatment had no effect on foliar N and P levels, and even the highest applications of these elements failed to raise foliar levels. Thus it is unlikely that an absolute soil deficiency is responsible for low foliar N levels in western hemlock. This is especially so given that the minimum average foliar N levels for Douglas-fir growing on the <u>same sites</u> are 1.8%. While soil data collected prior to planting (Table 4.1) indicates that N levels were slightly higher on unburnt sites (4.2 to 3.7 g kg^{-1}) compared to burnt sites (3.4 to 2.5 g kg^{-1}), it is unlikely that this difference is the major reason for western hemlock's low foliar N levels on burnt sites.

If N alone were limiting western hemlock growth response then high applications of N should have stimulated growth, or at least increased foliar N levels. This was not the case, and in fact high N applications resulted in reduced growth compared with milder N applications. This is clearly demonstrated in Fig. 4.1, and the highly significant quadratic response to N (Table 4.5) reflects the negative effect of the N2 level (relative to N1) in Fig. 4.1. Radwan et al. (1984) had previously concluded for western hemlock that no one form of N was superior, so it is unlikely that the form of N used in this study (ammonium nitrate) was responsible for western hemlock's erratic growth response and foliar N levels.

As mentioned previously, critical values for micronutrients in Douglas-fir and western hemlock are not known with any certainty. However, from the foliar data it is clear that Zn levels in western hemlock are low, and for burnt sites, probably below critical levels. Boehle and Lindsay (1969) and Marschner (1986) indicate that foliar Zn concentrations below 20 ug g^{-1} are approaching critical levels. Indeed, Zn levels in hemlock were significantly lower than those of Douglas-fir, and the question that must be considered is whether western hemlock Zn levels on burnt sites are sufficient to allow a growth response to P or N.

Zinc deficiencies can result in complex changes in plant metabolism. In particular, protein synthesis and protein content of plants is highly dependent on adequate Zn levels (Marschner 1986, Kitagishi and Obata 1986). Van Den Driessche (1984) reported that proteins are probably the most important N reserves in trees and may contain about 60% of all N in young trees. Hence, if protein synthesis is inhibited due to Zn deficiency, then foliar N levels will be greatly reduced. It is hypothesized that the low foliar N of western hemlock on burnt sites is due to insufficient Zn. When hemlock foliar data were analyzed using the

DRIS technique both N and Zn indices were negative for burnt sites (Zasoski and Porada 1986), which provides supporting evidence for a N-Zn relationship.

Fertilizer treatment had no significant effect on hemlock foliar Zn levels (Table 4.13 and Appendix 6B). The lack of a P effect on Zn may have been due to the already low foliar Zn levels, especially on burnt sites, and the fact that P application had no effect on P levels in western hemlock foliage. The lack of a plant-P-Zn interaction in western hemlock is important in that it may help to explain the lack of response to P by western hemlock growing in coastal soils. According to Van Den Driessche (1979) adequate foliar P levels for western hemlock are around 0.3%. Based on the data in Appendix 6B, a foliar response to P application should have occurred since seedlings had low initial foliar P levels (<0.18%).

Foliar data from Appendix 6A indicates that Fe levels in western hemlock are also low. When data from individual experimental units were examined, both burnt and unburnt sites had Fe levels (total Fe as opposed to active Fe) commonly less than 40 ug g^{-1}, and occasionally falling to around 20 ug g^{-1}. In the absence of more specific data for western hemlock such levels must be considered to be well below the critical level. According to Stone (1968) minimum Fe values in current foliage from mature western hemlock trees is in the range 40 to 60 ug g^{-1} and for seedlings expected levels are probably higher. Western hemlock foliar Fe levels were always significantly lower than those of Douglas-fir, and were also reduced by slash burning (Table 4.15).

Is it possible that other nutrients were inhibiting uptake of Zn and Fe by western hemlock? Olsen (1972) reported that high Mn levels could inhibit Zn and Fe uptake. Foliar data shows higher Mn levels in hemlock than Douglas-fir. However, the highest Mn levels occurred on unburnt sites, which also tended to have higher Fe and Zn levels. The physiological significance of Fe-Mn in plants has been outlined by Foy and Fleming (1978) and Marschner (1986) and such an interaction may be important for western hemlock. However, it is unlikely that high Mn levels *per se* had any effect on foliar Zn levels.

Nitrogen, as NH_4^+, can inhibit cation uptake (Marschner 1986), and has been found to reduce foliar Zn levels (Olsen 1972, Woods 1983). However, there is no conclusive evidence of an Fe-N interaction. In this study, seedlings were planted at least 6 months after slash burning and the overall effect of slash burning was to reduce foliar N levels. It is unlikely that high native N levels had an effect on foliar Zn or Fe levels in western hemlock. But, N application to western hemlock did significantly reduced foliar Fe levels, as shown in Fig. 4.4d. However, given the great variability of the foliar Fe data, the nutritional significance of this effect on western hemlock growth response is indeterminate. Nonetheless, this effect must not be overlooked in attempts to evaluate western hemlock nutrition. Iron, like Zn, is important in protein synthesis (Marschner 1986) and as indicated previously, factors that inhibit protein synthesis can have a major effect on foliar N levels. Hence, for western hemlock it is possible that a "finely tuned" interaction may exist between, for example, P-Zn-Fe-N levels.

Relative to other trace metals, Zn is readily soluble and mobile within the soil, and organic acids are particularly important in Zn mobilization and leaching (Kabata-Pendias and Pendias 1984). Lindsay (1972) listed some of the more important factors that contribute to Zn deficiency in plants, including:

1. Low soil Zn content
2. Soil pHs >7
3. Soils low in organic matter
4. Microbial inactivation of Zn in soil
5. Limited Zn uptake by roots due to a restricted root zone, or cool spring periods
6. Different plant species/genotype response
7. Antagonistic effects by other elements

Low soil Zn content on the acidic, coastal, western hemlock soils cannot be ruled out. Indeed, chemical analysis of the soils from the four sites used in this study revealed that total soil Zn levels (ie., $LiSO_4$-H_2O_4 extractable Zn) were in the range 8.5 to 14.8 ug g^{-1}, and the adequacy of such levels for growth response to fertilizer applications must be viewed with some concern. Alban (1969) reported that soils beneath old western hemlock were highly acidic. Otchere-Boateng and Ballard (1981) found that when urea-N was applied to soil columns containing western hemlock and Douglas-fir seedlings, significantly more Zn, Fe, and Al was leached from beneath hemlock than Douglas-fir; this cannot be related simply to the effect of urea, but must be related to a species influence. As Zn (and also Fe and Al) readily forms organic complexes, the above findings suggest that hemlock may play a major role in soil Zn losses, and hence sites dominated by hemlock over considerable periods of time may have low soil Zn levels in the surface horizons. Removal of the organic layer, e.g. by burning can thus have a major effect on plant available Zn levels. Lindsay (1974) has demonstrated the importance of chelators in supplying plants with micronutrients. The removal of the organic layer removes a ready source of natural chelators. Under natural conditions hemlock is known to root preferentially in the forest floor layer. Hence slash burning and planting of Douglas-fir and western hemlock in mineral soil may shift the nutrient balance from adequate to deficient, particularly with respect to Zn. This is supported by the soil chemical data (Table 4.1) which shows that burnt sites had higher total soil Zn levels than unburnt sites. Yet for these sites, foliar Zn levels for Douglas-fir and western hemlock were significantly lower compared with unburnt sites (Table 4.14 and 4.15).

No B, S, or Mo foliar analyses were carried out for Douglas-fir or western hemlock in this study. However, boron is highly mobile in acid soils under mesic conditions and there is some evidence from preliminary investigations suggesting foliar B levels may be low. As B deficiency symptoms may resemble those of Zn deficiency (Will 1985), low B availability on these coastal soils, or low tissue concentrations in Douglas-fir and western hemlock cannot be ruled out. Molybdate, like phosphate, is ready adsorbed in acid soils high in sesquioxides, while sulfate adsorption is generally much lower. However, based on the work of Turner and Lambert (1980) and more recent reports by Johnson (1984), it is unlikely that soil S levels are limiting growth, firstly because Douglas-fir showed a good response to P applications, and secondly

Douglas-fir had high foliar N levels (>1.8%). However, slash burning may have reduced available S levels due to volatilization and this may have contributed to lower foliar N levels on burnt sites.

For Douglas-fir it was apparent that Al had little direct impact on growth; P application caused a significant growth response and an increase in foliar P levels, and while a number of nutrient elements had low levels probably only Zn was approaching, or below, the critical level. However, for western hemlock the situation was not as straight forward, and there were indications suggesting that factors other than simply low soil nutrient levels, treatment effect or site preparation were influencing growth response and foliar nutrient concentrations.

Based on data reported by Van Den Driessche (1979), western hemlock P and N levels from this study were probably below the critical level for seedlings, but fertilizer treatment had no effect on the foliar level of these elements. In many instances on burnt sites, Fe was probably below the critical level, while all Zn levels on burnt sites are considered to be critically low, and may be approaching this level on unburnt sites as well. The uptake by plants of P, Zn, and Fe is an active process (Mengel and Kirkby 1983, Marschner 1986). Uptake of Ca and Mg also involves an active component (Mengel and Kirkby 1982). As well, the uptake of Ca, Mg, and Fe is strongly correlated to the root tip (Ferguson and Clarkson 1976, Clarkson and Sanderson 1978, Clarkson and Hanson 1980). Little is known about the zone of uptake for Zn, but based on information from Woolhouse (1983), Luttge (1983) and Marschner (1986) major uptake of Zn is most likely in the non-suberized region of the root tip (i.e., the zone of the primary endodermis). Therefore factors that influence the metabolism, development and/or morphology of roots, particularly in the region of the tip, may drastically effect the rate and efficiency of nutrient uptake. This will be most pronounced in plants where the ratio or number of root tips is low and shoot growth high (e.g. in seedlings).

Aluminum toxicity has been shown to have a major effect on root tip morphology and metabolism, with the root system as a whole appearing coralloid and with stubby lateral roots; such roots are inefficient in absorbing nutrients (Foy 1984). Aluminum also has a major inhibitory effect on uptake of P, Ca, Mg, Fe and Zn (Ryan 1983, Foy 1984), and hence their foliar levels. All of these elements were already low in western hemlock foliage and were even lower on burnt sites where there was a concomitant increase in foliar Al levels. Ryan et al. (1986a,b) showed western hemlock to be less tolerant of high Al levels than Douglas-fir. Also, western hemlock is reported to root preferentially in the forest floor layer (Heilman 1976); not only is this a zone of higher nutrient availability on coastal soils, but Al toxicity would also be reduced by the presence of higher cation concentrations and by complexation with organics.

On this basis there is a very strong possibility that Al is having a direct effect on western hemlock seedling growth. Observations from this study showed that greatest growth by western hemlock was on sites where a greater accumulation of organic matter occurred, regardless of treatment.

It is generally considered that P application can reduce Al toxicity while at the same time increasing foliar P levels (Tisdale et al.1985, Foy 1984). This was not the case for western hemlock in this study. In fact P, in the absence of N, caused an increase in foliar Al levels (e.g.

Fig. 4.3). It must be remembered that fertilizer was spot applied, rather than broadcast, in order to reduce the effect of P adsorption; in light of the high P retention found in soils from the study sites this probably explains why a positive and consistent growth response was observed in this study that was generally not seen in previous field trials. However, the spot application of P also meant that the surface area over which Al could be "detoxified" was reduced. Only a part of the roots would come into contact with the added fertilizer, the remainder would be in contact with the "natural" soil unimpacted by fertilizer treatment, the zone where little detoxification of Al would have occurred.

It is unlikely that fertilizer treatment per se depressed growth in western hemlock. Firstly, control treatments rarely grew better or had higher foliar nutrient levels, and secondly, unburnt sites showed healthier seedlings with better nutrient levels regardless of fertilizer treatment. Unburnt sites also had lower foliar Al levels.

Differential plant tolerance to elevated soil Al levels is most likely a reflection of different mechanisms or ability of nutrient uptake. Ryan (1983) found that western hemlock in the presence high H^+ concentrations had a higher root cation exchange capacity than Douglas-fir, but in the presence of Al this was reduced to or below that of Douglas-fir. Given the nature of the coastal soils, it is unlikely that N, P or N+P additions alone will increase western hemlock growth. Liming such vast areas in order to raise pH sufficiently to detoxify Al is not feasible and will likely exacerbate micronutritional problems. In fact Heilman and Eukan (1973) found liming to be detrimental to western hemlock growth in pot studies using coastal soils, and similar effects are commonly reported for a range of plant species (Kinzel 1983). Given the low total Zn levels in the soils of the study sites, any practices that could reduce the level of plant available Zn (eg. burning or liming), or inhibit plant uptake and translocation of Zn (eg. large N and P applications), may have a considerable effect on the ability of these soils to adequately supply Zn, particularly during periods of high plant growth.

It is clear that fertilization of western hemlock seedlings or young stands will require a more balanced nutritional approach. Almost certainly it will require additions of Fe and Zn; for seedlings this could be by root dipping or foliar spraying with a concentrated Fe+Zn solution prior to planting, while for younger stands foliar sprays would be the most efficient since additions to the soil might be lost or hence have to be unduly large. Secondly, slash burning should be avoided wherever re-establishment of hemlock is planned. Finally, the nutritional requirements of western hemlock, particularly in respect of the micronutrients and especially in regard to low pH and the presence of Al, requires urgent attention in order to understand hemlock's growth response on the coastal soils.

4.2 Hydroponic Solution Culture Studies

A series of four solution culture experiments were carried out to examine the effects of pH, and Ca:Al, P:Al and OH:Al mole ratios on root growth and elemental tissue composition of Douglas-fir and western hemlock. For each experiment, seedlings were grown for seven days in the treatment solutions. Apart from altering treatment ratios (and the concomitant change in pH) all other factors were maintained as constant as possible over the four experiments. The pH experiment was designed to provide reference points for growth due to H^+ because variations in Ca:Al, P:Al, and OH:Al ratios necessarily resulted in altered pH of the culture solutions. As well, these reference points allowed evaluation of the three ratio studies for relative root growth in the absence of added Al since there were no zero Al treatments. As mentioned previously, because of the obvious differences in initial seedling size and root length, root growth was analyzed on a percent relative basis:

$$\frac{(\text{Final root length} - \text{Initial root length}) \times 100}{\text{Initial root length}}$$

This allowed a more realistic species comparison on the effect of treatment on root growth.

4.2.1. Effect of pH

There was a marked difference in relative root growth between the two species when they were grown together at various pHs. In the statistical analysis for root growth the terms for species, solution pH, and species by solution pH interaction were highly significant ($p<0.01$). Solution pH *per se* had no significant effect on relative root growth in western hemlock. However, for Douglas-fir solution pH had a pronounced influence (Table 4.16); decreasing pH decreased relative root growth. At pH 3.0, Douglas-fir root growth was significantly lower than at pH 3.5. This dramatic effect was not evident in western hemlock. Greatest absolute root growth by Douglas-fir occurred at the nominal pH of 5.0, while the greatest absolute root growth for western hemlock occurred at the nominal pH of 4.5, although for western hemlock there was no significant difference in relative root growth at the range of pHs investigated (Table 4.16).

Plate I shows the effect of increasing solution pH on western hemlock (a) and Douglas-fir (b) root growth. For Douglas-fir the ameliorative effect of increasing pH from 3.0 to 4.0 is clearly apparent for absolute root growth, and also for the degree of root branch development. However, for western hemlock there is no apparent effect of increasing pH on root growth, corroborating to the statistical analyzes which showed no significant pH effect on root growth.

The effect of pH was also evident on elemental composition of root and foliar tissue, and Table 4.17 contains the mean concentration of elements over all pHs. Statistical analysis (MANOVA) was carried out to examine the effect of pH on the concentration of 10 cations and results are given in Table 4.18. A number of features stand out from the analyses. Firstly, except for root Zn levels, there were significant differences between species. Secondly, the effect of varying pH levels had a significant effect on root concentration for all the elements considered except K, Zn, and Na; for both species, as solution pH increased root concentrations of Al, P, Ca, Mg, Mn, Fe also increased. Finally, although no Al was added to any of the solutions, there was a significant difference in tissue Al concentrations when the two species are compared.

Table 4.16. Effect of pH on actual (mm) and relative (%) root growth for Douglas-fir and western hemlock over a 7 day period.

pH		Douglas-fir		Western Hemlock	
Init.	Final	(mm)	(%)	(mm)	(%)
3.0	3.0	5.6	.3a	4.1	8.9a
3.5	3.5	19.7	22.8b	4.7	9.8a
4.0	4.0	19.6	22.8b	5.4	12.4a
4.5	4.3	19.8	20.5b	5.8	11.7a
5.0	4.6	24.2	27.4c	5.5	11.4a

For percent relative response, vertical columns with the same letter indicate no significant difference when ranked using Duncan's Multiple Range Test (a=0.05).

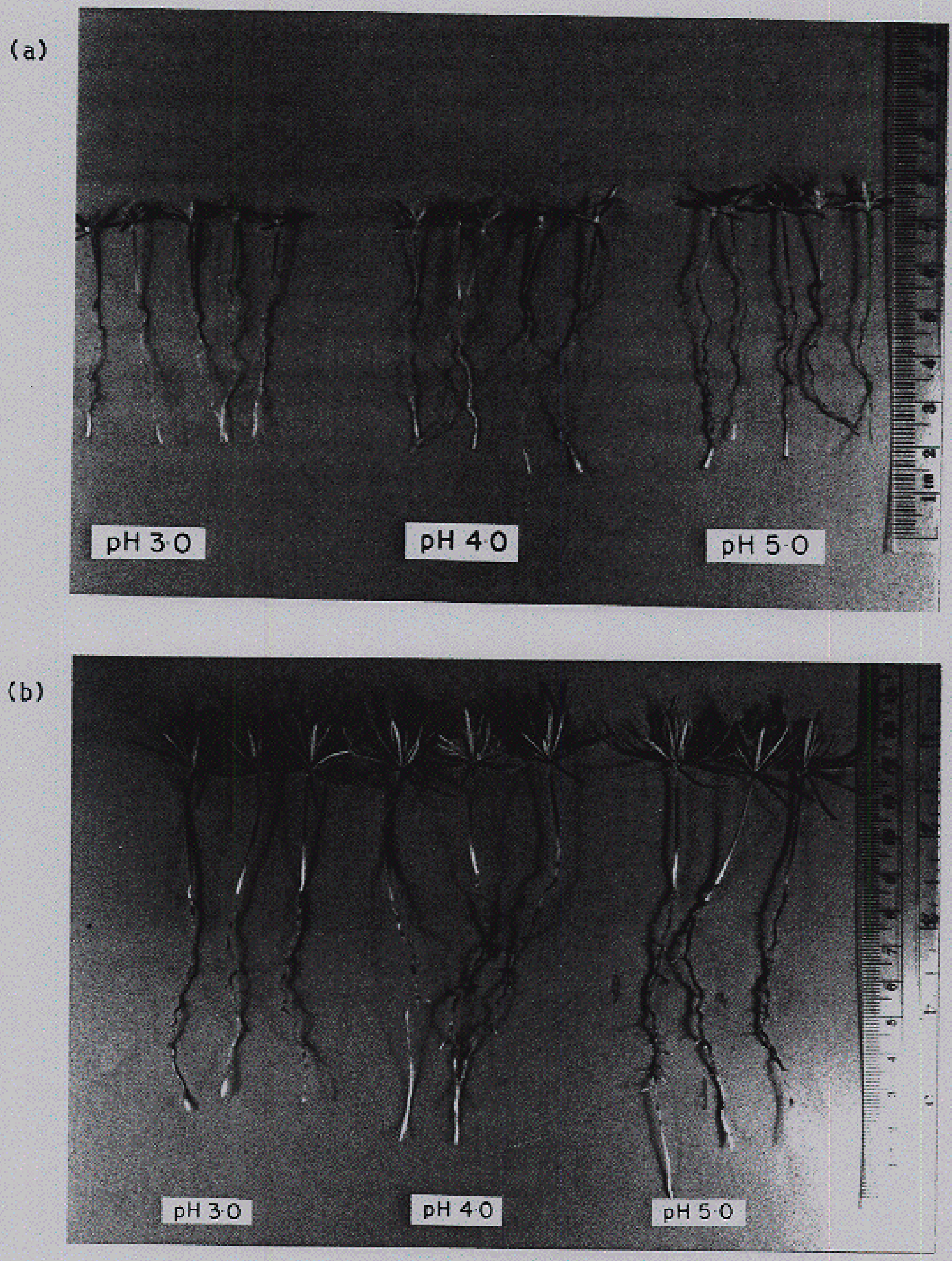


Plate I. The effect of increasing solution pH on western hemlock (a) and Douglas-fir (b) root growth and morphology.

Table 4.17. Mean concentration (ug g^{-1} dry weight) of elements for Douglas-fir and western hemlock averaged over all pH treatments.

Element	Douglas-fir		Western Hemlock	
	Foliage	Roots	Foliage	Roots
Al	132	531	317	795
P	4672	6359	3843	4893
K	5877	11078	6668	7987
Ca	1192	546	2282	774
Mg	1008	820	1377	935
Mn	96	26	269	37
Fe	86	1265	123	2019
Zn	46	82	36	76
Cu	31	101	60	84
Na	34	105	80	81

Except for root Zn concentrations, there were significant (a=0.01) differences for all elements between species both for foliage and roots.

Table 4.18. Summary MANOVA table of the effect of varying pH levels on the chemical composition of Douglas-fir and western hemlock root tissue.

		Significance of F									
Source	DF	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
Residual	9										
Replication	1	NS	NS	**	NS	NS	NS	NS	NS	NS	NS
Species	1	**	**	**	**	**	**	**	NS	**	**
pH	4	**	**	NS	**	**	*	**	NS	**	NS
Species by pH	4	NS	**	NS	NS	NS	NS	**	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05,
NS - non-significant at a=0.05.

From Table 4.18 it can be emphasized that a significant species by pH interaction occurred for root tissue Fe and P. This was examined in more detail and results shown in Table 4.19. The effect of pH on root Fe levels is most pronounced, increasing consistently with increasing pH; this effect was very much greater for western hemlock. Hydrogen ion concentration had no significant effect on Douglas-fir root P concentrations. However, for western hemlock, increasing pH resulted in an increased root P level up to pH 4.5. Root and foliar tissue data from the pH study are given in Appendix 7.

Table 4.19. Effect of pH on root Fe and P concentration (ug g^{-1} dry weight)) in Douglas-fir and western hemlock over a 7 day period.

Nominal pH	Douglas-fir		Western Hemlock	
	P	Fe	P	Fe
3.0	6178a	424a	3766a	301a
3.5	6114a	666b	3895a	779b
4.0	6327a	1181c	4857b	1951c
4.5	6767a	1814d	6076c	3290d
5.0	6408a	2241e	5871c	3776e

Vertical columns with the same letter indicate no significant difference when ranked with Duncan's Multiple Range Test (a=0.05).

There was no significant pH effect on foliar chemical composition. However, there was a significant species difference for <u>all</u> elements analyzed. Again, it is interesting that although no Al was added to the culture solutions, both species had noticeable foliar and root Al concentrations, and further, a significant species difference was evident. Two explanations are possible for the source of the Al. The first may be a carryover from seed. Secondly, there may have been some absorption from the silica sand in the germination boxes or from the tap water. The analyses of the culture solutions revealed that they were not contaminated and had <1 ug g^{-1} Al. The difference in Al concentration between the two species is most likely related to differences in ability, or mechanisms of cation uptake and is consistent with tissue concentrations of the base cations, as well as Mn and Fe concentrations.

4.2.2. Effect of Ca:Al Ratios

Table 4.20 outlines the initial experimental conditions for the Ca:Al solution culture experiment and the percent relative root growth for Douglas-fir and western hemlock. Of particular importance are the values for (Al^{3+}) activity, and the effect of increasing ionic strength (increasing Ca:Al mole ratios) on Al activity. Based on calculations from the GEOCHEM program (Sposito and Mattigod 1980)it was evident that Al^{3+} was the dominant Al species present. When Al was speciated using the method of Bloom et al. (1978) and James et al. (1983) no polymeric Al was found and all the added Al was in the monomeric form. Also, at the end of seven days, solution pH for any one treatment had changed less than 0.2 units, while changes in elemental concentrations were within experimental and detection error limits.

Table 4.20. Effect of initial Al concentration and Ca:Al ratios on selected chemical properties of the solution culture and on relative root growth (%) of Douglas-fir and western hemlock seedlings.

Ca:Al Mole Ratios	Initial Al Concentrations ug ml^{-1}				
	10 +(0.371)	25 (0.927)	50 (1.853)	75 (2.780)	100 (3.706)
			*Al^{3+} Activity ug ml^{-1}		
0.03	5.4 +(0.20)	11.5 (0.43)	18.7 (0.69)	24.1 (0.89)	28.9 (1.07)
0.15	5.3 (0.20)	11.1 (0.41)	18.7 (0.66)	22.7 (0.84)	26.5 (0.98)
0.75	4.7 (0.17)	9.0 (0.33)	17.7 (0.51)	17.1 (0.63)	19.9 (0.74)
			*Ionic Strength mM L^{-1}		
0.03	3.87	7.04	12.24	17.19	22.41
0.15	4.00	7.29	12.65	17.74	23.10
0.75	4.67	8.48	15.02	21.07	27.28
			Solution pH		
0.03	3.72	3.60	3.55	3.50	3.50
0.15	3.73	3.64	3.58	3.54	3.54
0.75	3.73	3.64	3.58	3.54	3.54
			Douglas-fir Relative Root Growth %		
0.03	8.2	11.4	7.9	4.5	3.4
0.15	10.1	12.7	10.2	9.5	8.3
0.75	11.9	13.8	19.2	14.8	18.3
			Western Hemlock Relative Root Growth %		
0.03	10.0	11.4	11.3	7.5	6.6
0.15	9.1	12.8	13.9	13.7	10.0
0.75	9.6	13.4	12.31	11.4	10.2

+ Values in brackets are concentrations in mM L^{-1}.

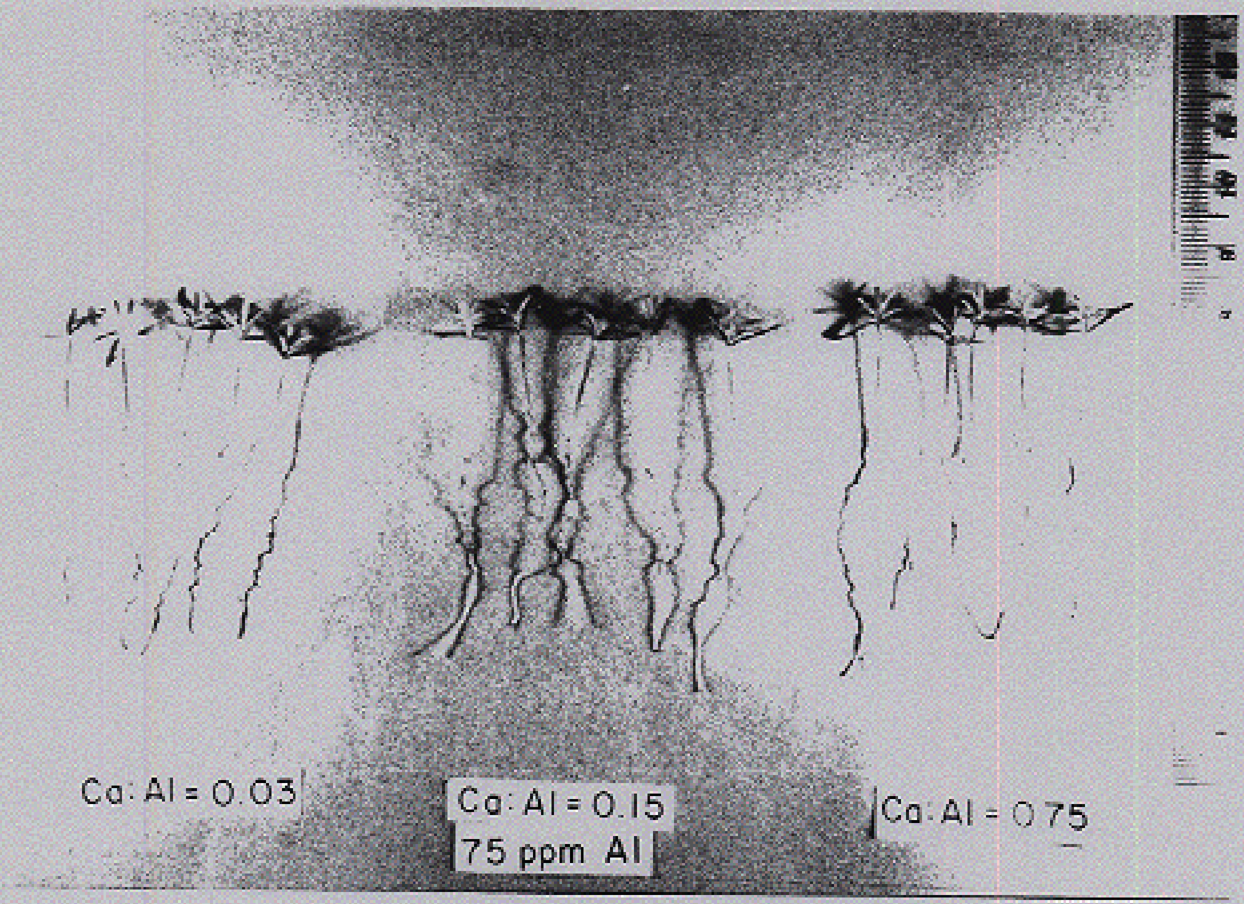
* Ionic strengths and free cation concentration data were obtained from program GEOCHEM (Sposito and Mattigod 1980). Activities were calculated using the equation of Guntelberg (Stumm and Morgan 1981) and data from GEOCHEM.

Statistical analyses of the effect of initial Al levels and Ca:Al ratios on relative root growth and tissue concentrations are given in Table 4.21. Initial Al levels and Ca:Al ratios had a significant effect on relative root growth. Although there was no difference between species at the main effect level, the two species did react differently to varying initial Al levels and to Ca:Al ratios, as indicated by the significant three way interaction. Examination of this interaction revealed that changes in solution Al levels and Ca:Al ratios had a major effect on Douglas-fir relative root growth when compared with western hemlock. For both species there was an increase in root growth up to 25 ug mg^{-1} Al in solution at the 0.03 and 0.15 Ca:Al ratios, and up to 50 ug ml^{-1} Al concentration for Douglas-fir at the 0.75 Ca:Al ratio; above these Al concentrations root growth declined steadily. Fig. 4.5 shows the species root growth response to Al levels and Ca:Al ratios. An interesting feature evident in Fig. 4.5 is that at the 0.03 Ca:Al ratio, Douglas-fir relative root growth was lower than that for western hemlock, while at the 0.75 Ca:Al ratio Douglas-fir relative root growth exceeded that of western hemlock.

Plate II shows the effect of increasing the Ca:Al ratio on western hemlock (a) and Douglas-fir (b). For Douglas-fir the ameliorative effect of increasing the Ca:Al ratio from 0.03 to 0.75 is clearly apparent, and supports the growth data in Table 4.20.

As indicated in Table 4.21, initial Al levels and Ca:Al ratios had a significant effect on the root tissue concentrations of all elements analyzed except Zn, Cu, and Na (although there were significant species differences in root tissue concentrations of these three cations). The

(a)



(b)

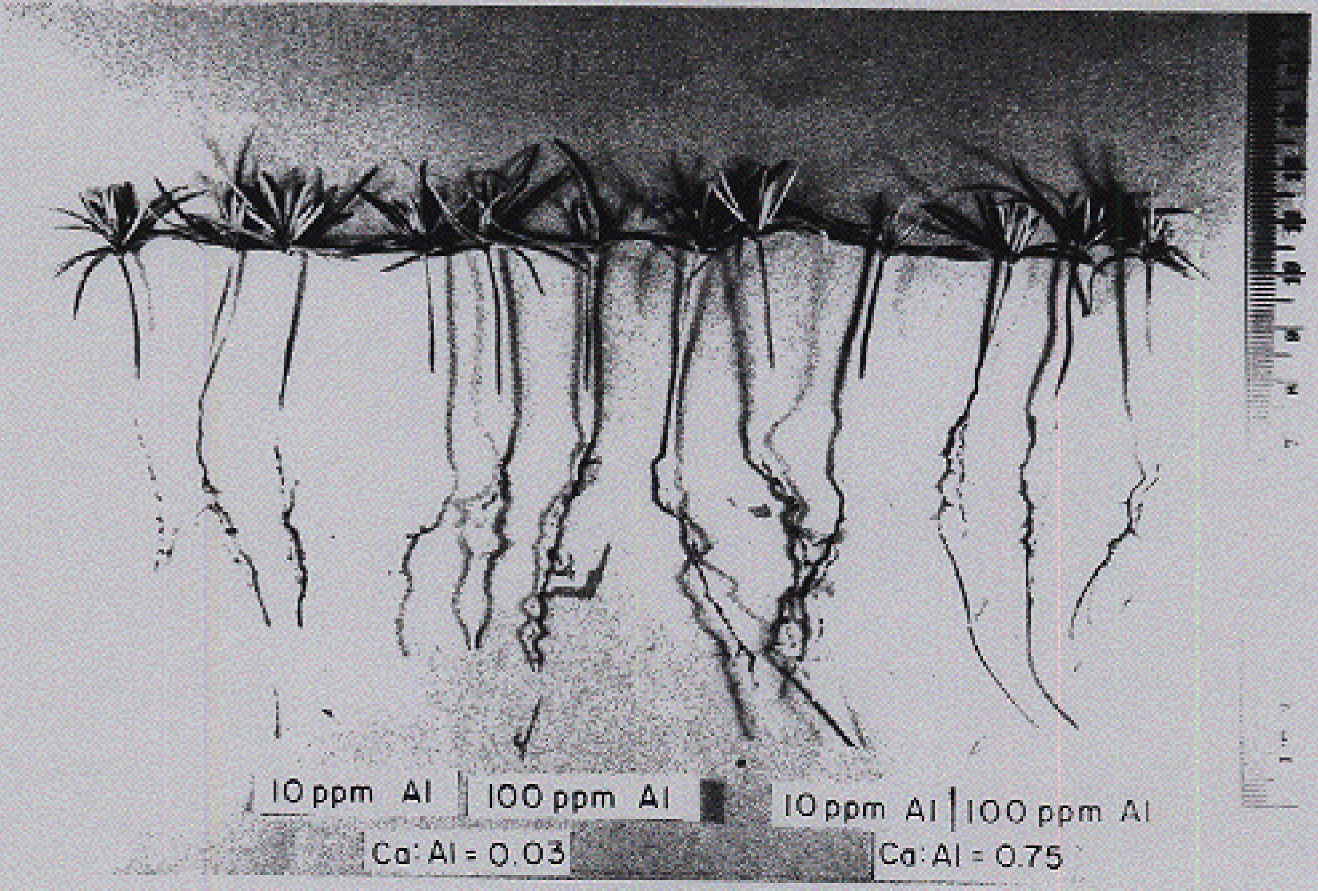


Plate II. The effect of increasing the Ca:Al mole ratio on western hemlock (a) and Douglas-fir (b) root growth and morphology.

Table 4.21. Summary MANOVA table of the effect of initial Al concentrations and Ca:Al ratios on the chemical composition and relative growth response of Douglas-fir and western hemlock seedling roots.

Source	DF	Significance of F										
		Rel. Root Growth	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
Residual	29											
Replication	1	**	*	*	NS	NS	**	**	NS	NS	NS	**
Species (Sp)	1	NS	**	**	**	**	**	**	NS	**	**	*
Ratios	2	**	NS	NS	**	**	**	*	NS	NS	NS	NS
Al Concentration (Alconc)	4	**	**	**	*	*	NS	NS	**	NS	NS	NS
Sp by Alconc	4	NS	**	NS	NS	NS	NS	NS	**	NS	NS	NS
Sp by Ratio	2	**	NS	NS	NS	NS	*	NS	NS	NS	NS	NS
Ratio by Alconc	8	*	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Sp by Alconc	8	**	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05, NS - non-significant

species by Al concentration interaction for root tissue Al and Fe concentrations are shown in Fig. 4.6. The overall similarity of the curves for both species is striking and suggests that the effect of solution Al on root Fe and Al adsorption and/or absorption may be the same for both elements and species.

Regardless of the Ca;Al ratio, increasing Al levels in the solution cultures did not result in an increase in root tissue Al levels. The proposed reason for this is that as solution Al levels increased above 25 ug ml^{-1} root tissue and cellular disruption, particularly in relation to the apoplast, began to take place allowing tissue Al to leak back into the bulk solution. This aspect is covered in more detail in Section 4.2.6 (p.179).

The effect of initial Al levels on root tissue concentrations was also significant for P, K, and Ca. Since there was no significant species interaction for the P, K, Ca, only main effects are presented. There was an increase in root tissue Ca levels for both Douglas-fir and western hemlock as solution Al levels increased. This was expected, because solution Ca levels increased with solution Al levels proportionate to the respective Ca:Al ratio. Root K concentrations increased gradually as solution Al increased to about 75 ug ml^{-1} and then remained constant. However, unlike Ca and K, root P levels dropped sharply as the Al concentration increased from 10 to 25 ug ml^{-1}. For instance, Douglas-fir root P concentrations dropped from 11200 to 8690 ug g^{-1}, while for western hemlock root P concentrations dropped from 9420 to 5790 ug g^{-1}. At solution Al levels above 25 ug ml^{-1} root P decreased more slowly.

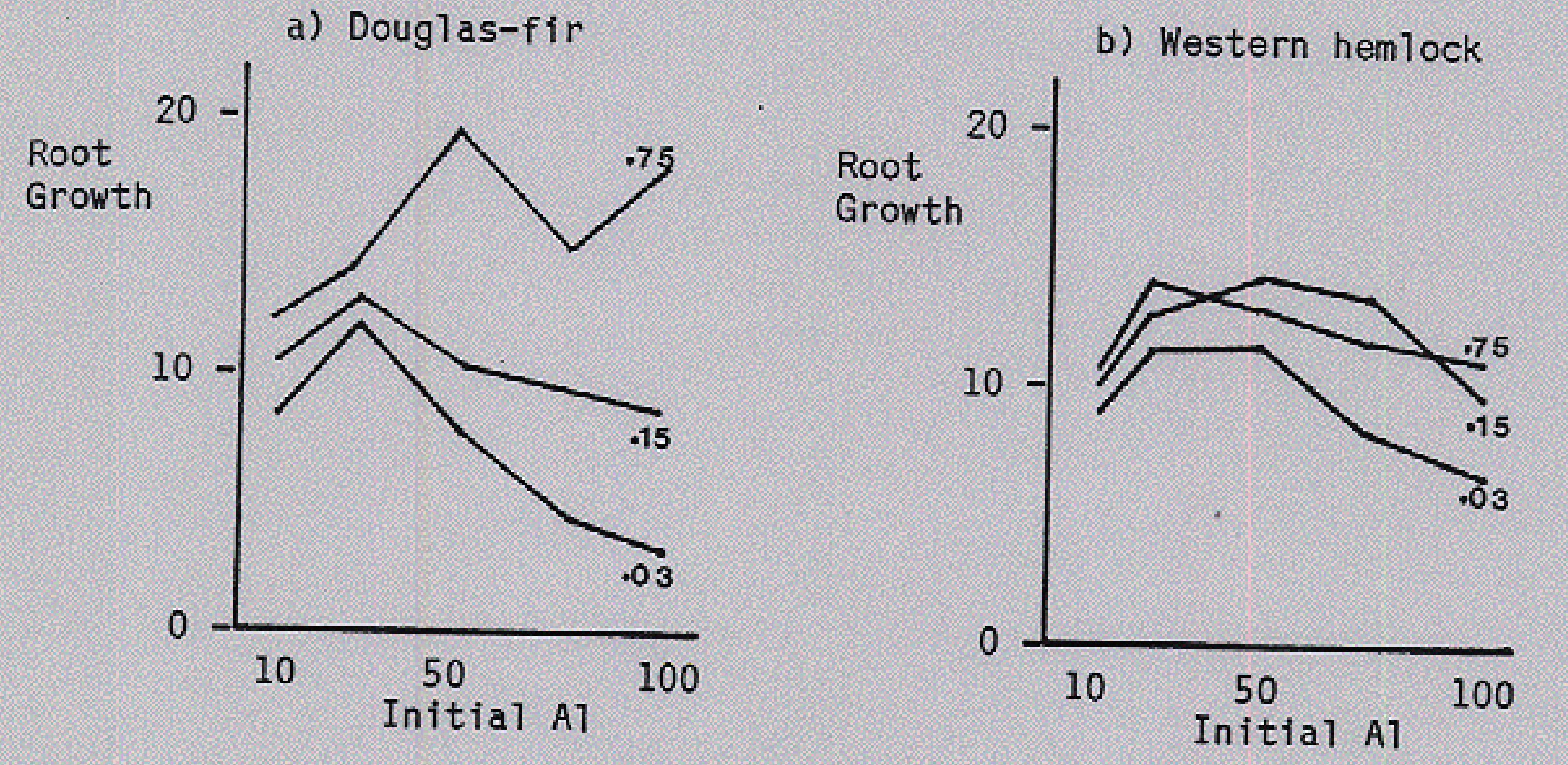


Fig. 4.5. The effect of varying initial Al concentration (ug ml^{-1}) and Ca:Al mole ratios on relative root growth (%) of a) Douglas-fir and b) western hemlock.

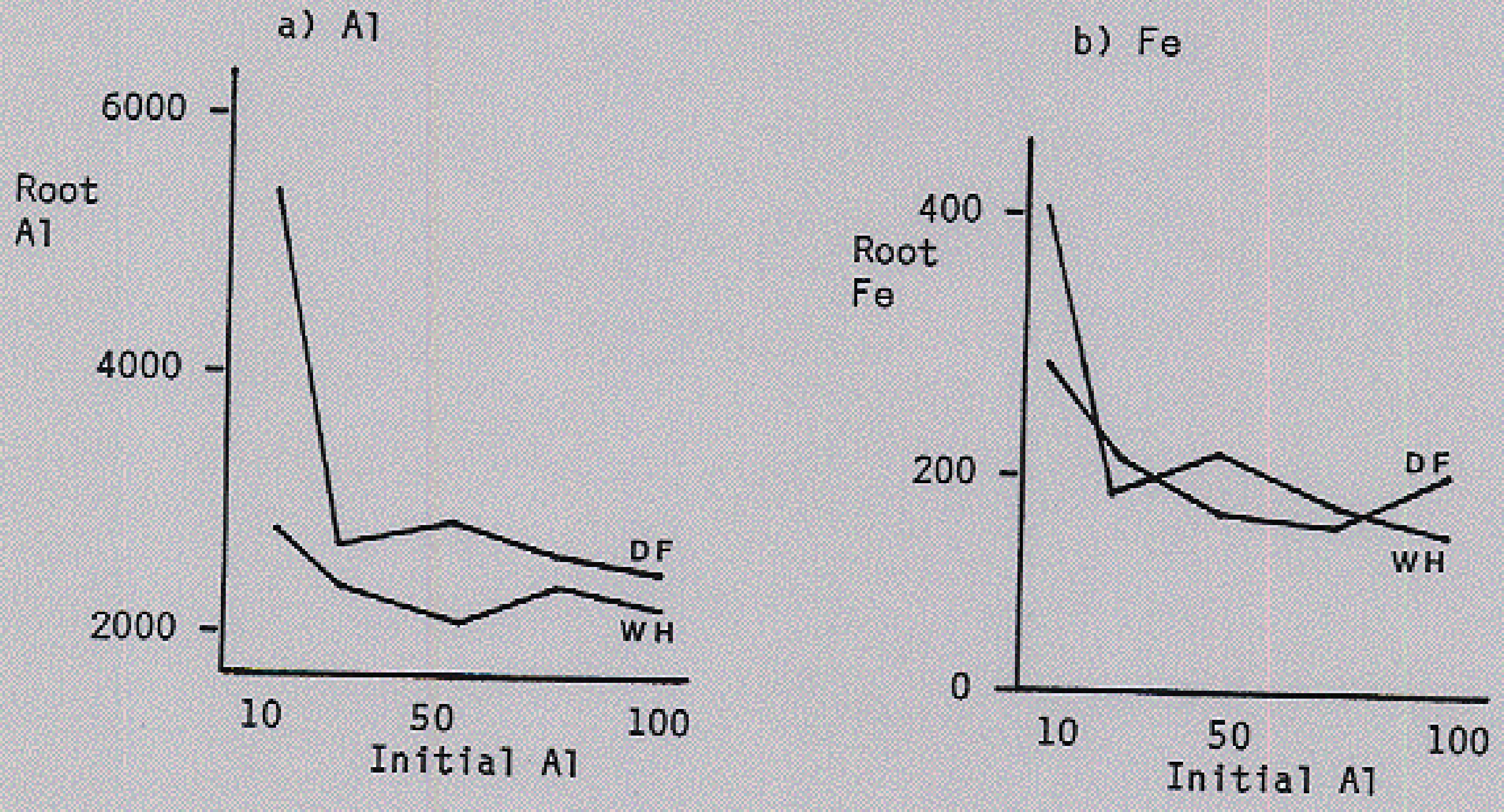


Fig. 4.6. The species by Al interaction for the Ca:Al ratio study showing the effect of initial solution Al concentration (ug ml^{-1}) on the concentration (ug g^{-1} dry weight) of a) mean root tissue Al and b) mean root tissue Fe for Douglas-fir (DF) and western hemlock (WH).

Varying the Ca:Al ratios had a significant effect on root tissue K, Ca, Mn, and Mg concentrations; for Mg, there was also a significant species by ratio interaction. Increasing Ca:Al ratios increased root tissue Ca levels, due to increasing Ca:Al ratios. However, K and Mn root tissue levels decreased significantly as the Ca:Al ratio increased. This is somewhat unusual for K in that K levels were increased with increasing solution Al levels. The significant species by ratio interaction for Mg was due to a decrease in root tissue Mg levels in Douglas-fir, whereas for western hemlock there was no significant change.

For all elements except Fe, a significant species difference in root tissue concentrations was found (Table 4.21), and this difference is clearly obvious from the foliar data in Appendix 8. Western hemlock had higher root levels of Al, Ca, Mn, Fe, and Na, and lower levels of P, K, Mg, Zn, and Cu compared with Douglas-fir.

Results from statistical analysis of initial Al concentrations and Ca:Al mole ratios on foliar levels are given in Table 4.23. In comparison with root tissue, foliar concentrations were not as much affected by the treatments. This is probably a reflection of tissue levels prior to treatment initiation, and the short duration of the study. However, except for K and Mg there was a significant species difference in foliar levels; western hemlock had higher foliar concentrations of Al, Ca, Mn, Fe, Cu, and Na, and lower concentrations of P and Zn compared with Douglas-fir. This trend in foliar tissue levels was similar to root tissue with the exception of Cu; while western hemlock had lower root Cu levels than Douglas-fir (42 vs 54 ug g^{-1}), it had higher foliar levels (59 vs 46 ug g^{-1}).

Table 4.22. Summary MANOVA table of the effect of initial Al concentrations and Ca:Al ratios on the foliar chemical composition of Douglas-fir and western hemlock seedlings.

Source	DF	Significance of F									
		Al	P	K	Ca	Mg	Mn	Fe	Zn	Ca	Na
Residual	29										
Replication	1	**	NS	NS	**	**	**	NS	**	*	**
Species (Sp)	1	**	**	NS	**	NS	**	**	**	**	**
Ratios	2	NS	NS	NS	**	NS	NS	NS	**	NS	NS
Al Concentration (Alconc)	4	**	NS	**	**	NS	NS	**	NS	NS	NS
Sp by Alconc	4	NS	NS	NS	**	NS	NS	NS	NS	NS	NS
Sp by Ratio	2	NS	NS	NS	*	NS	NS	NS	NS	NS	NS
Ratio by Alconc	8	NS	NS	NS	**	NS	NS	NS	NS	NS	NS
Ratio by Sp by Alconc	8	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05, NS - non-significant

Initial solution Al concentrations had a significant effect on foliar Al, K, Ca, and Fe levels, but as was the case for root tissue, foliar Ca levels were influenced by increasing solution Ca levels from the Ca:Al ratios. Increasing initial Al concentrations resulted in an increase in foliar Al levels up to solution Al concentration of 75 ug ml^{-1}, and then levelled off. For both species foliar Fe levels increased with increasing solution Al levels up to a solution concentration of 25 ug ml^{-1} and then declined steadily. Foliar Ca and K concentrations also increased up to a solution Al concentration of 25 ug ml^{-1}, but then plateaued.

There was a highly significant effect of Ca:Al ratios on foliar Zn levels. Although there was a significant difference in species foliar Zn level, the effect of varying the Ca:Al ratio was the same; as the Ca:Al ratio increased foliar Zn levels rose and the rate of increase was the same for both species.

The effect of the various treatments on foliar Ca levels was significant for all terms except the three way interaction (Table 4.23). Increasing the Ca:Al ratio resulted in an increase in foliar Ca levels in both species (Fig. 4.7). However with increasing Al in solution, Ca increased somewhat in Douglas-fir, but rose only a little and then declined in western hemlock (Fig. 4.7); this difference in response is the reason for the significant species by Al concentration interaction.

The reason for the significant ratio by Al concentration interaction is most likely the much greater foliar Ca concentration at higher Ca:Al ratios, particularly at the 0.75 ratio. In this respect the interaction probably reflects the large effect of higher Ca^{2+} activity on the activity of Al^{3+}, as well as on Ca availability for plant uptake, especially for Douglas-fir as a large increase in foliar Ca occurred for this species for all solution Al levels at the 0.75 Ca:Al ratio.

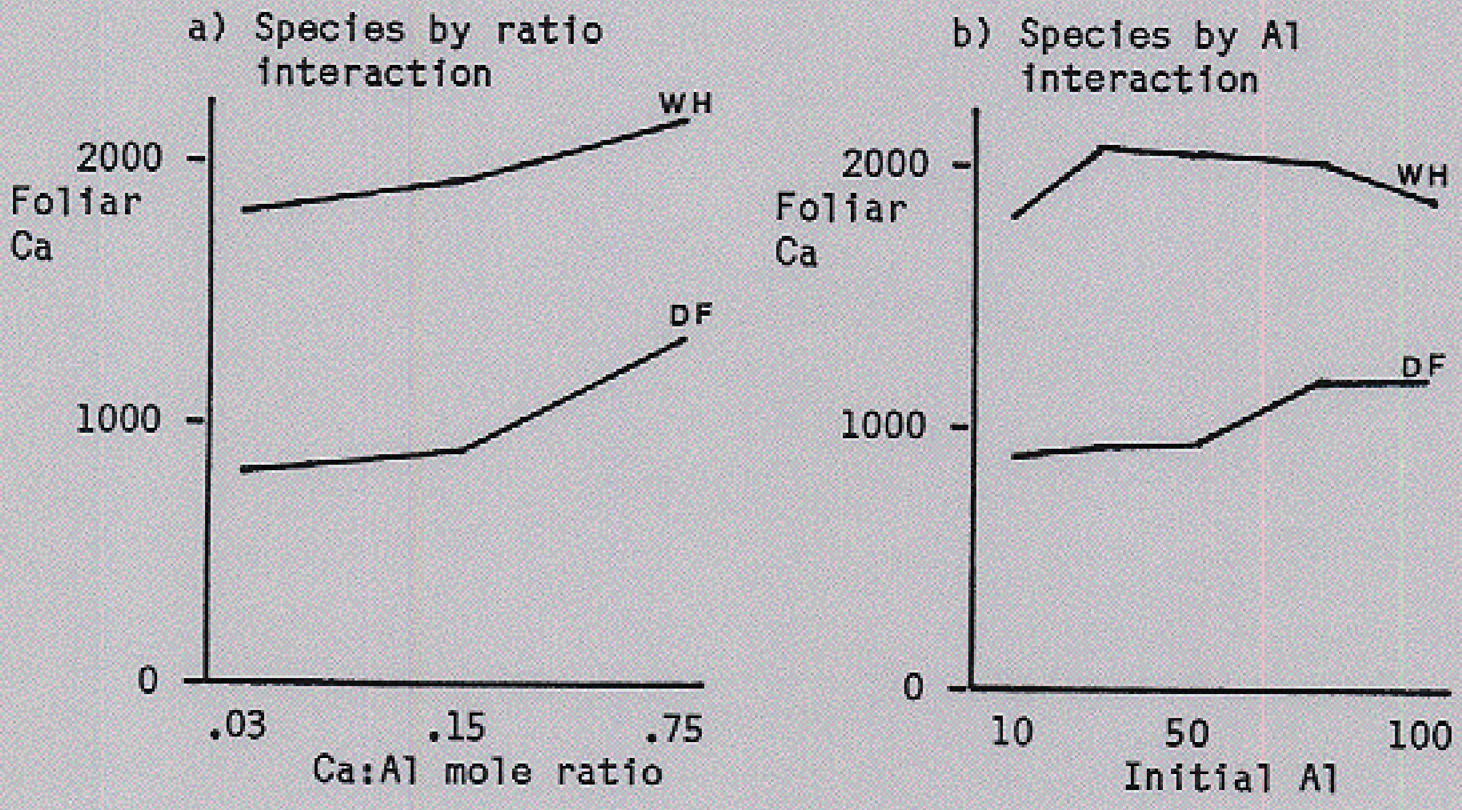


Fig. 4.7. Diagrammatic representation for Douglas-fir (DF) and western hemlock (WH) mean foliar Ca concentrations (ug g^{-1} dry weight) showing the interaction between a) species by Ca:Al mole ratio and b) species by initial Al concentration (ug ml^{-1}).

4.2.3. Effect of P:Al Ratios

Initial experimental conditions for the P:Al solution culture experiments as well as percent relative root growth after seven days of treatment for Douglas-fir and western hemlock are shown in Table 4.23. Unlike the Ca:Al study, in this experiment Al^{3+} activity did not change greatly with increasing P:Al ratios. However, there was a noticeable decrease in solution pH, from 4.36 for an initial Al concentration of 10 ug ml^{-1} for the lowest P:Al ratios down to pH 3.32 for the highest Al concentration and P:Al ratio. Under these conditions, treatment effects on root growth and foliar composition at pHs less than about 3.5 may be due as much to low pH effects (the effect of pH on growth was covered in Section 4.2.1) as to the effect of solution Al concentrations or P:Al ratios. Aluminum speciation by the method of Bloom et al. (1978) and James et al. (1983) again revealed that all added Al was in the monomeric form. Solution chemical composition at the end of seven days varied only minimally from the initial condition, for instance pH at the beginning and end of the experiments varied no more than pH differences between experimental replication (<0.1 pH units).

Results from the statistical analysis on the effects of initial Al levels and P:Al ratios on relative root growth and tissue concentrations of various elements are presented in Table 4.24. Both Al concentration and P:Al ratios had a highly significant main treatment effect on root growth. Although there was no significant difference between species at the main effect level, there was a highly significant species by initial Al concentration interaction.

Table 4.23. Effect of initial Al concentration and P:Al ratios on selected chemical properties of the solution culture and on relative root growth (%) of Douglas-fir and western hemlock seedlings.

P:Al Mole Ratios	Initial Al Concentrations ug ml^{-1}				
	10 +(0.371)	25 (0.927)	50 (1.853)	75 (2.780)	100 (3.706)
			*Al^{3+} Activity ug ml^{-1}		
0.0063	4.7 +(0.17)	10.7 (0.40)	17.9 (0.66)	23.6 (0.87)	28.2 (1.05)
0.025	4.8 (0.18)	10.9 (0.41)	18.3 (0.68)	24.1 (0.89)	28.9 (1.07)
0.1	5.1 (0.19)	11.5 (0.43)	19.2 (0.71)	24.7 (0.91)	29.5 (1.09)
			*Ionic Strength mM L^{-1}		
0.0063	3.68	6.69	11.81	16.68	21.82
0.025	3.72	6.84	11.98	16.93	22.20
0.1	3.84	7.04	12.33	17.42	22.73
			Solution pH		
0.0063	4.36	4.18	4.01	3.92	3.88
0.025	4.31	4.08	3.89	3.77	3.68
0.1	4.10	3.81	3.58	3.38	3.32
			Douglas-fir Relative Root Growth %		
0.0063	23.2	18.8	15.5	11.6	7.0
0.025	28.4	20.2	19.2	9.9	7.8
0.1	18.6	14.2	11.6	9.6	2.6
			Western Hemlock Relative Root Growth %		
0.0063	18.9	16.6	14.9	14.6	9.9
0.025	16.7	16.4	16.7	10.9	7.5
0.1	12.9	14.2	12.6	8.5	5.6

+ Values in brackets are concentrations in mM L^{-1}.

* Ionic strengths and free cation concentration data were obtained from program GEOCHEM (Sposito and Mattigod 1980). Activities were calculated using the equation of Guntelberg (Stumm and Morgan 1981) and data from GEOCHEM.

Examination of this interaction revealed that the major differences occurred at the lowest initial Al concentrations. Douglas-fir root growth decreased rapidly with increasing Al concentrations and the difference in response between the two species is shown in Fig. 4.8. The lack of a significant species by ratio interaction indicates that the response by both species to varying P:Al ratios was the same, and this is evident from the root growth data in Table 4.23. Although the root growth data for Douglas-fir suggests that the 0.025 P:Al ratio had an ameliorative effect on Al, that is, root growth was greatest for most Al concentrations at this ratio, this was not statistically significant. Increasing the P:Al ratio beyond 0.025 resulted in a significant reduction in root growth, particularly for Douglas-fir, and this is attributed mainly to the low solution pH at Al concentrations greater than 50 ug ml^{-1}.

Although there was no significant species by P:Al ratio interaction, comparison of relative root growth between Douglas-fir and western hemlock at the highest (0.1) P:Al ratio reveals that at solution Al concentrations above 25 ug ml^{-1}, western hemlock root growth exceeded that of Douglas-fir. This supports the earlier statement that the low root growth of Douglas-fir at the high P:Al ratio was due to a pH effect, as well as the earlier finding that western hemlock was more tolerant of low pH. It also raises the question of whether western hemlock is more tolerant of Al at low pH compared with Douglas-fir. However, at these low pHs the activity of other elements, particularly Cu, may also have increased to toxic levels and the greater root growth of western hemlock may be a reflection of greater tolerance to such levels.

Table 4.24. Summary MANOVA table of the effect of initial Al concentrations and P:Al ratios on the chemical composition and relative growth of Douglas-fir and western hemlock seedling roots.

		Significance of F										
Source	DF	Rel. Root Growth	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
Residual	29											
Replication	1	*	**	**	**	NS	NS	NS	**	**	NS	**
Species (Sp)	1	NS	**	**	**	**	**	**	**	NS	**	NS
Ratios	2	**	NS	**	NS	NS	NS	*	NS	NS	NS	NS
Al Concentration (Alconc)	4	**	*	NS	NS	*	NS	NS	**	NS	NS	NS
Sp by Alconc	4	**	**	NS	NS	NS	NS	*	**	NS	NS	NS
Sp by Ratio	2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Alconc	8	NS	**	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Sp by Alconc	8	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05, NS - non-significant

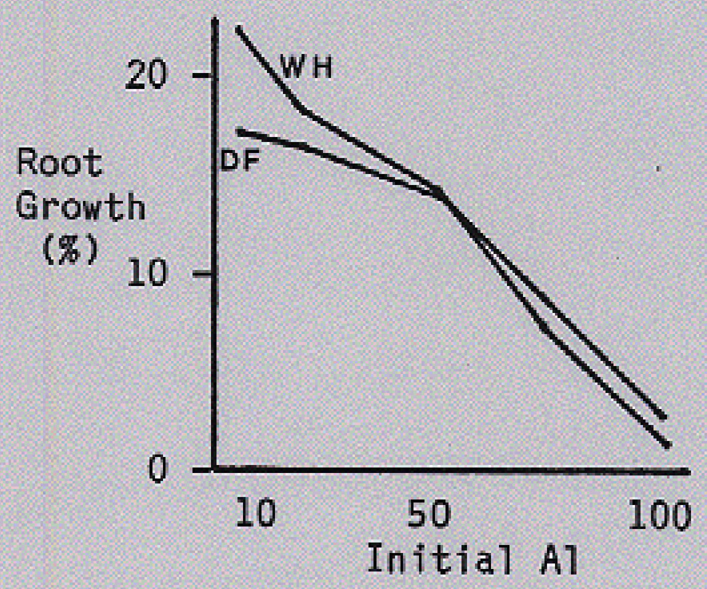


Fig. 4.8. The effect of increasing initial solution Al concentrations (ug ml^{-1}) in the P:Al ratio study on relative root growth (%) of Douglas-fir (DF) and western hemlock (WH).

Plate III shows qualitatively the effect of P:Al ratios and initial Al levels on Douglas-fir root growth. The major depressive effect of the high P:Al ratio is clearly evident in Plate III(a), while Plate III(b) shows the lack of an ameliorative effect by increasing the P:Al ratio. Although these effects were similar for western hemlock, they were not as pronounced.

Root tissue Al, P, Ca, Mn, and Fe levels were significantly affected by the treatment conditions (Table 4.24). For root tissue Al concentrations there were significant main effects for species and initial Al concentration, as well as a significant interaction between these terms. At the species level, western hemlock root tissue Al was always higher than that of Douglas-fir. When the interaction term was separated into species effects, the difference between Douglas-fir and western hemlock was most pronounced (Fig. 4.9). For western hemlock there was a sharp and consistent drop in root tissue Al levels as initial solution Al concentrations exceeded 25 ug ml^{-1}, while for Douglas-fir there was no consistent effect.

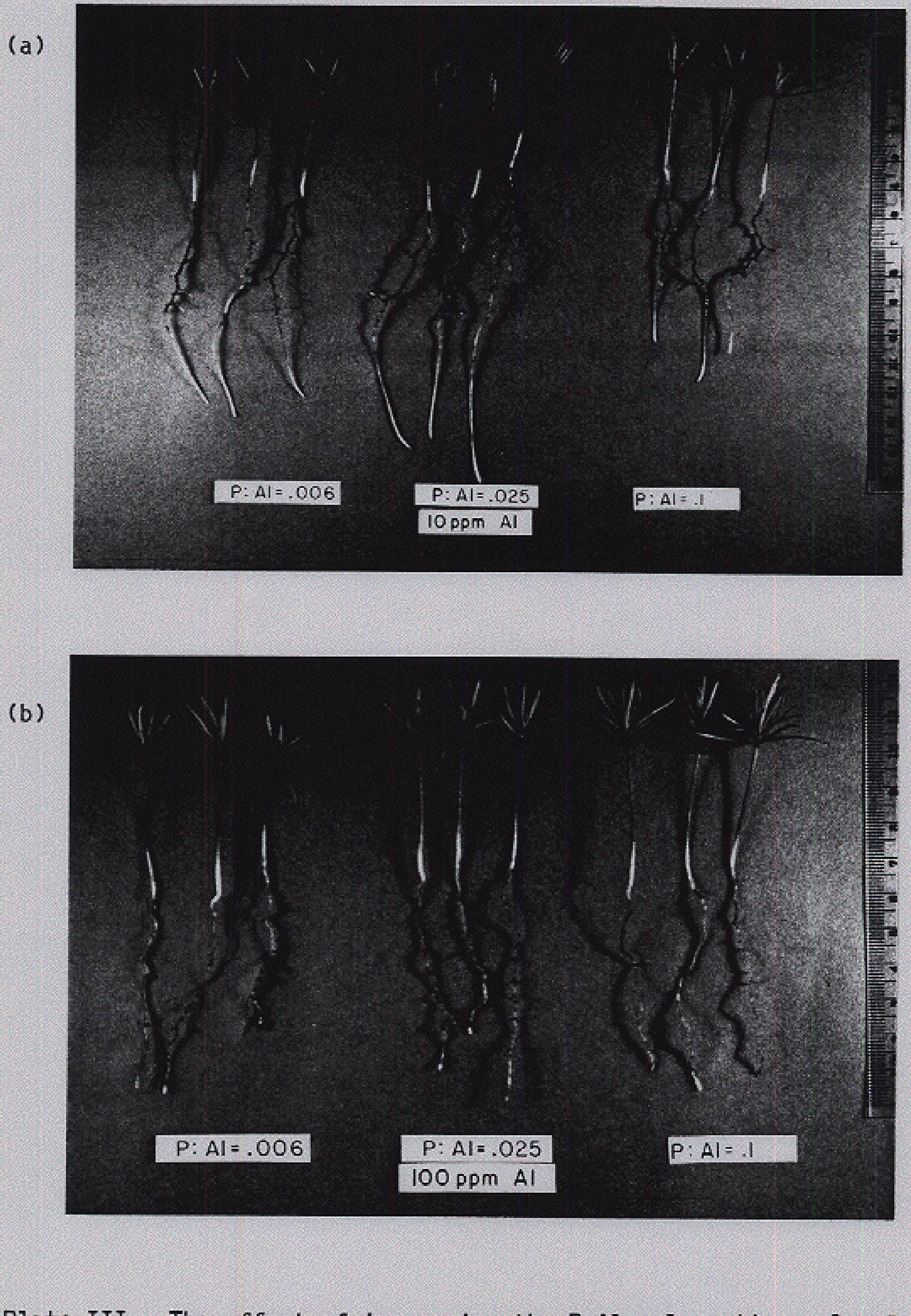


Plate III. The effect of increasing the P:Al mole ratio on Douglas-fir root growth at (a) 10 and (b) 100 ppm initial solution Al concentrations (ppm = ug ml^{-1}).

There was also a significant Al concentration by P:Al ratio effect on root tissue Al concentration (Fig. 4.9). At low P:Al ratios there was a gradual increase in root tissue Al concentrations. However, as the P:Al ratio increased there was an initial step wise increase in tissue Al concentration, but this increase then fell sharply and consistently for the two higher P:Al ratios. At solution Al concentrations of 10 and 25 ug ml^{-1} increasing the P:Al ratio increased tissue Al concentration, while at solution Al concentration above 50 ug ml^{-1} tissue Al concentrations decreased.

The highly significant effect of the P:Al ratios on root tissue P levels was due to increased tissue P levels as the P:Al ratio increased. This was expected as increasing the P:Al ratio resulted in an increase in solution P concentrations. The effect of increasing solution Al concentration on root tissue Fe and Mn levels is shown in Fig. 4.10, and the reason for the significant interaction can be seen by the magnitude of change in the concentration of both elements between the two species. For Fe, the interaction is due to the continuous sharp decrease in western hemlock's root tissue Fe levels. The Mn interaction is due to the rapid increase in Douglas-fir Mn levels at the highest solution Al concentration (100 ug ml^{-1}); at lower solution concentrations the lines for the two species were almost parallel.

Except for Zn and Na, there was a significant difference in the root tissue concentrations of elements between the two species. Douglas-fir had the highest root tissue P, K, Mg, and Cu concentrations and the lowest Al, Ca, Mn, and Zn concentrations compared with western hemlock.

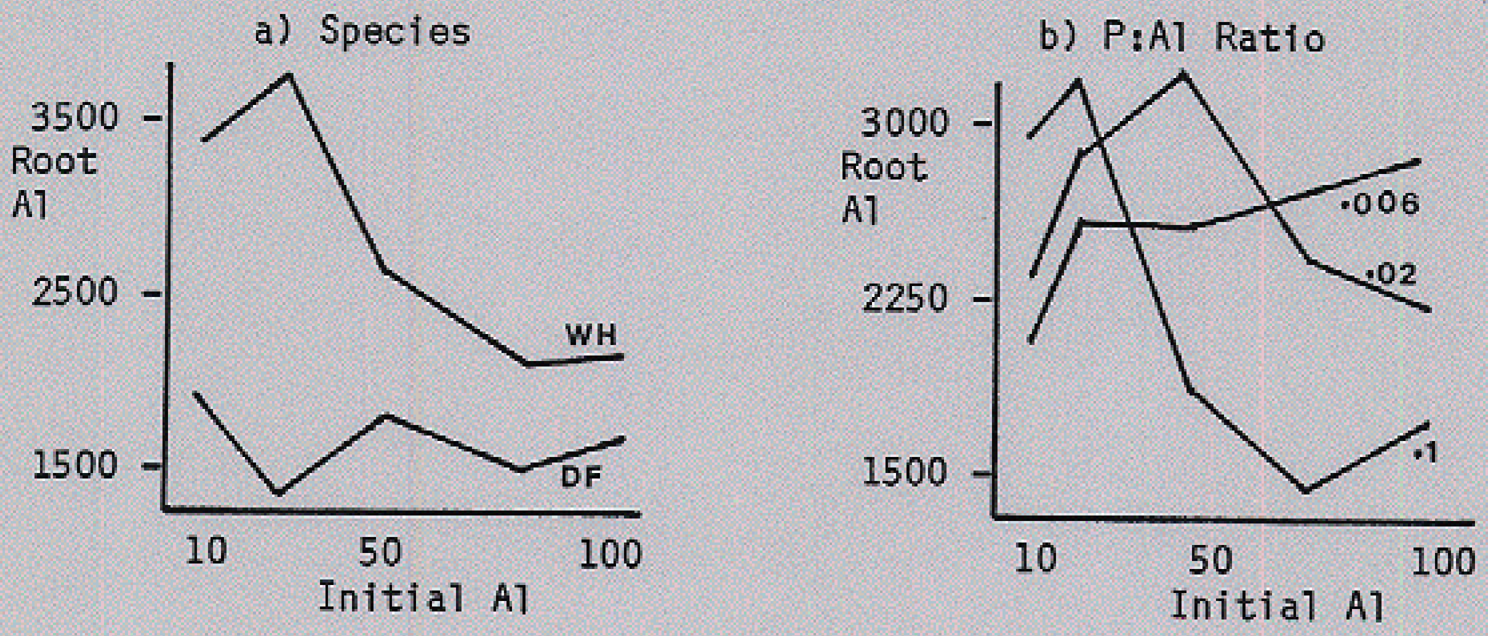


Fig. 4.9. The effect of increasing solution Al concentrations (ug ml^{-1}) on Douglas-fir (DF) and western hemlock (WH) mean root tissue Al concentration (ug g^{-1} dry weight) showing a) the difference between species and b) the influence of P:Al mole ratios.

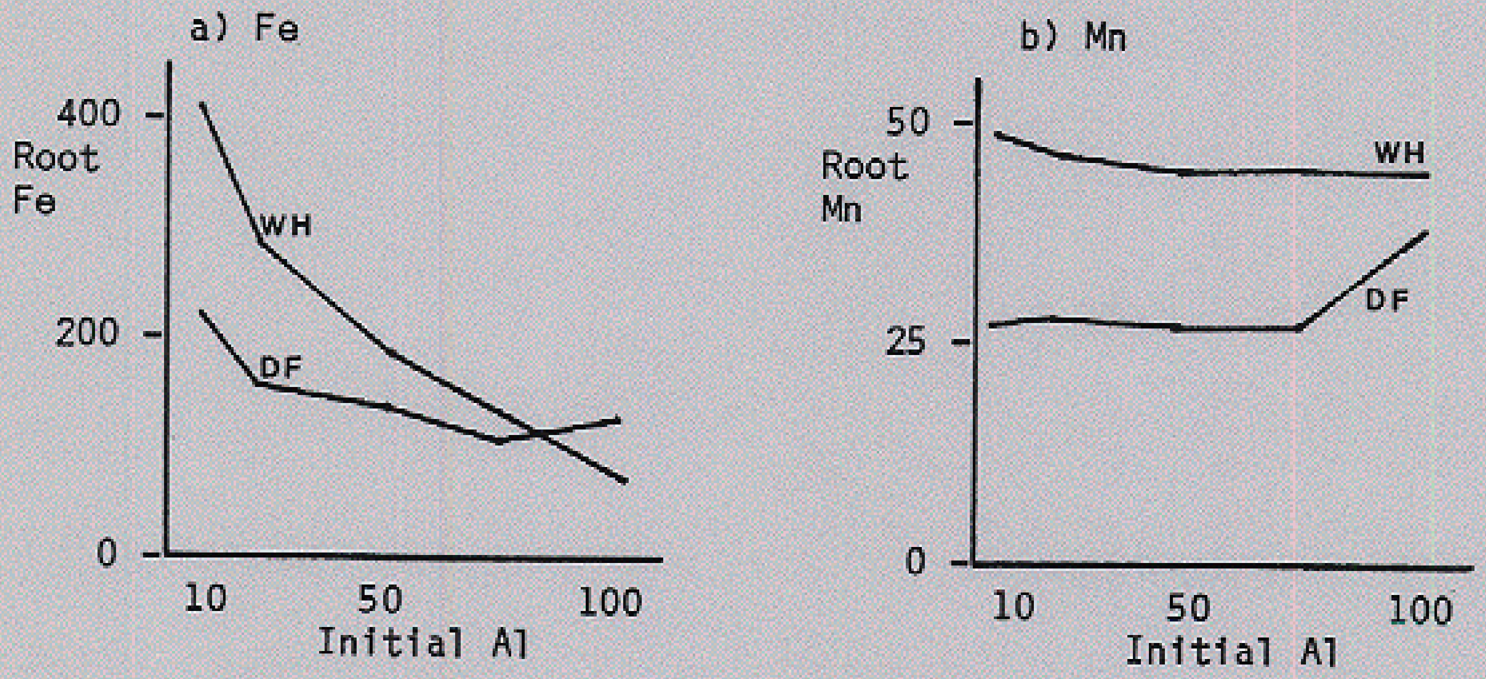


Fig. 4.10. Graphical representation of the species by initial Al concentration interaction in the P:Al ratio study for Douglas-fir (DF) and western hemlock (WH) a) root tissue Fe and b) root tissue Mn. Concentrations are in ug g^{-1} dry weight.

Table 4.25. Summary MANOVA table of the effect of initial Al concentrations and P:Al ratios on the foliar chemical composition of Douglas-fir and western hemlock seedlings.

		Significance of F									
Source	DF	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
Residual	29										
Replication	1	*	**	NS	**	NS	NS	NS	NS	**	**
Species (Sp)	1	**	**	**	**	**	**	**	**	**	**
Ratios	2	NS	**	NS	NS	NS	NS	NS	NS	NS	NS
Al Concentration (Alconc)	4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Sp by Alconc	4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Sp by Ratio	2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Alconc	8	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Sp by Alconc	8	NS	**	NS	NS	NS	NS	NS	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05, NS - non-significant

While there was a significant species difference in the mean foliar concentration of elements (Table 4.24), the only significant treatment effect was on foliar P levels. This was due to the P:Al ratio and was expected, since increasing the P:Al ratio increased solution P levels. Douglas-fir again had higher foliar concentrations of P, K, Mg, Zn, and Cu, and the lowest concentrations of Al, Ca, Mn, Fe and Na compared with western hemlock. It is worth noting that the concentrations of Al, Ca, Mn, and Na for western hemlock were virtually double those of Douglas-fir, so this difference between the two species is a major one under the treatment conditions of this experiment.

4.2.4. Effect of OH:Al Ratios

Initial experimental conditions for the OH:Al solution culture study, as well as percent relative root growth over the seven day treatment period are shown in Table 4.26. Unlike the previous solution culture experiments, in this experiment solution pHs increased with increasing solution Al for the 0.5 and 1.0 OH:Al mole ratios. This is evident from Table 4.1, and this pH change is a function of the OH:Al ratio. Activity of Al^{3+} was intermediate to the previous two studies. Aluminum speciation again revealed that all the Al added was in the monomeric form. This was unexpected, particularly at the higher pHs and Al concentrations, and this aspect is discussed in the following section. Like the preceding experiments there was good agreement between initial and final solution chemical composition and all pH differences were less than 0.2 pH units.

Table 4.26. Effect of initial Al concentration and OH:Al ratios on selected chemical properties of the solution culture and on relative root growth (%) of Douglas-fir and western hemlock seedlings.

OH:Al Mole Ratios	Initial Al Concentrations ug ml^{-1}				
	10 +(0.371)	25 (0.927)	50 (1.853)	75 (2.780)	100 (3.706)
			*Al^{3+} Activity ug ml^{-1}		
0	5.5 +(0.20)	11.35 (0.42)	18.7 (0.69)	24.1 (0.89)	28.9 (1.07)
0.5	5.3 (0.20)	11.1 (0.41)	17.7 (0.65)	22.5 (0.83)	26.3 (0.98)
1.0	5.3 (0.20)	10.6 (0.39)	16.7 (0.62)	21.0 (0.78)	24.6 (0.91)
			*Ionic Strength mM L^{-1}		
0	4.05	7.17	12.31	17.19	22.41
0.5	4.10	7.26	12.35	17.07	21.99
1.0	4.16	7.28	12.26	17.02	21.83
			Solution pH		
0	3.78	3.68	3.64	3.62	3.58
0.5	3.85	3.89	4.02	4.10	4.14
1.0	3.95	4.16	4.28	4.29	4.30
			Douglas-fir Relative Root Growth %		
0	29.8	27.6	15.4	8.5	2.8
0.5	34.6	27.1	29.7	20.6	12.8
1.0	34.6	40.4	31.4	24.3	13.7
			Western Hemlock Relative Root Growth %		
0	20.6	19.9	16.2	12.9	7.5
0.5	25.7	24.2	19.9	15.9	13.9
1.0	30.0	26.9	17.8	15.6	10.4

+ Values in brackets are concentrations in mM L^{-1}.

* Ionic strengths and free cation concentration data were obtained from program GEOCHEM (Sposito and Mattigod 1980). Activities were calculated using the equation of Guntelberg (Stumm and Morgan 1981) and data from GEOCHEM.

Results from the statistical analysis of the root data from the OH:Al study are presented in Table 4.27. The effect of varying the OH:Al ratios on root growth is clearly obvious from the number of highly significant terms for relative root growth. While all main effects were significant, there was also a significant interaction between species and initial solution Al concentration as well as species and OH:AL ratio. As a result of this interaction only the significant interactive terms are considered. The effects of initial solution Al concentration and OH:Al ratios on relative root growth are shown in Fig. 4.11. From this it can be seen that relative root growth was greater for Douglas-fir at all Al concentrations except at 100 ug ml^{-1}. The effect of increasing solution Al concentrations was to decrease root growth, however the rate of decrease was much greater in Douglas-fir (Fig 4.11). The effect of increasing the OH:Al ratio was to increase relative root growth. In other words, additions of NaOH to the culture solutions ameliorated the toxic effects of Al on root growth. While this effect was much greater for Douglas-fir than western hemlock when averaged over all solution Al concentrations, when individual treatment means are compared (Table 4.26) it can be seen that western hemlock's relative root growth exceeded that of Douglas-fir at initial solution Al concentrations above 25 ug ml^{-1} for the 0 OH:Al ratio. This difference in root growth cannot be entirely attributed to a pH effect because the experiment investigating the effects of pH in the absence of Al showed that for Douglas-fir there was no significant difference in relative root growth between pH 3.5 and 4.5.

Table 4.27. Summary MANOVA table of the effect of initial Al concentrations and OH:Al ratios on the chemical composition and relative growth of Douglas-fir and western hemlock seedling roots.

		Significance of F										
Source	DF	Rel. Root Growth	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
Residual	29											
Replication	1	*	*	*	NS	**	NS	**	*	**	*	NS
Species (Sp)	1	**	**	**	**	**	**	**	*	**	NS	*
Ratios	2	**	**	**	NS	NS	*	NS	**	*	NS	NS
Al Concentration (Alconc)	4	**	**	**	NS	NS	*	NS	**	*	NS	NS
Sp by Alconc	4	**	*	*	NS	NS	NS	NS	*	NS	NS	NS
Sp by Ratio	2	**	*	**	NS	NS	NS	NS	**	NS	NS	NS
Ratio by Alconc	8	NS	**	**	NS	NS	NS	NS	**	NS	NS	NS
Ratio by Sp by Alconc	8	NS	*	*	NS	NS	NS	NS	**	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05, NS - non-significant

While the interactive effect of Al and solution pH on relative root growth of Douglas-fir cannot be ruled out, linear regression analysis showed a high correlation between relative root growth and Al^{3+} activity for both species (r=0.85 for Douglas-fir and r=0.91 for western hemlock).

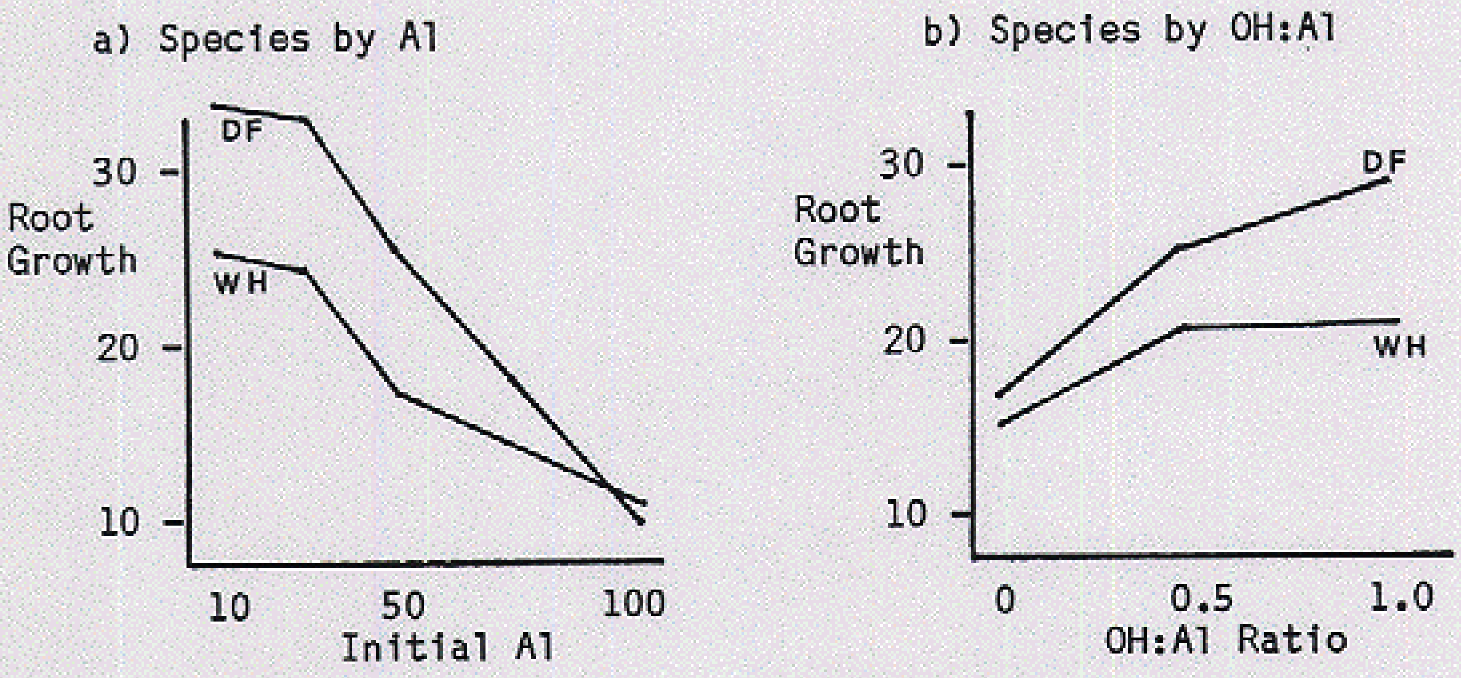


Fig. 4.11. Breakdown of the interaction between a) species by initial Al concentrations (ug ml^{-1}) and b) species by OH:Al ratios on the percent relative root growth of Douglas-fir (DF) and western hemlock (WH) for the OH:Al ratio study.

Plate IV shows the ameliorative effect of increasing the OH:Al mole ratio on Douglas-fir root growth. Note also the increased number of root branches at the highest OH:Al ratio; a similar effect was reported for increasing solution pH (section 4.2.1).

For root tissue Al, P, and Fe all terms from the MANOVA were significant (Table 4.27), and this indicates the complexity of the response pattern by the two species to changing solution Al levels and OH:Al ratios. Chemical analysis revealed unusually high concentrations

Plate IV. The ameliorative effect of increasing the OH:Al mole ratio on Douglas-fir root growth and morphology. Each group of three seedlings represents a single treatment. Treatments are, from left to right; 10 ug ml^{-1} initial solution Al concentration and 0 OH:Al ratio, 100 ug ml^{-1} initial solution Al concentration and 1.0 OH:Al ratio, and 100 ug ml^{-1} initial solution Al concentration and 0 OH:Al ratio. (Magnification 0.4x) of these elements at certain solution Al concentrations and OH:Al ratios (Appendix 10). While this is probably due to precipitation reactions at, or in the root, such effects make interpretation of the data difficult, particularly in light of the significant three-way interaction. As a consequence, the three-way interactions for root tissue Al, P, and Fe were examined by graphing the separate effects of initial solution Al concentrations and varying the OH:Al ratios. The results for Al and P are shown in Fig. 4.12 and Fig. 4.13.

For root Al concentrations the difference in response between the two species occurred at initial solution Al concentrations of 25 and 50 ug ml^{-1}. Douglas-fir root Al concentrations dropped to their lowest point at a solution Al concentration of 25 ug ml^{-1}, then rose progressively as solution Al concentrations increased to 75 ug ml^{-1}, before again declining. Alternately, western hemlock root Al concentration remained fairly constant up to a solution Al concentration of 25 ug ml^{-1}, dropped slightly at 50 ug ml^{-1}, rose to a maximum at 75 ug ml^{-1} and then fell sharply to the lowest root Al concentration at 100 ug ml^{-1} (Fig. 4.12). The effect of varying the OH:Al ratio on root tissue Al is also shown in Fig. 4.13, and the difference between the two species is clearly apparent. For western hemlock, root Al concentrations increased linearly with increases in the OH:Al ratio, yet this increase in root Al concentrations did not suppress root growth (Table 4.26). While Douglas-fir showed a similar increase up to the 0.5 OH:Al ratio, root Al concentrations dropped noticeably at 1.0 OH:Al ratio.

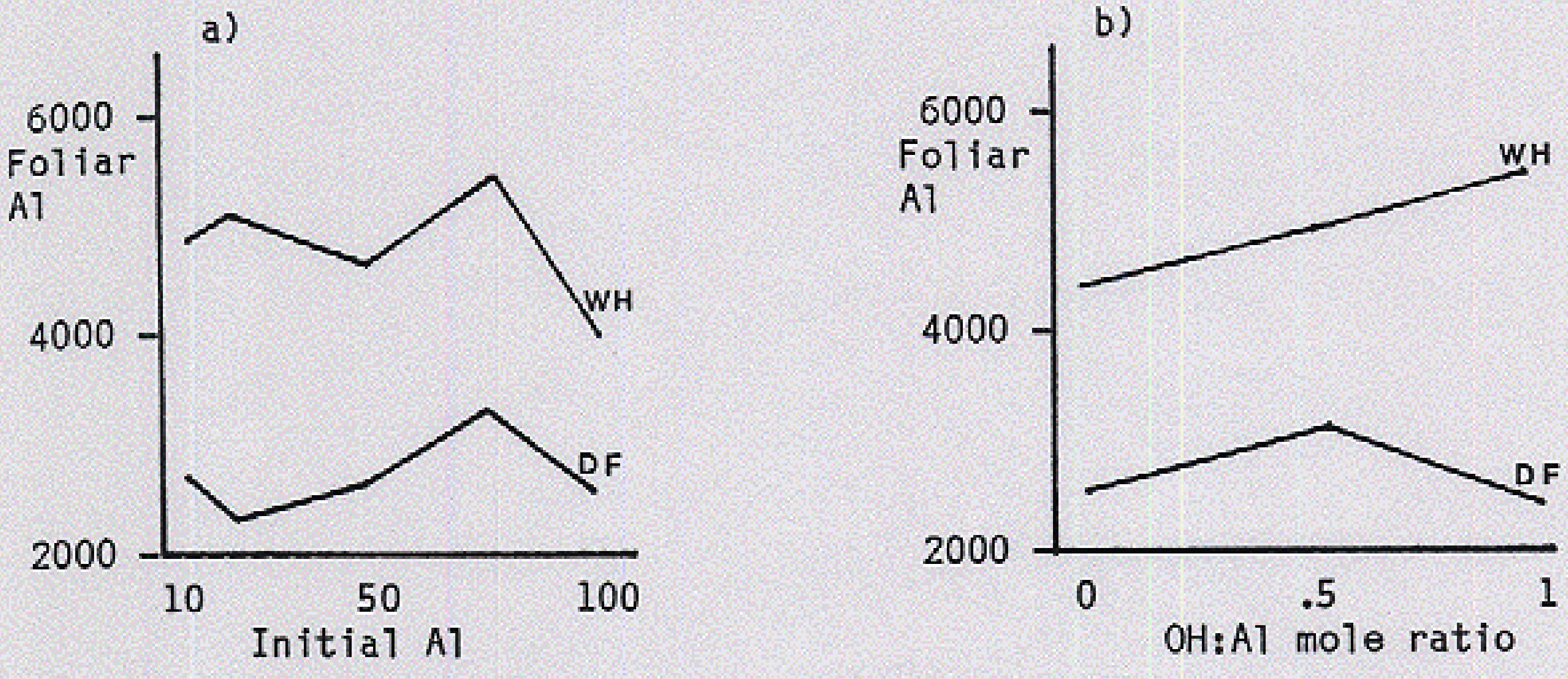


Fig. 4.12. The three-way interaction of species by solution Al concentration by OH:Al ratio for Douglas-fir and western hemlock root tissue Al concentrations (ug g^{-1} dry weight) showing the effect of increasing a) initial solution Al concentrations (ug ml^{-1}) and b) OH:Al mole ratios.

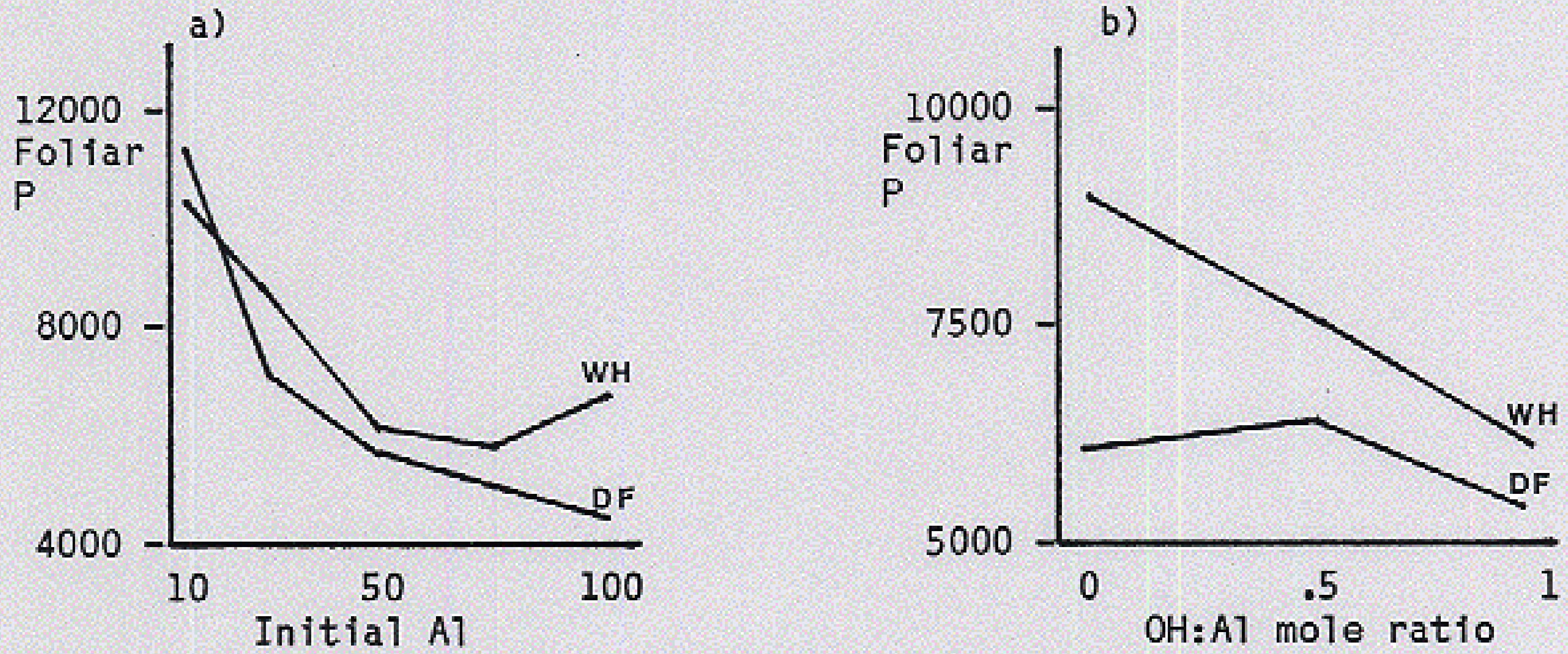


Fig. 4.13. The three-way interaction of species by solution Al concentration by OH:Al ratio for Douglas-fir and western hemlock mean root tissue P concentrations (ug g^{-1} dry weight) showing the effect of increasing a) initial solution Al concentrations (ug ml^{-1}) and b) OH:Al mole ratios.

Douglas-fir and western hemlock root P concentrations showed an almost identical response to solution Al concentration up to a concentration of 75 ug ml^{-1}. While root P concentrations continued to decline steadily beyond this in Douglas-fir, for western hemlock root P concentrations actually began to increase. This difference in response by the two species above a solution Al concentration of 75 ug ml^{-1} is most likely the main reason for the species by solution Al concentration interaction. From Fig. 4.13, the effect of varying the OH:Al ratio is readily apparent. But unlike root Al concentrations, root P concentrations in western hemlock decreased linearly as the OH:Al ratio increased, while for Douglas-fir the OH:Al ratio had no effect on root P concentrations.

The effects of initial solution Al concentrations and OH:Al ratios on root Fe concentrations in Douglas-fir and western hemlock are shown in Fig. 4.14. However, for Fe there is an interesting twist in the response pattern between the two species. While western hemlock had higher root Al and P concentrations over all solution Al concentrations and OH:Al ratios compared with Douglas-fir, this was not the case for Fe. Although western hemlock had the highest root Fe concentrations at the lowest solution Al concentration and OH:Al ratio, this was reversed at the higher solution Al concentrations and OH:Al ratios. Also, increasing solution Al concentrations above 50 ug ml^{-1} had little further effect on Douglas-fir root Fe concentrations, while for western hemlock root Fe concentrations continued to decline steadily.

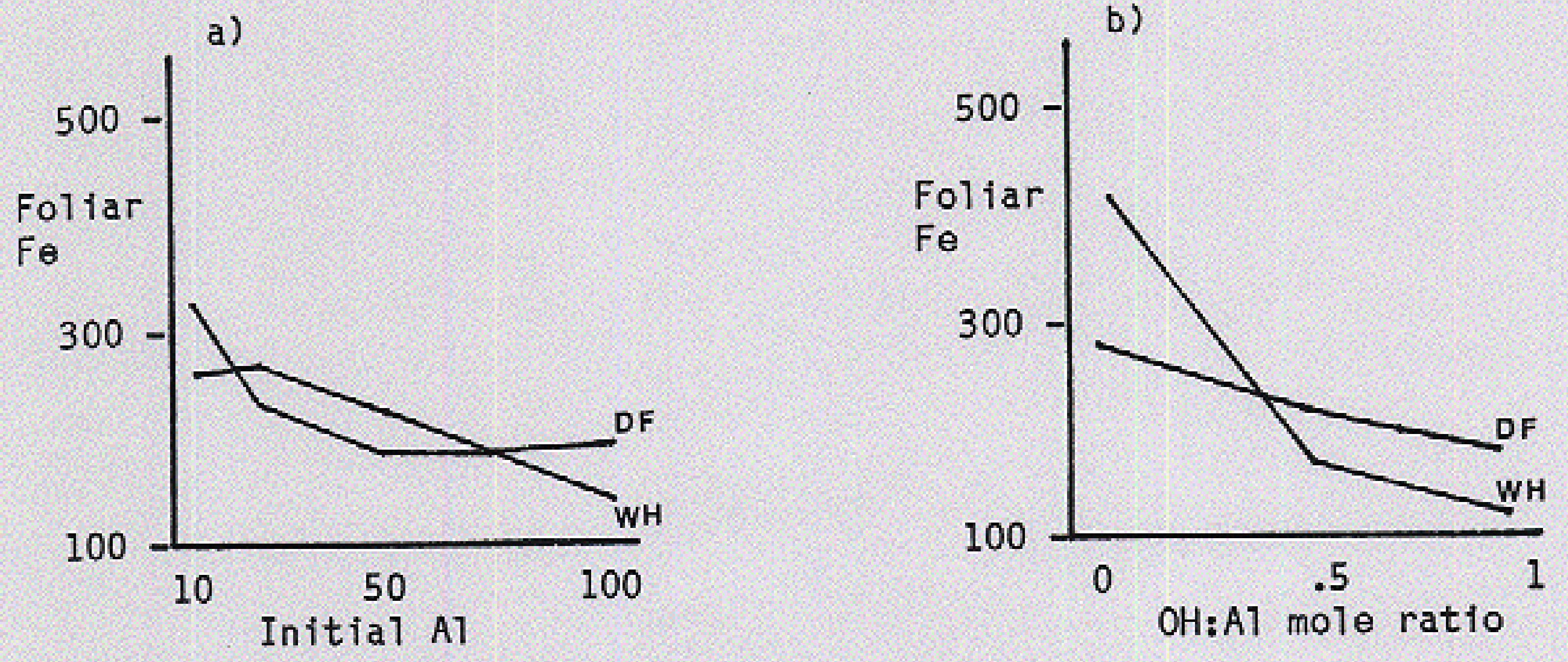


Fig. 4.14. The three-way interaction of species by solution Al concentration by OH:Al ratio for Douglas-fir (DF) and western hemlock (WH) mean root tissue Fe concentrations (ug g^{-1} dry weight) showing the effect of increasing a) initial solution Al concentrations (ug ml^{-1}) and b) OH:Al mole ratios.

Magnesium and Zn root concentrations also were significantly affected by treatment. But unlike root Al, P, and Fe, only the main effects of solution Al concentrations and OH:Al ratios were significant for Mg and Zn; there was no species interaction (Table 4.27). The general response pattern for both elements was that as the OH:Al ratio increased, root concentrations decreased. The effect of increasing solution Al levels was to cause an immediate drop in root Mg and Zn concentrations, followed by a gradual increase up to a solution Al concentration of 75 ug ml^{-1} before dropping to their lowest tissue levels.

There was a significant species difference in the root tissue concentrations of all ten elements. Douglas-fir had higher K, Zn, Cu and Na concentrations, and lower Al, P, Ca, Mg and Fe concentrations compared with western hemlock. The fact that P was higher in western hemlock root tissue is surprising as in all previous solution culture studies Douglas-fir had the highest P concentrations. This reversal of trends is probably related to adsorption/absorption of the unusually high concentrations of Al at or in western hemlock roots relative to Douglas-fir; such high Al concentrations would have the capacity to fix significant amounts of P.

Results from the statistical analysis of the foliar data are shown in Table 4.28. Initial solution Al concentrations and OH:Al ratios had a significant effect on foliar Al, P, K, and Fe concentrations. As solution Al concentrations increased so to did foliar Al concentrations, and the response pattern was the same for both species (there was no species by solution Al concentration interaction). But unlike root tissue Al concentrations, as the OH:Al ratio increased foliar Al concentrations decreased in western hemlock, while for Douglas-fir the OH:Al ratio had little effect on foliar Al concentrations. There was a significant main effect by the OH:Al ratio, as well as a significant species by solution Al interaction, on foliar P concentrations. As the OH:Al ratio increased, foliar P levels decreased, and this response was similar to that shown for root P levels (Fig. 4.15). For the species by solution Al concentration interaction, as solution Al concentration increased so to did foliar P concentrations in western hemlock. However, in Douglas-fir this trend was almost the opposite; a rapid decrease in foliar P levels occurred as solution Al concentrations approached 50 ug ml^{-1}, after which they varied little.

Table 4.28. Summary MANOVA table on the effect of initial Al concentrations and OH:Al ratios on the foliar chemical composition of Douglas-fir and western hemlock seedlings.

		Significance of F									
Source	DF	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
Residual	29										
Replication	1	NS	**	*	NS	NS	NS	NS	**	**	NS
Species (Sp)	1	**	**	**	**	**	**	**	**	**	**
Ratios	2	**	*	NS	NS	NS	NS	NS	NS	NS	NS
Al Concentration (Alconc)	4	**	NS	NS	NS	NS	NS	NS	NS	NS	NS
Sp by Alconc	4	NS	*	**	NS	NS	NS	**	NS	NS	NS
Sp by Ratio	2	**	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Alconc	8	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ratio by Sp by Alconc	8	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

** - significant at a=0.01, * - significant at a=0.05, NS - non-significant

Both K and Fe had significant species by solution Al concentration interactions. For western hemlock, foliar K concentrations decreased steadily as solution Al concentrations increased, while for Douglas-fir foliar K concentrations increased somewhat up to an initial solution Al concentration of 25 ug ml^{-1}, and then plateaued. The effect of solution Al concentrations on foliar Fe concentrations was nearly the opposite for the two species. As solution Al concentrations increased, foliar Fe concentrations decreased steadily in western hemlock. However, in Douglas-fir foliar Fe concentrations increased up to a solution Al concentration of 75 ug ml^{-1}, at which point Douglas-fir foliar Fe concentrations decreased at an almost identical rate compared with western hemlock.

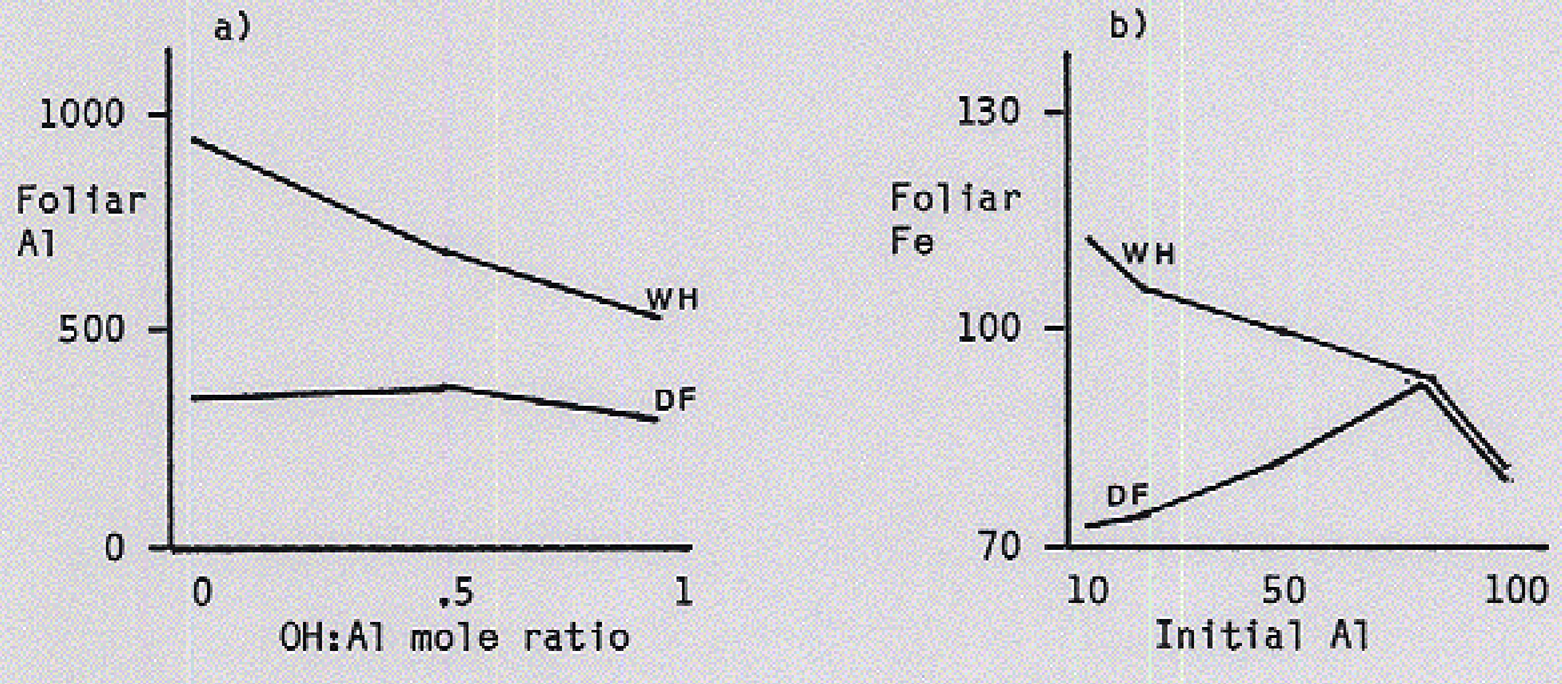


Fig. 4.15. Douglas-fir (DF) and western hemlock (WH): a) species by OH:Al ratio interaction showing the effect of increasing OH:Al mole ratios on foliar Al concentrations (ug g^{-1} dry weight); and b) species by Al concentration interaction showing the effect of increasing initial solution Al concentrations (ug ml^{-1}) on foliar Fe concentrations (ug g^{-1} dry weight).

There was a significant species difference in the foliar concentrations for all ten elements. On a relative basis western hemlock always had higher Al, K, Ca, Mg, Mn, Fe, Cu and Na concentrations, and lower P and Zn concentrations compared with Douglas-fir. Although western hemlock had higher root P levels, this was not reflected in the foliage, supporting the earlier statement that much of the root P in western hemlock was probably "fixed" as a consequence of high root Al levels.

4.2.5. Morphology - Foliage and Roots

There were no obvious foliage symptoms to increasing acidity or Ca:Al mole ratios in Douglas-fir and western hemlock. However, for the OH:Al and P:Al ratio experiments a number of symptoms were evident by the end of the seven day period. Douglas-fir foliage showed clear symptoms of necrosis from the apex of the cotyledons, grading into a distinct chlorotic band. For western hemlock, symptoms consisted mainly of necrosis in the cotyledons and then extending to the first flush of needles.

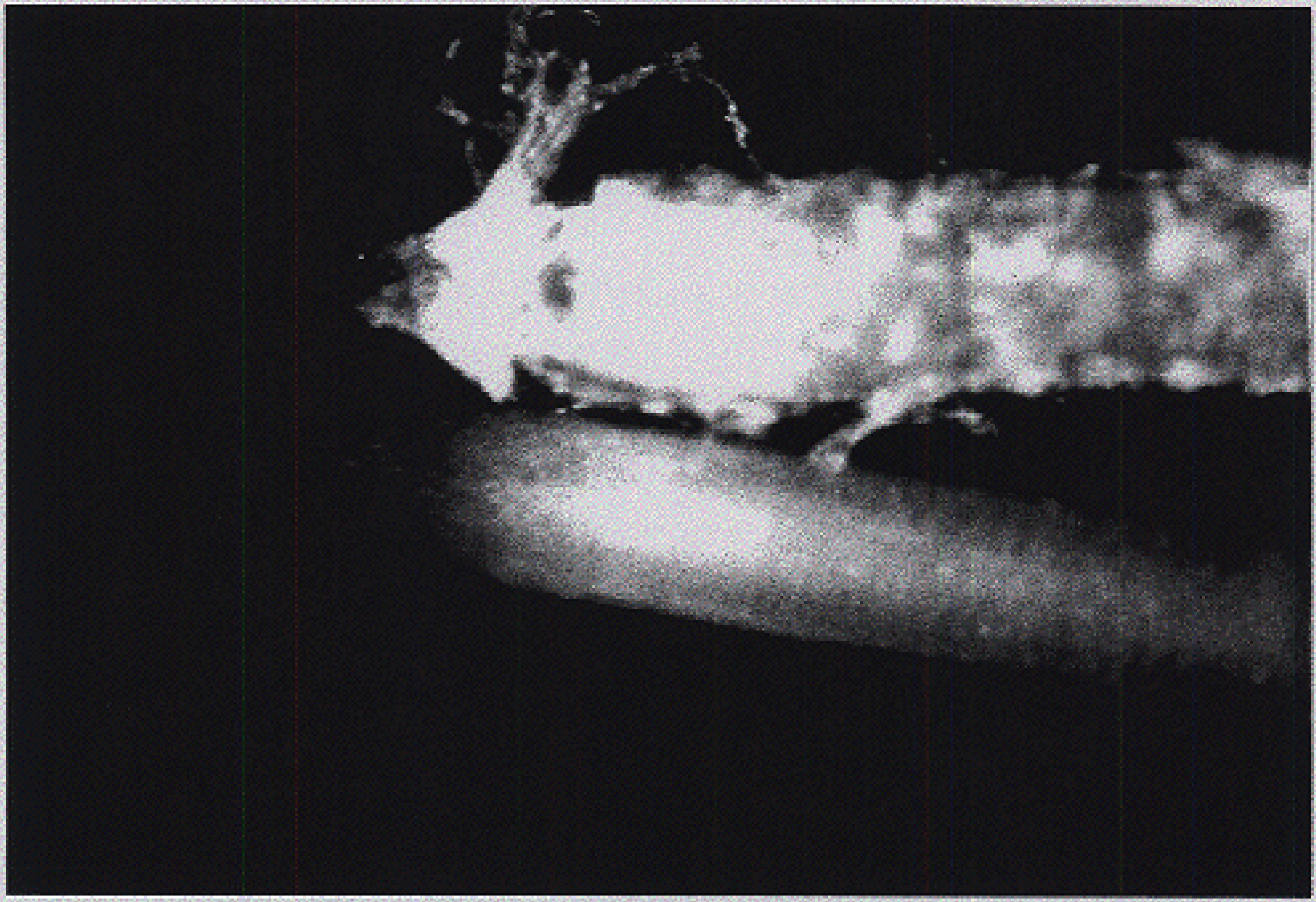
Symptoms of increased acidity on root morphology were most apparent at pH 3.0 (eg. Plate I). At the end of the seven day treatment period there was little evidence of active root elongation in Douglas-fir, and the entire root was dull brown in color, brittle, stunted, and with little root branch development. The only symptoms of pH on western hemlock root morphology was a noticeable fading of the crimson color of the root cap at pH 3.0. Regardless of solution pH, no root hair development was observed in either species.

There were no symptoms of Al toxicity on root morphology in Douglas-fir and western hemlock at solution Al concentrations of 10 and 25 ug ml^{-1}, except for Douglas-fir at the 0.03 Ca:Al ratio, where symptoms resembled those reported for pH 3.0 in the absence of Al. Plate V shows Douglas-fir (upper) and western hemlock root morphology at a solution Al concentration of 10 ug ml^{-1} and 0 OH:Al mole ratio. The crimson root cap and translucent zone of elongation in western hemlock, and the white silky color of the Douglas-fir root tip were indicative of actively growing roots.

At solution Al levels above 25 ug ml^{-1} a number of symptoms related to Al toxicity became evident, with maximum morphological development occurring at solution Al concentrations of 100 ug ml^{-1} for the 0.03 and 0.15 Ca:Al ratios, the 1.0 P:Al ratio, and the 0 OH:Al ratio. At the end of seven days, Douglas-fir roots were brittle, stunted, and with mottled brown bands of discoloration; bulbous, club-like root tips were common. When viewed under a dissecting microscope there was a distinct disintegration of the epidermal layer (Plate VI) and an absence of root hairs. For western hemlock the overall symptoms were similar to those reported for Douglas-fir, except for lighter shades of mottling; disintegration of the root tip was most pronounced in western hemlock (Plate VI).

Plate V. Morphological features of western hemlock (upper) and Douglas-fir (lower) roots grown at 10 ug ml^{-1} solution Al concentration and 0 OH:Al mole ratio. (Magnification 25x)

(a)



(b)

Plate VI. The effect of 100 ug ml^{-1} initial solution Al concentration and 0 OH:Al mole ratio on western hemlock (a) and Douglas-fir (b) root morphology. Lower root in Plate VI (a) is western hemlock grown at 10 ug ml^{-1} solution Al and 0 OH:Al mole ratio. (Magnification 25x)

4.2.6 Discussion - Solution Culture Studies

Addition of Ca or OH to the solution cultures did indeed ameliorate the effects of Al toxicity on Douglas-fir and western hemlock root growth, supporting hypothesis 2 in regard to Ca and OH. The ameliorative effect of Ca on the root growth of both species is particularly evident when comparing the 0.03 and 0.15 Ca:Al mole ratio. The reduced root growth of Douglas-fir at a solution Al concentration of 10 ug ml^{-1} and 0.03 Ca:Al ratio most likely reflects a Ca deficiency (the solution Ca concentration was only 0.5 ug ml^{-1}). At solution Al concentrations of 50 ug ml^{-1} and greater, the ameliorative effect of increasing Ca was clearly apparent (Table 4.20) and supports previous findings reported for crop plants (Johnson and Jackson 1964, Clarkson and Sanderson 1971). An aspect of particular relevance from Table 4.20 is that at Ca:Al mole ratios of 0.03 and 0.15, relative root growth of western hemlock exceeded that of Douglas-fir. This suggests that western hemlock may be more Al tolerant at low solution Ca concentrations compared with Douglas-fir. Ryan (1986a,b) reported that Douglas-fir was more tolerant of high Al concentrations (although both species were regarded as highly Al tolerant). However, the Ca concentrations of the solution cultures used by Ryan (1986a,b) were 16 and 5 ug ml^{-1} respectively, much higher than the Ca concentrations of the 0.03 Ca:Al mole ratio of this study. One of the mechanisms of Al tolerance is that plants may have a more efficient mechanism of Ca absorption and translocation, or else require lower levels of Ca (Foy 1984). Western hemlock always had higher tissue Ca levels compared with Douglas-fir, indicating that western hemlock may indeed have a greater ability to absorb and translocate Ca (eg. Fig 4.7).

Also, the large increase in root growth of Douglas-fir at the 0.75 Ca:Al ratio coincided with a sharp increase in tissue Ca, supporting not only the suggestion that Ca can ameliorate the toxic effects of Al, but also that Douglas-fir's tolerance to Al may be dependent upon higher levels of Ca compared with western hemlock. Ryan (1986a) had previously related western hemlock's tolerance of acid-Al conditions to it's low tissue requirements of Ca compared with Douglas-fir, and this is supported from the results of this study.

The ameliorative effect of the addition of Ca to solutions containing Al can be via two mechanisms. Firstly, by reducing the activity of Al due to solution ionic strength effects, and/or secondly, due to the physiological effect of increased Ca:Al ratios on the ability of Ca to compete with Al for membrane binding sites. However, when linear regression analyses were carried out root growth was poorly correlated with Al^{3+} activity ($R=-0.32$ and $R=-0.33$ for Douglas-fir and western hemlock respectively). Hence the ameliorative effect of Ca in this study is attributed mainly to its physiological effect.

Like Ca, the addition of OH to culture solutions containing Al had a significant ameliorative effect on root growth, particularly for Douglas-fir. This effect was most pronounced when the 0 and 0.5 OH:Al mole ratios were compared. Unlike Ca however, the addition of OH (as NaOH) did not involve changes in the concentration of essential elements in the solution culture. While the addition of OH raised solution pH and ameliorated the toxic effect of Al, it could not be determined whether this was due to differential toxicity of mononuclear Al species, or a physiological response to a pH and Al interaction (ie., increased susceptibility to Al as pH decreases).

Blamey et al. (1983) reported a similar ameliorative effect by OH on Al toxicity for soybean root growth and attributed this to a reduction in the concentration of monomeric Al in solution. In this study however, when solution Al was speciated all the Al was in the monomeric form. Because the addition of OH to the solution culture altered both pH and Al^{3+} activity, linear regression analysis was carried out to determine which of these two changes were most highly correlated with root growth. For Douglas-fir and western hemlock there was a high negative correlation between root growth and Al^{3+} activity ($R=-0.85$ and $R=-0.91$ respectively), and a low correlation with pH ($R=0.31$ for Douglas-fir and $R=0.06$ for western hemlock).

While the results from the linear regression analyses cannot be regarded as definitive evidence that Al^{3+} activity was the major factor influencing root elongation of Douglas-fir and western hemlock, nonetheless the results from the pH experiment showed that over the range 3.5 to 4.5 pH had no significant effect on root growth in both species and this corroborates results from the linear regression. These results are further supported by the earlier findings of Adams and Lund (1966) who reported that $Al^{3}+$ activity was highly correlated with the failure of cotton roots to penetrate acid subsoils, and by the more recent findings of Pavan and Bingham (1982) who reported that cotton root growth in solution culture (pH 4.0) was also highly correlated with Al^{3+} activity ($r=-0.99$).

Increasing the P:Al ratio did not ameliorate root growth in either Douglas-fir or western hemlock. Hence, under the treatment conditions used in this experiment, the hypothesis that additions of P to solutions containing Al can ameliorate root growth is rejected. While the growth results for the 0.025 P:Al ratio would suggest some ameliorative effect this was statistically not significant. The overall effect of increasing the P:Al ratio was to depress root growth, the opposite to that found by increasing the Ca:Al and OH:Al ratios.

Although these results appear to conflict with reports in the literature which indicated that the addition of P to solution cultures reduced the toxic effects of Al (Rorison 1958, Blamey et al. 1983, Bollard 1983, Alva et al. 1986), closer inspection of the data in Table 4.23 brings to light two important and related aspects that resolve much of this conflict. Increasing the P:Al ratio <u>increased</u> the Al^{3+} activity due to the <u>increased</u> acidity of the solution from the additions of P. Linear regression analysis showed a high correlation between root growth and Al^{3+} activity for Douglas-fir (R=-0.91) and western hemlock (R=-0.85). But unlike the previous Ca:Al and OH:Al ratio experiments, in the P:Al experiment root growth was also highly correlated with increasing solution pH (R=0.85 for both species).

It was suggested previously for the OH:Al ratio experiment that western hemlock may be more tolerant of Al at low pH compared with Douglas-fir. For that experiment however, there was no consistent change in solution pH with increasing Al concentration <u>and</u> increasing OH:Al ratios because of the 0 OH:Al ratio. But, in the P:Al ratio experiment this pH change was consistent and further, this change was about 1.0 pH units; there is a very strong indication in the P:Al ratio experiment that western hemlock may indeed be more tolerant of Al at low pH compared with Douglas-fir. Although this is confounded somewhat by the changes in solution P concentrations due to changes in the P:Al ratio (there may have been a species by P interaction), nevertheless as a generalization, at pHs less than about 3.8 western hemlock root growth was greater than that of Douglas-fir for each respective Al concentration.

Criticism has been leveled by a number of authors (Bollard 1983, Blamey et al. 1983, Alva et al. 1986) at solution culture experiments examining the toxic effects of Al because of the high solution P concentrations used in many of these experiments. According to these authors, this makes prediction of the actual toxic level of Al difficult and inaccurate because at solution P concentrations greater than about 1 ug ml^{-1} Al may be precipitated as aluminum phosphate. For instance, Munns (1965) suggested that solution P concentrations should be less than 0.7 ug ml^{-1} for a solution pH range 4.0 to 4.2 so as to avoid Al precipitation. In all the experiments in this study, Al speciation revealed that all the added Al was in the monomeric form, and hence still in solution. Further, when solutions were passed through columns containing highly acidic cation exchange resin (as a check on the speciation results), less than 5% of the added Al passed through the exchange column. This would indicate that for the duration and pH range over which these experiments were run no significant aluminum phosphate precipitation occurred.

Ferguson and King (1978) in a well presented review on the precipitation of P in waste water, reported that the pH range in which aluminum phosphate precipitation takes place was about 4.0 to 7.5, with greatest precipitation occurring between pH 5.0 and 6.0. While their results lend support to the results from this series of experiments in which pH was always less than 4.5, and mostly less than 4.0, there is an aspect of the paper by Ferguson and King (1978) that may be of importance to this study. These authors reported that at pHs less than 5.5 and with P in solution, the predominant form of P is the ion pair complex $AlPO_4^{2+}$. Thus it is possible that the Al speciation results may have included the Al from this ion pair. Because Al^{3+} activity was calculated based on results from Al speciation results as well as results from program GEOCHEM, the reported levels of Al^{3+} activity may be higher than that actually in solution. While the arguments of Blamey et al. (1983), Bollard (1983), and Alva et al. (1986) are valid, the paper by Ferguson and King (1978), as well as more recent reports by Robson and Pitman (1983), support the results from this study that Al precipitation was unlikely to have been a major confounding factor due to the low solution pHs used in these experiments.

For all three ratio experiments, the overall effect of increasing solution Al concentration was to decrease root growth in Douglas-fir and western hemlock. However, for the Ca:Al ratio experiment a consistent synergistic effect by Al at low concentrations was observed. Such an effect also was observed by Ryan (1986a,b) for Douglas-fir and western hemlock, and Foy (1984) cites numerous examples of this for crop plants. It is not clear why this effect was only evident for the Ca:Al ratio experiment (there was one other occurrence of this for Douglas-fir at the 1.0 OH:Al ratio), though the short term nature of these experiments or the changes in solution pH due to treatment effects may have restricted such effects from being manifested.

However, very high tissue Cu levels were recorded for both Douglas-fir and western hemlock in the pH experiment and in all three ratio experiments. At the low pHs of the solution cultures used in the experiments the "optimum" ratios of Ingestad (1979) may no longer be optimum due to the increase in activity of some elements, particularly Cu, which may be approaching toxic levels. Therefore, the "synergistic" effects of low Al levels may be related to a reduced Cu uptake due either to Al competing with Cu for common uptake sites, or by reducing Cu activity in solution due to increased solution ionic strength from the addition of Al. Although the tissue Al levels of both species were high, no one ratio study resulted in higher tissue Cu levels than those recorded for the most acid treatment of the pH study. This probably reflects the effect of Al on Cu uptake by Douglas-fir and western hemlock and the increasing ionic strength of the treatment solutions due to addition of Al. Thus, the high tissue Cu levels in both species are regarded as an overall effect of low solution pH, and the differences in pH within and between the various ratio studies are unlikely to have altered this overall pH effect.

Increasing solution Al levels did not lead to an increase in root Al concentrations. In fact the effect was the opposite, especially in western hemlock. For the Ca:Al ratio experiment there was a marked and immediate decrease in root Al concentrations after which they declined more slowly before levelling out. This effect was consistent for both species. A similar effect was also observed for western hemlock in the P:Al ratio experiment, although Douglas-fir showed no real effect to increasing solution Al concentrations. For the OH:Al ratio experiment, again there was no consistent response to increasing solution Al concentrations in Douglas-fir, while for western hemlock the lowest root Al levels occurred at the 100 ug ml^{-1} solution Al concentration; for this experiment the inconsistent results for both species are believed to reflect the differences in solution pHs as the OH:Al ratios increased from 0 to 1.

The antagonistic effect of increasing solution Al levels on root Al concentrations is explained as follows. At low levels (<25 ug ml^{-1}) Al was absorbed into the root cells and had little effect on root physiology. However, as solution Al levels increased above this, root cells began to break, down or membrane permeability was progressively reduced, such that Al began to leak out of the root tissue, particularly from the apoplast. As solution Al levels increased even further (>50 ug ml^{-1}), the epidermal layer and cortical cells (ie. the bulk of the apoplastic region) began to disintegrate, releasing cellular Al back into the bulk solution. This scenario appears reasonable, particularly in light of the effects of high solution Al levels on root morphology shown in Plate VI. The lack of a consistent response in Douglas-fir probably also reflects a greater resilience by this species to the disruptive cellular effects by Al; from Plate VI the disintegration of the epidermis was not as extensive as that in western hemlock.

The trend of decreasing root Al concentrations with increasing amounts of Al in solution raises a major issue. Previous studies investigating the effects of Al on tree species (McCormick and Steiner 1978, Steiner et al. 1980, Schier 1985, Ryan 1986a,b) have all suggested extremely high levels of Al tolerance. Yet from this study, if the suggestion that the decrease in root Al levels is indeed related to the physiological breakdown of the epidermal and cortical cells (as indicated in Plate VI), tolerance to Al may be at a much lower level than that previously reported. Only the short term nature of the experiments in this study prevented more obvious symptoms from becoming apparent at low solution Al concentrations.

Unlike the effect on root Al levels, as solution Al concentrations increased so to did foliar Al levels. This was consistent over all the experiments involving Al, although in the P:Al ratio experiment this effect was only significant at p=0.06.

Neither root Zn, Cu, nor Na concentrations were influenced by solution Al levels or Ca:Al and P:Al ratios. Of the three elements only root Zn concentrations were reduced by increasing OH:Al ratios and increasing levels of solution Al. The reason for the OH:Al ratio effect is uncertain as pH _per se_ had no significant effect on root Zn concentrations. A noticeable feature of the results was that root Fe and P levels were depressed by increasing amounts of Al in solution; while this trend was consistent for both species, such antagonistic effects were most pronounced in western hemlock. Ryan (1986a,b) reported an antagonistic effect by Al on root Ca, Fe, Mn, and Cu concentrations in Douglas-fir and western hemlock. Although such an effect was only found to be statistically significant (a=0.05) for root P and Fe levels in this study, it must be remembered that treatments were over seven days, while those of Ryan (1986a,b) exceeded 45 days. As well, there was a major difference in seedling size between the two studies.

An interesting effect arising from increasing the Ca:Al ratio was the depression of root K, Mg, and Mn levels. This effect occurred only for the Ca:Al ratio study and may reflect the increased levels of Ca in solution competing for uptake sites, or else depressing the activity of K, Mg, and Mn in solution. Such findings have been reported by Mengel and Kirkby (1982) and Robson and Pitman (1983).

The effect of increasing the Ca:Al, P:Al, and OH:Al ratios, as well as increasing the amount of Al in solution, must be viewed with reference to the effect solution pH *per se*. In the pH experiment , increasing acidity decreased root levels of Al, Ca, Mg, Mn, Fe, and Cu in both species. Such an effect by low pH (high H^+ ion concentrations) on root cation levels has been commonly reported (Moore 1974, Kinzel 1983, Foy 1984), and has been attributed to the effect of excess H^+ ions on root membrane permeability, competition with other cations for uptake sites, interference with ion transport, and inducing membrane leakiness (Mengel and Kirkby 1982, Foy 1984, Marschner 1986). As well, root P levels in western hemlock were also significantly depressed by increasing solution acidity. Thus the effect of any Al treatment on root and foliage nutrient levels must be viewed in two parts. Firstly, did treatment application depress solution pH below some threshold level? Secondly, were root or foliage nutrient levels similar with and without Al present in solution?

Increasing the Ca:Al ratio had little effect on solution pH, while increasing the P:Al and OH:Al ratio had opposing effects; increasing the P:Al decreased solution pH, whereas increasing the OH:Al ratio increased pH. When the mean root tissue nutrient levels of each of the four studies are compared (Appendices 7 to 10), the presence of Al in the solution cultures did indeed have an effect over and above that which could be directly related to pH alone. Root tissue Ca, Mg, Fe, Zn, and Cu levels were lower for all experiments where Al was added to the solutions. However, because of the confounding nature of the data (ranges in solution pH, treatment effects on solution Ca and P concentrations, absence of a zero Al control for the three ratio studies) no statistical analyzes of the data were carried out. Even so, the overall trends in the data are supported by the consistency of the results for both Douglas-fir and western hemlock, and from reports in the literature. For instance, Ryan (1986a) found a significant antagonistic effect by Al on root Ca, Mg, Fe, and Cu levels in Douglas-fir and western hemlock, and Foy (1984) cites similar examples for a range of crop plants.

Due to the overall variability in the data, no definitive comment can be made when comparing the pH and Al effects on root P and K levels. However, unlike the results reported by Ryan (1986a) there was no dramatic reduction in the root tissue levels of P or K when Al was present in the solution culture.

From the results in Section 4.2.1, pH had no effect on root Zn concentrations in Douglas-fir and western hemlock. Hence it would be reasonable to expect that over the range of pHs in the experiments incorporating Al, root Zn levels should be comparable with those from the pH experiment. This was not the case when the data in Appendices 7 to 10 were compared. Both Douglas-fir and western hemlock had markedly lower root Zn levels in the presence of Al, and for western hemlock root Zn levels were found to be significantly lower than those of Douglas-fir, yet there was no significant species difference in the absence of Al. However, the overall significance of the effect of Al on root Zn levels is indeterminate; when the foliar data were compared there was little evidence that the presence of Al in solution had any marked effect on foliar Zn levels in either species, though Douglas-fir always had the highest foliar Zn levels.

Treatment effects on foliar nutrient concentrations were not as evident as those for roots. Also, there were no pronounced differences in foliar nutrient levels when the pH treatment was compared to the Ca:Al, P:Al, and OH:Al ratio experiments. This is a reflection of the short duration of the various experiments. For the OH:Al experiment, foliar P, K, and Fe levels were significantly depressed by increasing amounts of Al in solution, and this was most obvious for western hemlock. A similar effect for both species was also evident in the Ca:Al ratio study. This is consistent with reports in the literature (Alam and Adams 1979, Foy 1984, Ryan 1986a,b, Pegtel 1986, Marschner 1986), and has been related to the interference by Al with the reduction of Fe^{3+} to Fe^{2+} (Kinzel 1983, Foy 1984). Grime and Hodgson (1969) hypothesized the existence of a constitutive binding (chelating) system whereby plants can detoxify Al. But as indicated by Kinzel (1983), plants with a large capacity for binding trivalent ions may also bind a relatively large fraction of Fe^{3+}; under conditions of limited Fe supply and in the presence of Al, plants may bind sufficient Fe to cause an Al-induced Fe deficiency. Kinzel (1983) outlines some of the ecologically important aspects of the Al-Fe interaction in plants.

The morphological symptoms of Al toxicity found in this study are similar to those reported in the literature (McCormick and Steiner 1978, Steiner et al. 1980, Foy 1984, Ryan 1986a). While morphological symptoms at moderate solution Al concentrations could not be easily discerned from those related to pH or low Ca levels (root brittleness, brown discoloration, and stunted growth), at higher solution Al levels (>50 ug ml^{-1}) the influence of Al on root morphology could not be mistaken. Common symptoms included bulbous, club-like root tips, distinct mottling and discoloration in the region of the primary meristem, and disintegration of the epidermal layer in the region of the root tip (Plate VI). The development of such morphological symptoms in the presence of Al was rapid, often evident in under three days. This is much more rapid than that reported by Ryan (1986a). However, in this study, Douglas-fir and western hemlock seedlings were only five weeks old whereas those used by Ryan (1986a) were one year old. Thaworuwong and Van Diest (1974) reported that younger seedlings were generally more susceptible to Al than older plants, and this is borne out when the results of this study are compared to those reported by Ryan (1983, 1986a).

CHAPTER V

SUMMARY AND EVALUATION OF THE HYPOTHESES

5.1 Summary of Results

The distinguishing features of the Oregon and Washington coastal soils include high acidity, low exchangeable bases and high exchangeable Al. Under such conditions Al can dominate the soil solution, and this Al domination can be a major factor influencing plant growth. Two experiments were initiated to investigate the role of Al in the growth and nutrition of two commercially important tree species, Douglas-fir and western hemlock. The first experiment was an *in situ* fertilizer trial at four coastal locations to determine whether applications of N, P, or N+P would result in significant growth responses of the species. The second experiment was a series of solution cultures to determine whether increasing Ca:Al, P:Al, and OH:Al mole ratios could ameliorate effects of Al on Douglas-fir and western hemlock root growth. This chapter concatenates the results of the two experiments into a concise summary to evaluate the hypotheses presented in Chapter I.

To state that coastal soils of Oregon and Washington are infertile would oversimplify a complex ecological system. While these soils have a number of properties indicative of good tree growth (high total P, relatively high levels of soil N, low C:N ratios, relatively deep soil profiles and good moisture holding capacity), they are dominated by Al. As outlined in the literature review, high levels of reactive Al in the soil can have a profound influence on soil fertility and plant growth. Aluminum dominance in the coastal soils is almost certainly the major factor responsible for the high level of P sorption (>93%) found in this study. Chemical properties of these soils show striking similarities to those of the nonallophanic Andosols of Japan. Properties of such Japanese soils (Al dominated exchange system, high P sorption, low base status) are a major deterrent for plant growth.

High P sorption capacity of these soils has a number of important management implications. When growth data from the coastal study were evaluated, P application always resulted in a significant, positive growth response, <u>but only in Douglas-fir</u>. In this study all fertilizers were spot applied and hence the effect of P sorption was reduced. However, broadcast applications of highly soluble P fertilizers on the coastal soils will result in considerable amounts being adsorbed onto soil sorption sites, thus reducing the efficiency of such applications. Instead, spot applications at, or shortly after planting, or broadcast application of less soluble P fertilizers (eg. rock phosphate) may be a better management alternative. Also, application of large amounts of N were found to depress foliar P levels in Douglas-fir and this may explain some of the inconsistent responses to N application previously reported for Douglas-fir growing in these soils. Based on data from this study, application of N alone is unlikely to result in large growth responses, and under current conditions would not appear to be an efficient management practice.

Although the response by Douglas-fir to P applications was consistent over all sites, the magnitude of the response for the "best" treatment (N2P2) was lower on burnt sites (26%) compared with unburnt sites (52%). However, the diminution of response to fertilizer application on burnt sites was due to increased growth of the control plots, and this was probably due to increased levels of available P as a result of slash burning.

Unlike Douglas-fir, growth response by western hemlock to fertilizer application was inconsistent; there was an absence of a strong growth response to P, as well as a depressive (negative quadratic) growth effect of high N applications. Western hemlock growth response to fertilizer applications was particularly erratic on burnt sites. When the foliar data were examined two possible explanations were immediately apparent. Both N and Zn levels were depressed in western hemlock foliage on burnt sites, and were considered to be near or below critical levels. However, N application had no effect on foliar N levels in western hemlock, indicating that lack of available N was not the factor responsible for this species' low foliar N levels; this is further supported by the high foliar N levels (>1.8%) of Douglas-fir growing on the same sites. Such high N levels indicate that S availability is adequate for plant growth based on the N-S relationship proposed by Turner and Lambert (1981). It is hypothesized that Zn deficiency is the major reason for western hemlock's low foliar N levels, and for the general lack of response to P applications.

The effect of slash burning on micronutrient availability raises an important question; namely, why are foliar levels of Zn, Cu, and Fe significantly reduced in Douglas-fir and western hemlock on burnt sites compared to unburnt sites? By agronomic standards, both sites are highly acidic and availability of Zn, Cu, and Fe would not normally be considered a nutritional problem. While the increase in surface soil pH may have had some effect on micronutrient availability, in the case of Zn total levels were actually higher on burnt sites. Also, while foliar Al levels were higher in Douglas-fir and western hemlock on burnt sites, results from the solution culture studies showed no effect of Al on tissue Zn levels in either species. However, increased levels of foliar Al in both species on burnt sites may have had an antagonistic effect on foliar Fe and Cu levels, as this effect was observed in the solution culture studies and was also reported by Ryan (1986a, b) for these two species.

The increase in tissue Al levels, plus the significant decrease in tissue Zn, Fe, and Cu in Douglas-fir, and particularly the decrease in tissue Zn and Cu levels in western hemlock on burnt sites indicate that one of the major effects of slash burning may be to greatly reduce the level of natural chelates in the soil. As pointed out by Lindsay (1974), metal ion chelation plays an important part in supplying nutrients to plants. Were it not for this, many soils would be restricted in their ability to support plant growth because Fe, Zn, and Cu levels cannot be maintained at adequate levels in the soil solution.

In the solution culture studies, where an "optimum" nutrient balance was used, Douglas-fir consistently had higher tissue Zn levels than western hemlock. Western hemlock however, tended to have higher tissue Fe and Cu levels. But when these species were grown *in situ* on the coastal soils, Douglas-fir *always* had higher tissue Fe, Cu, and Zn levels. Not only does this indicate a greater Zn uptake ability in Douglas-fir, but it also indicates a greater ability for Fe and Cu uptake under conditions pertaining to the coastal soils used in this study. On this basis it is hypothesized that western hemlock relies greatly on the presence of an adequate supply of soluble nutrients and on the presence of natural chelates for transport of Zn, Fe, and Cu to the root surface, whereas Douglas-fir has a greater capacity to produce chelating agents and hence to maintain adequate foliar micronutrient levels. Although not conclusive, data from the fertilizer study and solution culture experiments do provide strong circumstantial evidence in support of this hypothesis.

Results from the solution culture studies revealed that increasing the P:Al ratio did not ameliorate the toxic effects of Al. This was attributed to the large drop in solution pH with increasing P levels; concomitant with this there may have been an increase in the availability of Cu. In fact, very high (toxic?) tissue Cu levels in both Douglas-fir and western hemlock were recorded in the solution culture studies. At the low pHs of the solution culture studies the "optimum" nutrient ratios reported by Ingestad (1979) may no longer be optimum and elements such as Cu may be approaching toxic levels. Thus, the antagonistic effect of Al on the uptake of Cu also may be the reason for the "stimulatory" effects of low levels of Al on root growth observed for Douglas-fir and western hemlock in the Ca:Al ratio experiment in this study, as well as those reported by Ryan (1986a, b) for these species grown in the same nutrient medium.

Increasing the OH:Al and Ca:Al ratios inhibited the effects of Al on root growth, particularly in Douglas-fir. Increasing the OH:Al ratio raised solution pH and, because all the Al in solution was found to be in monomeric form , the conclusion from this and from the P:Al ratio experiment is that there may be a very strong Al by pH interaction on

Douglas-fir root growth. In the Ca:Al ratio experiment, the main effect of increasing Ca appears to be a physiological one, rather than on depressing solution Al activity. The effect of increasing solution Ca levels was particularly evident in Douglas-fir, suggesting that this species' tolerance to high solution Al levels may be more dependent on an adequate availability of Ca than western hemlock.

Both Douglas-fir and western hemlock accumulated considerable levels of Al in their tissue, even though the duration of the experiments was seven days. Western hemlock always had significantly higher tissue Al levels than Douglas-fir, and this difference was most apparent when root tissue Al levels were compared. From the solution culture experiments, western hemlock is considered more tolerant to pHs less than about 3.8, and appears more tolerant of Al at low pHs and low solution Ca levels compared with Douglas-fir.

Beaton et al. (1965) and Krajina (1970) reported that nutrient levels in western hemlock were low relative to other indigenous conifers, and from this they hypothesized that this species' total nutrient requirements were low. This was not borne out in the present study. While Douglas-fir had consistently higher foliar N, Fe, Cu, and Zn levels compared with western hemlock when grown _in situ_ on the coastal soils, and higher P and Zn levels when grown in solution culture, western hemlock had higher foliar levels of Ca, K, Mg, Mn, and Na. While western hemlock's foliar P levels were comparable to those of Douglas-fir when the two species were grown together in the coastal soils, this is most likely due to a P dilution effect in Douglas-fir foliage as a result of a much higher growth response. The solution culture studies showed that

Douglas-fir had a much greater P absorption capacity compared with western hemlock. It must be remembered, however, that the above results were obtained using seedlings, whereas the results reported by Beaton et al. (1965) and Krajina (1970) were for mature stands. Thus it is possible that at a mature stage western hemlock may have a broader tolerance to low nutrient levels than Douglas-fir, though this is not synonymous to a lower nutrient requirement. During stages of more vigorous growth the nutrient requirements of western hemlock appear comparable to those of Douglas-fir.

5.2 Evaluation of the Hypotheses

Because of the close relationship between hypothesis 1 and corollary A the two are evaluated together, and are restated below.

Hypothesis 1: The coastal soils of Oregon and Washington are reported to have "andic" soil properties - high levels of exchangeable aluminum and sesquioxides, and high levels of phosphate adsorption. Under such conditions applications of P, rather than N, will result in significant growth responses in Douglas-fir and western hemlock.

Corollary A: The levels of plant available N and micronutrients are sufficient in the coastal soils to sustain a growth response to P applications.

Results from the fertilizer trial and soil analyses, and points bought out in the discussion support the above hypothesis. This is particularly so for Douglas-fir, and this species always showed a consistent, positive response to P applications. The high P sorption capacity of these soils, plus the low levels of available P lend added support to the hypothesis. While western hemlock's response to fertilizer application was erratic, especially on burnt sites, there was however, a more consistent response to P, rather than N, on unburnt sites. The high tissue N levels in Douglas-fir, and lack of a significant growth response to N application further support the hypothesis. As well, although western hemlock had low (deficient) N levels on burnt sites (probably due to a Zn deficiency), application of N had no effect either on growth or foliar N levels, indicating that a N deficiency *per se* is unlikely to be the reason for this species' low N levels.

Based on the levels of total soil N and C:N ratios the availability of N in these soils appears adequate, and supports corollary A. This is corroborated by the general lack of a positive growth response by either species to N applications, and the relatively high foliar N levels in Douglas-fir. However, the low tissue Zn levels in western hemlock, particularly on burnt sites, plus the low soil ($LiSO_4$-H_2SO_4 extractable) Zn levels on all four sites do not support corollary A, at least for Zn availability and western hemlock, and it is suggested that the lack of a response by this species to P applications is due to a Zn-N deficiency interaction.

Hypothesis 2: Applications of OH, P, or Ca to the growth medium can ameliorate the toxic effects of Al in Douglas-fir and western hemlock grown under controlled conditions.

Results from the OH:Al and Ca:Al ratio experiments support the above hypothesis. However, it was indicated that the mechanism by which OH (and P) could ameliorate the toxic effects of Al is by complex ligand formation; this did not appear to be the case in the OH:Al experiment. Here all the added Al was found to be in the monomeric form. Based on the maximum pH of the solutions (pH 4.3) and the discussion on Al chemistry in the literature review, most of the Al in solution was considered to exist as the Al^{3+} ion. Thus the main effect of OH was to raise the solution pH, indicating that for Douglas-fir in particular, a major Al by pH interaction may exist in relation to this species' Al tolerance.

For the Ca:Al ratio experiment the main mechanism by which Ca ameliorated the toxic effects of Al appears to be a physiological one, rather than by reducing the activity of toxic Al species. Again, the effect of increasing solution Ca levels was most pronounced for Douglas-fir, suggesting that this species' ability to tolerate high levels of Al may be more dependent on an adequate Ca supply when compared with western hemlock.

Increasing the P:Al ratio did not ameliorate the toxic effects of Al, and there was no indication of complex ligand formation. The effect of increasing solution P levels was to lower solution pH levels and raise Al^{3+} activity. Because of the high Al-tolerance of both species, it is unlikely that additions of P to solution cultures would show any marked ameliorative effect, as large additions of P can greatly decrease solution pH, inhibiting formation of Al-P complexs and increasing Al^{3+} activity. Thus the above hypothesis is rejected in relation to P.

Hypothesis 3: Western hemlock has foliar cation concentrations (requirements) comparable to those of Douglas-fir when grown in the same medium.

When the two species were grown together in solution culture over a series of four different experiments, western hemlock usually had higher tissue concentrations of Al, K, Mg, Mn, Fe, Cu, and Na, while Douglas-fir invariably had higher tissue Zn and P concentrations. For some elements the tissue concentrations in western hemlock were twice that of Douglas-fir, indicating a major difference in cation uptake between the two species. Except for Zn, such results clearly support the above hypothesis.

When the foliar data from the fertilizer trial were compared, the foliar levels of Ca, Mg, Mn, K, Al,and Na in western hemlock were similar to or higher than those of Douglas-fir, providing further support for the hypothesis. However ,in the field study, Douglas-fir always had higher foliar concentrations of N, Zn, Fe, and Cu.

Corollary B: Douglas-fir and western hemlock have different mechanisms or abilities of ion uptake under similar environmental conditions.

There were a number of obvious differences in nutrient concentrations between the two species when grown in the same medium. Notably, Douglas-fir had consistently higher Zn levels (and N levels in the fertilizer trial) while western hemlock had higher Ca, Mg, Mn, Na, and Al levels. Ryan (1983) reported that western hemlock had a greater root cation exchange capacity under acid conditions compared with

Douglas-fir. However, this difference in the passive ability of cation uptake extends beyond root cation exchange capacity. From the results it appears that there is a major difference between the two species in their ability to acquire or absorb Zn, and perhaps also Fe and Cu under conditions pertaining to the coastal soils. It is hypothesized that this difference is a physiological one, and is related to the greater ability of Douglas-fir to produce chelating compounds that can increase the solubility and transport of less soluble ions of low concentration in the soil solution.

Although western hemlock had noticeably lower foliar N levels compared with Douglas-fir, particularly on burnt sites, this has been attributed to an induced N deficiency as a result of deficient Zn levels. The predominant form of N in forest soils occurs as the cation NH_4^+, and hence western hemlock, because of its higher root cation exchange capacity should have similar foliar N levels compared with Douglas-fir. However, under conditions of low tissue Zn levels, N levels may be greatly reduced due to a reduction in protein synthesis. Therefore it is hypothesized that the main reason for Douglas-fir's higher foliar N levels may be its greater ability to absorb Zn.

5.3 Ecological and Management Significance, and Conclusions

The effects of high soil acidity and toxic levels of elements such as Al are first expressed at the plant root (Foy 1984). As roots are the primary organ for water and nutrient uptake, factors that inhibit normal root growth and function will have a major effect on plant growth and development, and ultimately survival. Young seedlings are reported to be more susceptible to the effects of Al than older plants (Thaworuwong and Van Diest 1974). Thus a species tolerant of low pH, and tolerant of Al at low solution Ca levels will have a distinct competitive advantage.

In this study, four week old western hemlock seedlings were found to be more of tolerant of low pH, and more Al-tolerant at low Ca levels than Douglas-fir seedlings of similar age. Such features give western hemlock a distinct competitive advantage to survive and grow in the acidic forest floor organic layers of the coastal soils. This competitive advantage is further extended by western hemlock's high shade tolerance (Minore 1979).

The high tissue Al levels found in western hemlock will also be reflected in the forest floor organic layers, resulting in reduced decomposition rates due to the toxic effects of Al on soil micro-organisms (Alexander 1980). Thus once established western hemlock may be able to maintain this acidic environment via the accumulation of Al-rich organic matter, and thereby maintain its competitive advantage. However, as indicated in the literature review, the activity of toxic forms of Al in the forest floor will be reduced due to the presence of humic and fulvic acids. Heilman (1976) reported that for the coastal soils of the Pacific Northwest the levels of exchangeable bases and available P were higher in the acidic organic layers compared to the mineral soil. Because western hemlock is capable of maintaining active root development under acid conditions in the presence of moderate levels of Al (<50 ug g^{-1}), this species may also have a competitive advantage in nutrient interception and uptake.

However, the results from the coastal study, and those reported by Ryan (1983), indicate that western hemlock's competitive advantage is dependent on the presence of an acidic organic layer. On burnt sites the growth of western hemlock, even with the application of P or N, was greatly reduced when compared with unburnt sites, and it was postulated that this was due to a Zn deficiency. In comparison, Douglas-fir had adequate Zn levels and showed a consistent, positive response to P applications. From this it was hypothesized that Douglas-fir had a greater capacity to acquire Zn, as well as Fe and Cu, due to its ability to produce chelating compounds. The removal of the acidic forest floor organic layer, plus the reduction in natural chelating compounds has shifted the competitive advantage away from western hemlock to Douglas-fir. Therefore the management and regeneration of western hemlock will require the exclusion of fire, and the application of more balanced fertilizer mixes if this species' productivity is to be maintained on the coastal soils.

The application of P always gave a consistent growth response by Douglas-fir, and based on the high foliar N levels and lack of a response to N applications, there appears little value in continued N application in the absence of P. However, the high P sorption capacity of the coastal soils implies that application of less soluble forms of P fertilizers, or spot application at or shortly after planting may be a better management alternative than broadcast applications of highly soluble P fertilizers. But the high P sorption and total P levels of these soils also indicate that response to P application is unlikely to be longlived.

Both Douglas-fir and western hemlock are well adapted to the acidic coastal soils of the Pacific Northwest. However, based on the results from this study, there appear to be distinct differences in their ability or to mechanism for nutrient uptake. Given the economic and ecological importance of the two species in the Pacific Northwest there is still a paucity of information on the physiology and nutrient requirements of the two species growing on the acidic, Al dominated coastal soils of Oregon and Washington. The importance of the Oregon and Washington coastal zone is well recognized for its forest productivity, ecological, and scientific values. However, to ensure that these values are maintained a fuller understanding is required of the factors influencing soil fertility, and on the physiology, nutrition, and mycorrhizal relationships of Douglas-fir and western hemlock.

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Appendix 1 Composition of nutrient solutions used in this study. (From Ryan 1983).

Stock Reagent	Nutrient Solution			Stock 20x	1/3 Stock 20x
	$^{+}$MW	mM.L^{-1}	mgL^{-1}	(g18L^{-1})	(g18L^{-1})
NH_4NO_3	80.05	2.5	200.1	72.0	24.0
$NaH_2PO_4H_2O$	137.99	0.65	89.7	32.3	8.3
KNO_3	101.11	1.5	151.7	54.6	18.2
$Ca(NO_3)_2.4H_2O$	236.1	0.4	94.4	34.0	11.3
$MgSO_4.7H_2O$	246.5	0.4	98.6	35.5	11.8
NaCl	58.45	0.1	5.8	2.1	0.70
$MnCl_2.4H_2O$	197.91	0.007	1.38	0.5	0.17
$CuCl_2.2H_2O$	170.48	0.0005	0.068	0.03	0.01
ZnCl	136.28	0.0005	0.068	0.02	0.01
H_3BO_3	61.84	0.02	1.24	0.44	0.15
$NaMoO_4.2H_2O$	241.95	0.00007	0.017	0.006	0.002
$^{*}FeSO_4.7H_2O$	278.03	0.009			

$^{+}$MW: Molecular weight

$^{*}FeSO_4.7H_2O$ was added to the tanks (nutrient culture) to give this final concentration using a 5% Fe stock solution in 0.01N HCL. This process avoided precipitation in the 20x stock solution.

185.3 mM stock solutions of $AlCl_3$ $6H_2O$ were made up as required.

Appendix 2. Chemical and physical properties, and description of a soil pedon near the four study sites. (From S.C.S 1975).

SOIL Pedon 10
Andic Dystrochrept SOIL Nos. S64Wash-14-3 LOCATION Grays Harbor County, Washington

SOIL SURVEY LABORATORY Riverside, California LAB. Nos. 64374 - 64378

Depth (cm)	Horizon	1B1b								Size class and particle diameter (mm) 3A1						Coarse fragments 1A2a		
		Total			Sand					Silt								
		Sand (2-0.05)	Silt (0.05-0.002)	Clay (<0.002)	Very coarse (2-1)	Coarse (1-0.5)	Medium (0.5-0.25)	Fine (0.25-0.1)	Very fine (0.1-0.05)	(0.05-0.02)	Int. III (0.02-0.002)	Int. II (0.2-0.02)	2-0.1			> 2 Pct. of whole soil	2-19	19-76
		Pct. of <2 mm															Pct. of <76mm	
0-15	A1	19.2	41.2	39.6	2.1	3.8	3.3	5.4	4.6	11.2	30.0	18.6	11.8			1	1	
15-38	A3	24.2	50.3	25.5	1.2	4.3	3.9	7.6	7.2	16.6	33.7	27.9	12.9			1	1	
38-76	B21	23.7	50.4	25.9	0.9	3.9	4.1	7.6	7.2	15.6	34.8	27.0	12.3			1	1	
76-110	B22	23.4	47.4	29.2	1.1	3.9	4.1	7.5	6.8	13.8	33.6	24.8	12.4			0	0	
110-165	IIC	24.1	42.6	33.3	0.5	2.7	3.5	8.5	8.9	13.3	29.3	27.1	10.3			2	2	

Depth (cm)	6A1a	6B1a	C/N	6C2a	Carbonate as $CaCO_3$		Bulk density			3B2	Water content			4D1	4D1	pH		
	Organic carbon a/ Pct.	Nitrogen Pct.		Ext. Iron as Fe Pct.	6E1b <2 mm Pct.	3A1a <0.002 mm Pct.	4A1f 1/3-bar g/cc	4A1h Oven-dry g/cc	g/cc	Cm	4B1c 1/3-bar Pct.	4B2 15-bar Pct.	4C1 1/3-to 15-bar cm/cm	Extensibility COLEf cm/cm	Extensibility COLE cm/cm	8C1b Saturated paste	8C1a H_2O 1:1	8C1d NaF (2 min)
0-15	8.05	0.358	22	6.2			0.89	1.07		1.00	54.4	29.1		0.063	0.063		4.5	9.9
15-38	2.68	0.179	15	5.8			0.93	1.05		1.00	50.1	24.9		0.041	0.041		4.9	10.7
38-76	1.53	0.100	15	5.9			1.04	1.16		1.00	43.4	23.1		0.037	0.037		5.0	10.6
76-110	1.22	0.074	16	5.6			0.92	1.01		1.00	49.1	22.3		0.032	0.032		5.0	10.9
110-165	0.46			5.0			1.27	1.41		0.99	37.5	23.6		0.036	0.036		4.9	10.0

Appendix 2 continued.

Depth (cm)	Extractable bases 6N2a Ca 5B3a	6O2a Mg 5B3a	6P2a Na 5B1a	6Q2a K 5B1a	Sum of bases	6H2a Ext. acidity	Cation exch. capacity 5A6a NH$_4$OAc	5A3a Sum of cations		6G1e KCl exc. Al +++	Ratios to clay 8D1 CEC sum	Ext. iron	15-bar water				Base saturation 5C3 Sum of cations Pct.	5C1 NH$_4$ OAc Pct.
	meq/100g																	
0-15	0.6	1.1	0.3	0.2	2.2	52.6		54.8		9.1	1.38	0.16	0.73				4	
15-38	0.1	0.6	0.3	0.1	1.1	38.6		39.7		4.6	1.56	0.23	0.98				3	
38-76	tr.	0.4	0.2	0.1	0.7	34.6		35.3		5.6	1.36	0.23	0.89				2	
76-110	tr.	0.3	0.1	0.1	0.5	32.7		33.2		6.5	1.14	0.19	0.76				2	
110-165	tr.	0.5	0.2	0.1	0.8	29.1		29.9		11.6	0.90	0.15	0.71				3	

Depth (cm)	b/ Clay fraction mineralogy 3A1 7A2 X-ray c/	7A3 DTA Pct.
0-15	VR3, KH3	
15-38	VR3, KH3	
38-76	VR3, KH3	
76-110		
110-165	VR3, KH3	

a/25.2 kg of organic carbon per square meter to a depth of 1 meter.

b/Mineral code:

VR = vermiculite

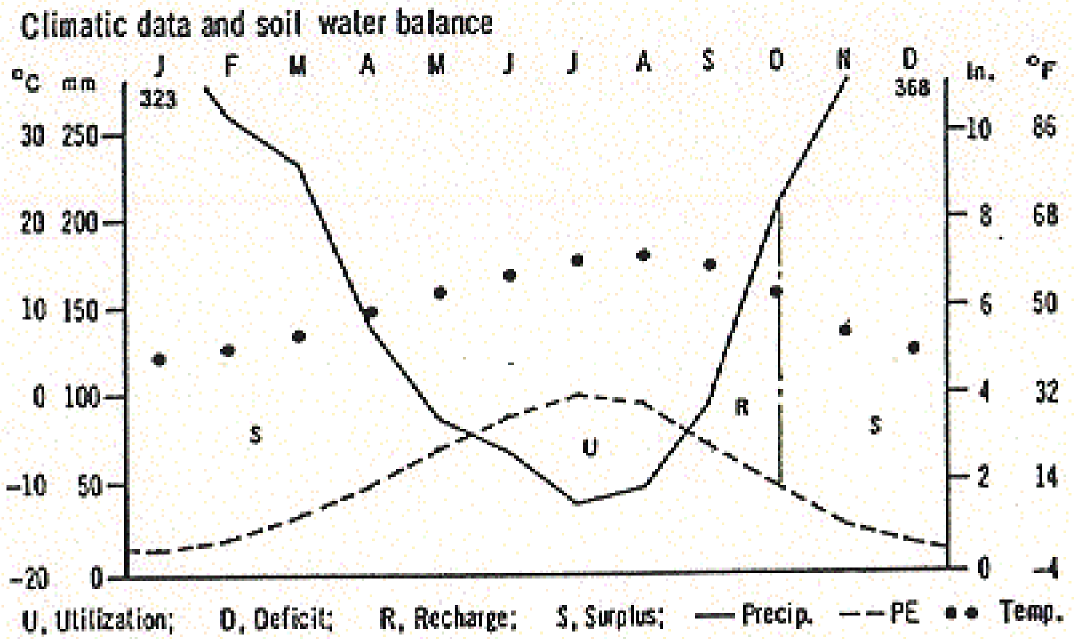
KH = halloysite

c/Approximate weight fraction (X-ray):

3 = one-fifth to one-third

Appendix 2 continued.

Pedon 10


Climatic data and soil water balance

Classification: Andic Dystrochrept, thixotropic, mesic.

Location: Grays Harbor County, Wash. 14.5 km northwest of Hoquiam to the junction of county road 101 and Grass Creek, thence 0.3 km south to just beyond the curve on Grass Creek road and 30 m southeast into woods. Central NW1/4 NE1/4 sec. 10, T. 18 N., R. 11 W.

Physiographic position: Terrace, elevation about 9 m.

Topography: Nearly level with cradle-knoll microrelief from hemlock tipover.

Drainage: Well drained; slow surface runoff; moderately slow permeability.

Vegetation: 60-year old hemlock (Tsuga heterophylla); sparse understory of vine maple (Acer circinatum), sword fern (Nephrolepis exaltata) and moss.

Parent material: Glaciofluvial deposits of late Wisconsin age overlying older glaciofluvial deposits. Deposits consist of moderately fine textured sediments partly derived from basalt. Very deep underlying deposits of glaciofluvial compacted to cemented gravel, lacustrine and residuum of tertiary sandstone, siltstone, and shale.

Sampled by: K. W. Flach, R. W. Chapin, Carl McMurphy, August 29, 1964.

Remarks: The soil temperature was 11.5° C at 50 cm and 10.5° C at 150 cm when the soil was sampled. Five to 15 cm diameter root channels filled with surface horizon material and 5YR colored material (burned roots) extend to a depth of 110 cm in one side of the pit. They were not sampled. All horizons are thixotropic. The soil does not disperse well, hence field estimates of texture are given in the profile description.

Soil No.: S64Wash-14-3.

Appendix 2 continued.

Colors are for the moist soil unless otherwise indicated.

01 5-3 cm (2-1 in.). Conifer needles, twigs, bark, live moss.

02 3-0 cm (1-0 in.). Dark reddish brown (5YR 2/2) decomposed needles, thixotropic.

A1 0-15 cm (0-6 in.). Dark brown (10YR 3/3) silt loam, brown (10YR 4/3) dry; moderate coarse granular and moderate fine subangular blocky structure; hard (dry), very friable (moist), slightly sticky, plastic and thixotropic (wet); many fine tubular and many medium vesicular pores; abundant coarse, medium and fine roots; dark brown (7.5YR 3/2) organic stained ped surfaces; few very fine unweathered pebbles, 7 percent iron cemented aggregates; clear wavy boundary.

A3 15-38 cm (6-15 in.). Dark brown (7.5YR 3/4) silt loam, yellowish brown (10YR 5/4) dry; moderate very fine subangular blocky structure; slightly hard (dry), friable (moist), sticky, plastic and thixotropic (wet); many fine tubular and many medium vesicular pores; abundant coarse, medium and fine roots; few unweathered pebbles and 5 percent iron cemented aggregates; gradual, wavy boundary.

B21 38-76 cm (15-30 in.). Dark brown (7.5YR 3/4) silty clay loam, light yellowish brown (10YR 6/4) dry; moderate very fine and weak fine subangular blocky structure; hard (dry), friable (moist), sticky, plastic and thixotropic (wet); common medium and fine tubular and common medium and fine vesicular pores; common medium and fine roots; few unweathered pebbles; diffuse wavy boundary.

B22 76-110 cm (30-44 in.). Dark brown (7.5YR 3/4) silty clay loam, yellowish brown (10YR 5/4) dry; weak very fine subangular blocky structure; hard (dry), friable (moist), very sticky, plastic and thixotropic (wet); common medium and fine tubular and many coarse vesicular pores; common medium and fine roots; smooth cutans on ped faces; few unweathered pebbles; clear, wavy boundary.

IIC 110-165 cm (44-64 in.). Yellowish brown (10YR 5/4) silty clay, light yellowish brown (10YR 6/4) dry; common medium distinct yellowish red (5YR 4/6) and light olive brown (2.5Y 5/4) mottles, strong brown (7.5YR 5/8) and light gray (2.5Y 7/2) dry; massive; very hard (dry), friable (moist), very sticky, plastic and thixotropic (wet); few medium tubular and many coarse vesicular pores; few fine roots to 165 cm; 1 percent very fine unweathered gravel by volume.

Appendix 3A MANOVA statistics on Douglas-fir and western hemlock seedling height growth to fertilizer application and site preparation.

Source of Variation	DF	Significance of F		
		First Year	Second Year	Two Year
Error 1	6	--	--	--
Site preparation (Sprep)	1	.033	.436	.818
Error 2	6	--	--	--
Species	1	.010	.241	.829
Species by Sprep	1	.027	.075	.365
Error 3	48	--	--	--
Treatment (Treat)	8	.014	.031	.010
Treat by Sprep	8	.904	.765	.890
Error 4	48	--	--	--
Treat by Species	8	.521	.074	.223
Treat by Species by Sprep	8	.497	.484	.939

Appendix 3B MANOVA statistics on Douglas-fir and western hemlock seedling diameter growth to fertilizer application and site preparation.

Source of Variation	DF	Significance of F		
		First Year	Second Year	Two Year
Error 1	6	--	--	--
Site preparation (Sprep)	1	.507	.128	.184
Error 2	6	--	--	--
Species	1	.005	.001	.000
Species by Sprep	1	.314	.031	.012
Error 3	48	--	--	--
Treatment (Treat)	8	.000	.002	.000
Treat by Sprep	8	.815	.547	.439
Error 4	48	--	--	--
Treat by Species	8	.637	.012	.125
Treat by Species by Sprep	8	.895	.024	.159

Appendix 4A. Mean height growth (cm) of Douglas-fir and western hemlock for the first, second, and two year growth periods.

Mean First Year Height Growth

Site Prep	Species	Treatment									Total
		Ctrl	P_1	P_2	N_1	N_1P_1	N_1P_2	N_2	N_2P_1	N_2P_2	
Unburnt	Douglas-fir	10.2	11.6	10.7	10.7	11.1	12.8	10.8	12.1	13.5	103.4
	Western hemlock	10.3	10.2	13.2	11.1	13.2	12.7	10.6	13.6	12.7	107.4
	Total	20.5	21.7	23.8	21.7	24.2	25.5	21.4	25.7	26.2	210.8
Burnt	Douglas-fir	11.6	13.1	15.2	12.1	12.5	12.2	12.2	12.9	15.7	117.5
	Western hemlock	12.6	13.7	13.7	15.0	18.2	15.9	15.0	16.6	20.1	141.0
	Total	24.2	26.8	28.9	27.1	30.7	28.1	27.2	29.5	35.8	258.5
Total	Douglas-fir	21.9	24.7	25.9	22.7	23.6	24.9	23.0	24.9	29.1	221.0
	Western hemlock	22.9	23.9	26.8	26.1	31.4	28.6	25.6	30.2	32.8	248.4
	Total	44.8	48.6	52.8	48.8	56.9	53.6	48.6	55.2	62.0	469.4

Appendix 4A Continued

Mean Second Year Height Growth

Site Prep	Species	Treatment									Total
		Ctrl	P_1	P_2	N_1	N_1P_1	N_1P_2	N_2	N_2P_1	N_2P_2	
Unburnt	Douglas-fir	29.0	37.7	43.0	30.2	40.1	41.0	34.4	41.0	45.8	342.2
	Western hemlock	36.4	36.4	33.2	41.2	41.8	41.8	31.5	47.4	38.6	348.3
	Total	65.4	74.1	76.2	71.4	81.9	82.8	65.9	88.4	84.4	690.5
Burnt	Douglas-fir	34.9	37.9	36.4	34.1	41.4	37.7	38.7	41.0	43.0	345.1
	Western hemlock	34.6	31.3	34.0	34.8	36.6	35.5	32.3	34.1	35.0	308.2
	Total	69.5	69.2	70.4	68.9	78.0	73.2	71.0	75.1	78.0	653.3
Total	Douglas-fir	63.9	75.6	79.4	64.3	81.5	78.7	73.1	82.0	88.8	687.3
	Western hemlock	71.0	67.7	67.2	76.0	78.4	77.3	63.8	81.5	73.6	656.5
	Total	134.9	143.3	146.6	140.3	159.9	156.0	136.9	163.5	162.4	1343.8

Appendix 4A Continued

Mean Two Year Height Growth

Site Prep	Species	Treatment									Total
		Ctrl	P_1	P_2	N_1	N_1P_1	N_1P_2	N_2	N_2P_1	N_2P_2	
Unburnt	Douglas-fir	39.2	49.3	53.8	40.9	51.2	53.7	45.2	53.1	59.3	445.7
	Western hemlock	46.7	46.6	46.4	52.2	55.0	54.6	42.1	61.0	51.3	455.9
	Total	85.9	95.9	100.2	93.1	106.2	108.3	87.3	114.1	110.6	901.6
Burnt	Douglas-fir	46.5	51.0	51.6	46.2	53.9	49.9	50.9	53.9	58.7	462.6
	Western hemlock	47.1	45.0	47.7	49.9	54.8	51.5	47.3	50.7	55.1	449.1
	Total	93.6	96.0	99.3	96.1	108.7	101.4	98.2	104.6	113.8	911.7
Total	Douglas-fir	85.7	100.3	105.4	87.1	105.1	103.6	96.1	107.0	118.0	908.3
	Western hemlock	93.8	91.6	94.1	102.1	109.8	106.1	89.4	111.7	106.4	905.0
	Total	179.5	191.9	199.5	189.2	214.9	209.7	185.5	218.7	224.4	1813.3

Appendix 4B. Mean diameter growth (cm) of Douglas-fir and western hemlock for the first, second, and two year growth periods.

Mean First Year Diameter Growth

Site Prep	Species	Treatment									Total
		Ctrl	P_1	P_2	N_1	N_1P_1	N_1P_2	N_2	N_2P_1	N_2P_2	
Unburnt	Douglas-fir	.24	.27	.30	.29	.34	.38	.27	.33	.48	2.90
	Western hemlock	.20	.19	.25	.21	.27	.26	.23	.28	.28	2.17
	Total	.44	.46	.55	.50	.61	.64	.50	.61	.76	5.07
Burnt	Douglas-fir	.22	.20	.25	.25	.34	.29	.26	.31	.35	2.47
	Western hemlock	.22	.17	.21	.22	.24	.24	.20	.24	.28	2.02
	Total	.44	.37	.46	.47	.58	.53	.46	.55	.63	4.49
Total	Douglas-fir	.46	.47	.55	.54	.68	.67	.53	.64	.83	5.37
	Western hemlock	.42	.36	.46	.43	.51	.50	.43	.52	.56	4.19
	Total	.88	.83	1.01	.97	1.19	1.17	.96	1.16	1.39	9.56

Appendix 4B Continued

Mean Second Year Diameter Growth

Site Prep	Species	Treatment									Total
		Ctrl	P_1	P_2	N_1	N_1P_1	N_1P_2	N_2	N_2P_1	N_2P_2	
Unburnt	Douglas-fir	.85	1.12	1.07	.84	1.11	1.05	.95	1.05	1.12	9.16
	Western hemlock	.78	.68	.64	.73	.85	.89	.62	.93	.82	6.94
	Total	1.63	1.80	1.71	1.57	1.96	1.94	1.57	1.98	1.94	16.10
Burnt	Douglas-fir	.74	.77	.81	.71	.76	.80	.74	.84	.80	6.97
	Western hemlock	.60	.65	.66	.72	.64	.70	.59	.68	.77	6.01
	Total	1.34	1.42	1.47	1.43	1.40	1.50	1.33	1.52	1.57	12.98
Total	Douglas-fir	1.59	1.89	1.88	1.55	1.87	1.85	1.69	1.89	1.92	16.13
	Western hemlock	1.38	1.33	1.30	1.45	1.49	1.59	1.21	1.61	1.59	12.95
	Total	2.97	3.22	3.18	3.00	3.36	3.44	2.90	3.50	3.51	29.08

Appendix 4B Continued

Mean Two Year Diameter Growth

Site Prep	Species	Treatment									Total
(A)	(B)	Ctrl	P_1	P_2	N_1	N_1P_1	N_1P_2	N_2	N_2P_1	N_2P_2	
	Douglas-fir	1.10	1.39	1.37	1.13	1.46	1.43	1.22	1.38	1.60	12.08
Unburnt	Western hemlock	.98	.87	.88	.94	1.13	1.15	.85	1.21	1.10	9.11
	Total	2.08	2.26	2.25	2.07	2.59	2.58	2.07	2.59	2.70	21.19
	Douglas-fir	.95	.97	1.06	.96	1.10	1.09	1.01	1.15	1.15	9.44
Burnt	Western hemlock	.81	.82	.87	.94	.88	.94	.79	.91	1.05	8.01
	Total	1.76	1.79	1.93	1.90	1.98	2.03	1.80	2.06	2.20	17.45
	Douglas-fir	2.05	2.36	2.43	2.09	2.56	2.52	2.23	2.53	2.75	21.52
Total	Western hemlock	1.79	1.69	1.75	1.88	2.01	2.09	1.64	2.12	2.15	17.12
	Total	3.84	4.05	4.18	3.97	4.57	4.61	3.87	4.65	4.90	38.64

Appendix 5A. Douglas-fir height and diameter growth response (% of control) for unburnt and burnt sites.

Douglas-fir Unburnt Sites

Treatment	Height			Diameter		
	First Year	Second Year	Two Year	First Year	Second Year	Two Year
Ctrl	100a	100a	100a	100a	100a	100a
P1	113a	130bcd	125bcd	113a	132b	126bc
P2	105a	149cd	137cd	125a	126b	125bc
N1	104a	104ab	104ab	121a	98a	103a
N1P1	108a	138cd	131cd	142ab	131b	133c
N1P2	124a	142cd	137cd	158ab	124b	130bc
N2	105a	119abc	115abc	113a	112ab	111ab
N2P1	120a	142cd	135cd	138ab	124b	125bc
N2P2	133a	158d	151d	200b	132b	145c

Vertical columns with the same letter indicate no significant difference at a=0.10 using Duncan's Multiple Range Test.

Appendix 5A continued.

Douglas-fir Burnt Sites

Treatment	Height			Diameter		
	First Year	Second Year	Total	First Year	Second Year	Total
Ctrl	100a	100ab	100a	100ab	100a	100a
P1	113ab	109ab	110ab	91a	104a	102a
P2	131ab	104ab	111ab	114ab	109a	116a
N1	104ab	98a	99a	114ab	96a	101a
N1P1	107ab	131ab	116ab	155ab	103a	116a
N1P2	105ab	124ab	107ab	132ab	108a	115a
N2	105ab	112ab	a09ab	118ab	100a	106a
N2P1	111ab	124ab	116ab	141ab	114a	121a
N2P2	135b	132b	126b	159b	108a	121a

Appendix 5B. Western hemlock height and diameter growth response (% of control) for unburnt and burnt sites.

Western Hemlock Unburnt Sites

Treatment	Height			Diameter		
	First Year	Second Year	Total	First Year	Second Year	Total
Ctrl	100a	100ab	100ab	100a	100bcd	100abc
P1	99a	100ab	100ab	95a	87ab	89a
P2	128a	91ab	100ab	125a	82ab	90ab
N1	108a	113ab	112ab	105a	94abc	96ab
N1P1	128a	115ab	118ab	135a	109cd	115bc
N1P2	124a	115ab	117ab	130a	114cd	117bc
N2	103a	87a	90a	115a	79a	87a
N2P1	132a	131b	131b	140a	119d	123c
N2P2	124a	106ab	110ab	140a	105bcd	112bc

Vertical columns with the same letter indicate no significant difference at a=0.10 using Duncan's Multiple Range Test.

Appendix 5B continued.

Weatern Hemlock Burnt Sites

Treatment	Height			Diameter		
	First Year	Second Year	Total	First Year	Second Year	Total
Ctrl	100a	100a	100a	100ab	100a	100a
P1	109ab	90a	96a	87a	108a	101a
P2	109ab	98a	101a	95ab	110a	107a
N1	119abc	100a	106a	100ab	120a	116a
N1P1	145bc	106a	116a	109ab	107a	109a
N1P2	127abc	103a	109a	109ab	117a	116a
N2	120abc	93a	100a	91ab	99a	98a
N2P1	132abc	99a	108a	109ab	113a	112a
N2P2	160c	101a	117a	127b	128a	136a

Appendix 6A. Mean foliar concentration of elements (ug g^{-1} dry weight) for Douglas-fir on unburnt and burnt sites - Fall sampling 1985 of current foliar increment.

MEAN CONCENTRATION OF ELEMENTS (UG/G) - FALL SAMPLING OCTOBER 1985
DOUGLAS-FIR UNBURNT SITES (PLOTS 1&2)

TREAT -MENT	N(%)	AL	P	K	CA	MG	MN	FE	ZN	CU
CTRL	2.347	351	1521	7128	1771	866	534	110.9	32.1	5.01
P1	2.118	330	1635	7582	2046	845	532	101.7	29.4	5.93
P2	2.240	336	1808	6932	1996	864	394	107.0	27.1	5.06
N1	2.570	325	1663	7277	1741	863	521	155.8	28.8	5.74
N1P1	2.043	335	1734	7396	1879	820	504	110.4	27.8	4.73
N1P2	2.225	309	1830	7743	2058	889	582	137.2	27.8	4.59
N2	2.400	350	1533	7675	1701	873	579	111.7	30.6	5.40
N2P1	2.015	330	1614	7141	1683	783	481	107.1	25.4	4.31
N2P2	2.140	371	1682	7215	2071	907	535	117.7	24.9	5.64
MEAN	2.233	337	1669	7343	1883	857	518	117.7	28.2	5.16

MEAN CONCENTRATION OF ELEMENTS (UG/G) - FALL SAMPLING OCTOBER 1985
DOUGLAS-FIR BURNT SITES (PLOTS 3&4)

TREAT -MENT	N(%)	AL	P	K	CA	MG	MN	FE	ZN	CU
CTRL	1.965	344	1709	6533	1605	820	536	72.1	24.4	4.25
P1	1.955	345	1841	7407	1830	944	510	84.1	26.8	4.03
P2	1.857	313	1786	7023	1644	884	431	80.6	20.3	3.87
N1	1.890	317	1516	6213	1330	754	403	81.5	23.0	3.97
N1P1	1.855	335	1861	6473	1693	807	578	79.8	22.5	3.84
N1P2	1.807	308	1805	6052	1671	835	507	78.1	20.8	3.77
N2	1.940	314	1476	7463	1739	746	443	66.6	23.6	3.96
N2P1	1.855	330	1570	5560	1817	855	517	77.5	21.6	3.84
N2P2	1.765	312	1738	7362	1877	856	540	66.9	21.0	3.53
MEAN	1.877	324	1700	6676	1690	833	496	76.4	22.7	3.90

Appendix 6B. Mean foliar concentration of elements (ug g^{-1} dry weight) for western hemlock on unburnt and burnt sites - Fall sampling 1985 of current foliar increment.

MEAN CONCENTRATION OF ELEMENTS (UG/G) - FALL SAMPLING OCTOBER 1985
WESTERN HEMLOCK UNBURNT SITES (PLOTS 1&2)

TREAT -MENT	N(%)	AL	P	K	CA	MG	MN	FE	ZN	CU
CTRL	1.955	368	1926	9016	2005	994	770	60.8	17.2	4.08
P1	1.650	400	2047	8922	2069	1064	743	56.5	16.9	6.75
P2	1.517	344	1799	8251	1787	1060	614	47.8	13.7	3.31
N1	1.910	364	1889	9278	1958	1060	653	52.9	18.7	3.86
N1P1	1.838	380	2069	8002	1969	1145	654	60.0	17.7	3.72
N1P2	1.902	412	2292	8753	2358	1203	871	65.6	18.3	3.84
N2	1.745	355	1827	8261	2052	1067	793	61.2	16.8	3.99
N2P1	1.880	443	2284	8442	2388	1127	848	95.9	19.4	4.06
N2P2	1.785	435	2113	7363	2204	1255	927	85.2	17.5	3.84
MEAN	1.798	389	2027	8476	2088	1108	764	65.1	17.4	4.16

MEAN CONCENTRATION OF ELEMENTS (UG/G) - FALL SAMPLING OCTOBER 1985
WESTERN HEMLOCK BURNT SITES (PLOTS 3&4)

TREAT -MENT	N(%)	AL	P	K	CA	MG	MN	FE	ZN	CU
CTRL	1.099	546	1544	8814	1661	983	720	66.5	11.9	3.19
P1	1.027	584	1745	8324	1622	1100	529	56.9	10.3	2.87
P2	1.092	590	1831	8280	1722	1080	621	74.0	11.8	3.35
N1	1.040	533	1647	7444	1814	1043	625	64.0	12.9	2.88
N1P1	1.200	451	1910	7398	1854	1046	680	83.8	11.8	2.90
N1P2	1.037	522	1733	7222	1731	1127	597	58.1	12.1	2.91
N2	1.182	391	1486	8260	1537	932	482	48.1	11.8	3.05
N2P1	.986	388	1628	6519	1549	977	508	46.1	11.4	3.08
N2P2	1.269	412	1704	7048	1632	1129	634	50.7	12.3	3.00
MEAN	1.104	491	1692	7701	1680	1046	600	60.9	11.8	3.02

Appendix 7. Effect of solution pH on the mean concentration of elements (ug g^{-1} dry weight) in Douglas-fir and western hemlock root and foliar tissue.

Nominal pH	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
	ug g^{-1} dry weight basis									
					Douglas-fir Root Tissue					
3.0	415	6180	10200	399	741	21	424	90	53	108
3.5	398	6110	11300	446	756	27	666	87	84	112
4.0	530	6330	11700	530	791	25	1180	78	95	102
4.5	627	6770	11200	654	900	27	1810	80	129	100
5.0	690	6410	10900	702	912	30	2240	74	144	103
Mean	531	6360	11100	546	820	26	1270	82	101	105
					Douglas-fir Foliar Tissue					
3.0	135	4800	5950	1100	938	87	78	47	28	34
3.5	126	4680	5960	1180	950	97	80	45	32	34
4.0	150	4640	5980	1140	984	100	90	46	30	33
4.5	133	4640	5780	1270	1090	102	95	48	34	38
5.0	118	4600	5710	1250	1080	97	88	43	31	33
Mean	132	4670	5880	1190	1010	96	86	46	31	34

Appendix 7 continued.

Nominal pH	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
	ug g^{-1} dry weight basis									
	Western Hemlock Root Tissue									
3.0	459	3760	8080	692	870	34	301	78	54	84
3.5	591	3900	8080	695	901	37	779	69	63	87
4.0	844	4860	7810	751	948	37	1950	74	78	78
4.5	996	6080	8170	830	977	39	3290	84	110	73
5.0	1090	5870	7800	906	981	42	3780	77	117	85
Mean	795	4890	7990	774	935	37	2020	76	84	81
	Western Hemlock Foliar Tissue									
3.0	324	3800	6400	2210	1320	265	104	35	54	83
3.5	352	3930	6930	2280	1390	270	112	41	55	85
4.0	310	3800	6580	2280	1360	266	116	33	60	79
4.5	311	3940	6730	2400	1450	289	141	39	66	77
5.0	290	3750	6700	2240	1371	256	142	34	63	75
Mean	317	3840	6670	2280	1380	269	123	36	60	80

Appendix 8. Effect of initial solution Al levels (ug ml^{-1}) and Ca:Al mole ratios on tissue levels of elements (ug g^{-1} dry weight) in Douglas-fir and western hemlock.

Treat -ment	Douglas-fir Root Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	2639	10886	10847	211	822	29	360.4	52.3	57.02	122
2	1678	8388	12262	222	826	26	209.7	55.5	51.20	104
3	1545	8021	13277	233	804	27	186.7	53.9	54.99	114
4	1590	7965	12920	273	844	29	145.4	60.7	54.88	123
5	1921	7682	13792	298	757	28	185.1	57.5	50.38	129
6	2013	10940	12329	289	787	25	278.0	63.0	55.87	111
7	1461	7911	12853	321	719	23	188.1	59.8	53.12	112
8	1631	7955	14794	490	690	23	183.6	56.8	51.46	105
9	2415	7653	14114	477	787	23	179.7	69.9	51.90	146
10	1900	7299	13813	503	726	25	205.7	71.8	56.08	116
11	2338	11694	13010	499	658	20	296.4	52.3	59.50	112
12	2170	9782	14663	551	727	24	320.4	52.7	58.07	117
13	1375	7907	16129	818	698	21	177.5	51.8	49.42	129
14	1502	8024	16005	851	639	21	167.8	54.1	47.35	130
15	1947	7295	15389	981	640	18	215.4	62.3	63.53	137
MEAN	1875	8627	13746	468	741	24	220.0	58.3	54.32	120

Treatment groups 1-5, 6-10, and 11-15 represent the 0.03, 0.15, and 0.75 Ca:Al mole ratios respectively. Within each group the following Al levels were applied (in numerical order): 10, 25, 50, 75, and 100 ug ml^{-1} (eg. treatments 1, 6, and 11 each had the same solution Al levels (10 ug ml^{-1}) but differed in their respective Ca:Al ratios).

Appendix 8 continued.

Treat-ment	Douglas-fir Foliar Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	232	5059	6264	864	1206	100	69.2	48.2	42.46	45
2	241	5348	6542	856	1215	116	82.8	47.0	42.62	33
3	321	4893	6541	890	1137	121	62.1	45.5	46.91	38
4	387	5041	6379	986	1214	109	69.0	47.8	47.16	39
5	308	4640	6651	833	1104	114	56.5	43.3	36.00	29
6	209	4975	6362	846	1131	117	73.5	48.0	39.95	31
7	272	4834	6463	927	1182	101	83.9	50.9	82.73	59
8	261	5008	6593	880	1189	103	62.2	46.6	36.97	32
9	496	5076	7021	1053	1242	117	65.2	52.7	46.00	45
10	487	5016	6669	1045	1232	106	65.9	53.8	48.26	37
11	211	4884	5929	902	1147	102	74.5	45.2	41.18	40
12	262	5170	6749	1087	1170	103	71.1	54.4	50.48	38
13	300	4950	6962	1182	1170	108	63.5	49.1	46.61	39
14	435	5461	7456	1540	1337	119	63.8	54.2	42.40	45
15	519	5326	6992	1717	1228	135	58.3	50.9	39.58	44
MEAN	329	5045	6638	1040	1193	111	68.1	49.2	45.95	39

Treatment definitions are given on p.240 of Appendix 8.

Appendix 8 continued.

Treat -ment	Western Hemlock Root Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	5439	8586	8256	414	694	49	435.0	48.1	42.11	151
2	2162	5220	9826	903	592	41	197.1	48.2	46.03	124
3	1986	5281	9516	482	607	42	158.4	49.8	44.12	149
4	2333	5260	8053	435	511	40	161.9	37.2	35.33	153
5	1825	5127	9004	805	565	36	125.9	37.7	37.60	106
6	5360	9183	8008	570	673	44	437.7	50.7	37.54	106
7	2868	6824	9631	620	595	46	238.0	45.0	42.80	136
8	2897	5379	9787	759	591	42	277.6	42.4	37.04	119
9	2401	4404	10692	562	591	42	167.6	45.9	48.12	198
10	1424	5267	10299	800	548	39	97.8	71.2	46.74	166
11	6224	10494	9139	649	605	39	521.7	48.9	40.58	150
12	2001	5321	10427	792	591	40	215.6	43.7	36.22	115
13	2616	5188	11419	1136	614	42	229.9	54.2	49.14	180
14	2241	4556	9956	1236	551	34	185.4	45.3	53.22	164
15	1598	4700	9862	911	492	36	109.7	43.0	34.71	145
MEAN	2892	6053	9592	738	588	40	237.3	47.4	42.09	144

Treatment definitions are given on p.240 of Appendix 8.

Appendix 8 continued.

Treat -ment	Western Hemlock Foliar Tissue (ug g^{-1} dry weight) Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	359	3048	6149	1753	1126	229	94.3	27.7	63.18	93
2	507	4197	7294	2049	1342	291	111.8	27.9	64.80	115
3	474	3331	6360	1756	1149	247	81.7	25.5	60.13	85
4	548	3244	6579	1954	1162	262	86.7	24.3	62.29	98
5	598	3373	6566	1752	1127	252	73.5	25.3	47.88	101
6	386	2884	6076	1753	1146	255	126.0	28.9	62.97	102
7	442	3801	7002	2060	1248	251	106.6	33.8	69.57	99
8	604	3221	7432	2059	1258	269	99.7	29.9	67.95	108
9	555	3629	7412	2063	1182	265	82.2	29.2	59.66	93
10	544	3374	6830	1790	1172	263	75.8	32.8	51.20	81
11	382	3348	6379	1818	1170	238	89.1	27.3	54.90	94
12	454	3481	6947	2114	1195	251	91.4	27.8	64.24	104
13	513	3212	7180	2240	1237	253	89.7	27.6	53.16	114
14	682	3088	7189	1989	1136	242	95.3	25.8	54.18	95
15	505	3251	7188	2172	1177	254	76.4	26.9	48.55	89
MEAN	503	3365	6839	1955	1188	255	92.0	28.0	58.98	98

Treatment definitions are given on p.240 of Appendix 8.

Appendix 9. Effect of initial solution Al levels (ug ml^{-1}) and P:Al mole ratios on tissue levels of elements (ug g^{-1} dry weight) in Douglas-fir and western hemlock.

Treat-ment	Douglas-fir Root Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	1178	4190	14436	378	833	33	236.1	53.0	50.99	106
2	1608	4128	12740	380	801	34	199.5	51.1	48.29	105
3	1392	4508	13358	345	782	35	125.0	57.3	46.79	112
4	1852	4318	12768	303	726	34	178.7	52.8	43.91	86
5	2271	4694	13114	306	790	44	202.8	58.8	47.11	116
6	1002	4791	13151	380	799	30	217.0	56.5	53.38	123
7	1403	5654	13513	346	802	30	156.2	76.8	51.30	99
8	2450	6332	14242	325	833	34	220.4	56.0	47.91	114
9	1696	5463	11634	280	745	31	123.3	50.7	43.34	95
10	1565	5737	12159	280	774	32	137.9	51.1	43.67	123
11	1404	6826	11700	345	686	26	214.1	48.8	47.61	119
12	1383	7674	12182	322	750	28	152.8	49.8	48.16	119
13	1638	8826	13298	320	779	29	152.4	60.2	47.61	118
14	1437	7739	12273	304	770	23	141.8	60.3	50.65	124
15	1653	6570	11540	393	683	38	129.1	58.8	56.04	107
MEAN	1595	5830	12807	334	770	32	172.5	56.1	48.45	111

Treatment groups 1-5, 6-10, and 11-15 represent the 0.0065, 0.025, and 0.1 P:Al mole ratios respectively. Within each group the following Al levels were applied (in numerical order): 10, 25, 50, 75, and 100 ug ml^{-1} (eg. treatments 1, 6, and 11 each had the same solution Al levels (10 ug ml^{-1}) but differed in their respective P:Al ratios).

Appendix 9 continued.

Treat -ment	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
	Douglas-fir Foliar Tissue (ug g^{-1} dry weight)									
1	301	3903	6069	1051	1018	116	83.2	46.0	36.35	37
2	269	3837	5763	1166	974	112	56.6	44.5	38.90	40
3	337	4055	6354	1147	1068	118	65.1	48.8	38.88	39
4	318	3755	5665	1037	961	98	59.8	41.6	34.06	35
5	361	4061	6225	1003	1013	102	50.5	43.4	30.96	38
6	271	3973	6012	1102	1021	105	79.6	45.0	35.77	38
7	292	3993	6001	1115	993	110	66.3	42.2	34.70	36
8	426	4506	6828	1141	1064	119	74.5	48.2	34.23	42
9	435	4583	6511	1153	1104	116	64.2	49.5	38.22	43
10	339	4356	6138	1128	998	105	57.6	44.5	37.23	38
11	255	4199	6218	1145	1031	110	85.9	46.2	40.35	43
12	238	4485	6060	1099	1006	95	62.9	45.0	34.54	40
13	257	4583	5947	1111	977	92	52.7	44.6	36.67	40
14	323	5214	6472	1092	1095	103	55.3	48.0	33.44	39
15	335	4591	6416	1186	1014	95	52.3	47.2	41.25	47
MEAN	317	4273	6178	1112	1022	106	64.4	45.6	36.37	39

Treatment definitions are given on p.244 of Appendix 9.

Appendix 9 continued.

Treat -ment	Western Hemlock Root Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	2866	3036	9758	524	638	47	439.6	50.0	44.57	84
2	3074	2984	10379	515	601	45	273.2	54.4	43.89	96
3	3137	3434	10184	495	608	45	196.8	52.8	39.57	76
4	2942	3165	9912	542	579	46	188.3	57.3	44.71	134
5	3145	3568	10075	510	603	47	229.8	54.4	43.09	91
6	3498	4560	10514	519	660	47	478.6	47.5	48.60	137
7	3905	4505	10008	576	620	46	279.7	55.1	44.05	111
8	3611	4672	10589	501	563	43	266.5	46.1	40.14	77
9	2921	4223	9673	483	526	43	161.5	47.0	40.32	108
10	2815	4699	11298	511	606	51	197.0	56.9	47.89	94
11	4117	6617	9833	576	650	46	430.9	43.6	44.12	124
12	4538	6565	10865	551	691	50	341.4	50.4	47.45	122
13	2299	5502	10583	517	566	44	152.6	50.3	39.32	113
14	1572	4237	10595	502	543	45	118.6	47.2	40.76	102
15	2033	5783	10126	391	646	33	166.8	61.9	65.56	101
MEAN	3098	4503	10293	514	606	45	261.4	51.7	44.94	104

Treatment definitions are given on p.244 of Appendix 9.

Appendix 9 continued.

Treat -ment	Western Hemlock Foliar Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	386	2795	6962	2124	1251	233	78.2	30.2	59.92	99
2	642	2896	7075	1997	1262	245	92.2	31.9	59.68	88
3	728	2643	6633	2057	1159	235	105.1	32.5	60.03	104
4	1223	3007	7005	1950	1205	238	154.3	32.4	53.67	103
5	1000	2767	7181	2013	1249	255	90.3	32.3	57.03	103
6	489	2870	6990	2023	1260	242	108.2	31.2	58.23	92
7	1080	2865	6866	2028	1244	233	145.9	31.3	62.04	100
8	870	2876	6869	2008	1179	232	85.3	31.4	58.86	100
9	891	3303	7022	2009	1252	250	89.8	30.3	61.16	103
10	947	3248	6797	1924	1179	240	79.3	31.0	60.43	102
11	423	3151	7026	2151	1313	246	93.1	32.1	63.75	110
12	666	3334	7764	2231	1247	246	107.8	33.3	64.56	102
13	665	3383	7301	1921	1188	233	82.9	28.8	51.07	102
14	591	3163	6994	2129	1158	220	74.5	31.6	69.07	110
15	648	3075	6818	1951	1130	236	71.9	34.6	61.53	115
MEAN	750	3025	7020	2034	1218	239	97.3	31.7	60.07	102

Treatment definitions are given on p.244 of Appendix 9.

Appendix 10. Effect of initial solution Al levels (ug ml^{-1}) and OH:Al mole ratios on tissue levels of elements (ug g^{-1} dry weight) in Douglas-fir and western hemlock.

Treatment	Douglas-fir Root Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	2950	5800	15400	451	516	22	230	58	52	156
2	2190	8580	15700	432	490	37	260	67	49	104
3	2210	6860	15000	401	521	29	252	79	46	83
4	2640	6170	14900	403	525	37	282	74	47	99
5	2420	5620	13500	367	433	30	329	60	39	94
6	3470	11000	17300	437	531	28	338	70	49	127
7	2430	7570	16000	382	457	25	299	71	40	81
8	3020	6650	15600	406	466	32	140	67	43	125
9	3610	5860	15800	411	422	35	130	68	50	141
10	2760	4430	15600	327	325	31	153	61	32	113
11	1960	9010	16900	439	543	32	214	67	48	93
12	2370	6280	15800	385	384	31	237	53	35	104
13	3000	3800	16400	397	382	28	165	55	35	164
14	3700	4080	14600	415	400	25	153	65	40	178
15	2300	4210	14400	411	413	26	86	66	42	136
Mean	2740	6390	15500	404	454	30	218	66	43	120

Treatment groups 1-5, 6-10, and 11-15 represent the 0, 0.5, and 1.0 OH:Al mole ratios respectively. Within each group the following Al levels were applied (in numerical order): 10, 25, 50, 75, and 100 ug ml^{-1} (eg. treatments 1, 6, and 11 each had the same solution Al levels (10 ug ml^{-1}) but differed in their respective OH:Al ratios).

Appendix 10 continued.

Treatment	Douglas-fir Foliar Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	298	7150	4580	1090	1010	116	74	48	15	67
2	316	6400	5610	941	1080	118	71	49	16	44
3	475	5320	6340	973	1100	117	75	50	19	37
4	351	6310	5760	1090	1180	123	110	49	18	32
5	403	6300	5970	933	1090	117	94	49	15	36
6	290	7310	5420	949	1160	109	67	47	14	53
7	286	5820	6480	1010	1130	122	71	50	15	41
8	447	5520	5750	1000	1140	115	86	49	18	52
9	408	5030	5810	1030	1140	122	80	51	14	50
10	515	4740	6020	888	1100	122	68	46	14	55
11	303	5930	6220	1040	1160	127	72	49	15	41
12	331	5350	5370	1030	1092	110	76	46	14	40
13	423	4380	5910	1020	1060	108	89	48	16	68
14	408	4410	5680	1010	1220	115	86	46	15	69
15	338	4690	6100	1020	1100	118	80	49	16	63
Mean	373	5640	5800	1000	1120	117	80	49	16	50

Treatment definitions are given on p.248 of Appendix 10.

Appendix 10 continued.

Treatment	Western Hemlock Root Tissue (ug g^{-1} dry weight)									
	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
1	7030	11000	9850	488	563	39	639	45	39	83
2	4560	9850	9980	484	500	48	411	46	39	59
3	3740	7900	9000	577	559	51	464	61	56	146
4	3280	8280	8670	506	596	44	327	63	40	81
5	2720	7090	10200	539	559	36	322	45	38	120
6	4230	10700	11700	518	487	39	338	48	34	74
7	4550	9460	10300	633	571	37	139	38	34	63
8	5200	6040	10600	525	532	42	156	47	33	90
9	7490	4990	10800	514	502	42	121	52	37	91
10	3590	6320	9690	492	508	46	108	45	36	148
11	3940	10100	11300	528	581	54	188	44	54	89
12	6430	6870	12000	524	514	40	194	41	32	78
13	5200	3570	10100	584	493	44	86	45	27	96
14	6310	4320	9652	619	605	44	119	53	26	110
15	5940	4460	8530	558	519	45	75	42	38	79
Mean	4840	7350	10100	538	539	43	243	48	37	96

Treatment definitions are on p.248 of Appendix 10.

Appendix 10 continued.

Treatment	Al	P	K	Ca	Mg	Mn	Fe	Zn	Cu	Na
	Western Hemlock Foliar Tissue (ug g^{-1} dry weight)									
1	636	3880	10200	3220	1630	253	120	37	68	177
2	919	4490	9930	3110	1620	282	111	40	57	163
3	942	4870	9070	3870	1700	255	121	43	59	171
4	1170	4830	9580	3280	1710	293	95	42	60	151
5	978	4960	8530	2890	1690	289	84	37	53	147
6	616	3980	10200	3190	1590	237	116	42	71	143
7	607	4430	9500	3800	1640	241	105	44	65	146
8	727	4180	9480	2750	1480	257	98	35	54	120
9	726	4040	9320	3300	1610	278	97	40	68	130
10	765	4860	8960	3420	1670	277	80	45	74	152
11	535	4720	11000	3940	1870	288	123	46	60	162
12	493	4020	9370	2940	1560	298	130	35	56	124
13	485	4300	8290	3190	1540	261	87	41	71	123
14	624	3620	9000	3100	1610	254	90	35	60	157
15	801	4410	7710	3760	1690	251	87	41	61	172
Mean	734	4370	9340	3320	1640	267	103	40	62	149

Treatment definitions are given on p.248 of Appendix 10.

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