INVESTIGATION OF INORGANIC FACTORS IN SOIL LIMITING THE GROWTH OF SITKA SPRUCE

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DEDICATION

To my Father who warned me to beware of the bad in the best of us.

To my Mother who taught me to look for the good in the worst of us.

With all my love

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CONTENTS

SUMMARY

High amounts of allophane as measured by the sodium fluoride test were found in the brown forest soils and B horizons of podzols developed on basalt and basalt till. High organic matter levels and phosphate retention in these soils were found to be due to their high allophane content.

Spruce can grow on soils with a range of physical and chemical properties. Chemical tests have been studied for reliability in predicting deficiency of phosphate in spruce needles, and high levels of soluble or exchangeable aluminium in soils, particularly in Fiunary and Savary Glen Forests. These findings led to the conclusion that aluminium toxicity was the cause of the phosphate deficiency. In addition to direct effects on the chemical status of other essential nutrients.

Trees responded rapidly to fertilizer giving measurable differences in the growth. Fertilization markedly increased the amount of (phosphorus, nitrogen and potassium) accumulate in the current year's needles.

A comparison was made of various methods for estimating available phosphorus in soil. The choice of a particular method was dependent upon its reproducibility and sensitivity freedom from interfering ions and stability of colour.

The correlation coefficients between available phosphorus values obtained by these methods, and total phosphorus in the soils, with the uptake of phosphate by spruce trees were calculated. The resin method gave

better correlations with phosphorus uptake by spruce than other chemical methods. The anion-exchange resin method for soil-phosphate extraction was investigated on four different soils. The amount of phosphorus extracted was dependent on the anionic form of the resin. It was concluded from the results given that the strong base anion-exchange resin affects the pH of soil-water suspensions.

The Cl^- form of AER caused a decrease in the pH of all soils, whereas the OH^- and HCO_3^- forms increased the pH of acid soils. Phosphorus extracted by HCO_3-resin was greater than Cl-resin from acid soils.

It is thus recommended that resin in the bicarbonate form should be used for both routine as well as more advanced analyses to test the ability of soils to supply phosphate to plants.

The reproducibility of the ascorbic acid method was superior to that of the stannous chloride process, in addition to having the advantages of stable colour for a long period, and excellent colour and sensitivity.

A study was made of the possible interference of silicon on the determination of phosphorus. The results indicated that a range of silicon (Si) concentrations do not affect the phosphorus values.

This investigation set out to devise a suitable and rapid method for determining the silicon in soil and plant tissues. There are many methods available varying in principle and technical detail for determining silicon in soil and plant materials. Several methods have been compared and their relative efficiencies judged for accuracy and reproducibility.

Rapid decomposition of silicates is achieved in teflon vessels with sealed lids to prevent volatilization losses using hydrofluoric acid at $240^{\circ} \pm 10^{\circ}C$. Hydrofluoric acid and a second mineral acid is an effective and powerful decomposing agent for the complete dissolution of silicate materials without loss of silicon by evaporation provided the containers are cooled at $-18^{\circ}C$ for two hr. before opening.

The boric acid is present to suppress HF interference during analysis. The borate removes interference from excess fluoride by forming fluoroboric acid. Silicon (Si) (present as fluorosilicic acid) can then be determined spectrophotometrically as the yellow β-silicomolybdic acid. The reduction of silicomylybdic acid to molybdenum blue by using metol solution as reductant instead of 1-amino-2-naphthol-4-sulphoric acid is also recommended. Alternatively, the silicon can be determined directly by atomic absorption spectrophotometry.

A pH of 1.9 is recommended for solutions of molybdosilicic acid on the ground of reproducibility.

The most important sources of interference likely to be encountered in most work are due to phosphorus and iron. It was found that 0.5 ppm of silicon could be determined in the presence of 22 ppm of phosphorus.

Suppression of phosphorus was achieved by the addition of oxalic acid solution. Mullin and Riley (1955) found that by reducing iron with hydroxylamine hydrochloride, 0.2 ppm silicon could be determined in the presence of 100 ppm ferric iron with an error of less than 1%.

The growth of sitka spruce seedlings on acid soils were significantly improved by ectomycorrhiza. Seedlings with this ectomycorrhizal

fungus have a root system that was physiologically capable of tolerating adverse soil conditions, and increasing absorption of essential nutrients from low concentrations.

The uptake of nutrients from soil and litter from the relatively large inter-root distances of trees is achieved by longevity of mycorrhizal roots and particularly by growth of mycelial strands into soil. The implications of longevity for transfer in the soil are the same for both diffusive and convective flow. Increasing nutrient uptake and efficiency of nutrient use is only one aspect of tree growth. It has to be integrated into such other aspects as tree demand for nutrients under a particular situation. Increasing nutrient uptake is not likely to be of much relevance in a situation where some other factor is limiting growth.

Mycorrhiza influence nutrient uptake, carbohydrate distribution and growth substance production, and increase host-plant resistance to drought, and eventually eliminate aluminium soil toxicity. A priority should be to understand how these factors are integrated in plant growth in soil.

Analysis of several plant polysaccharides confirmed the presence of silicon in all pectin samples analysed and revealed its presence in potato starch, and it revealed the presence of phosphorus in all pectin, and potato starch samples. In the latter case, the silicon was concentrated in the amylopectin fraction.

The range of silicon values found, based on dry weight of polysaccharide analysed was:-

(a) for pectin 1.40 - 2.30 mg g^{-1} DW.

(b) for potato starch 0.47 - 0.80 mg g^{-1}.

Other samples analysed contained less than 0.10 mg g^{-1}.

It would appear that most of the silicon present in potato tubers is located in the starch grain and some of the properties of potato starch traditionally attributed to phosphate could be influenced by the silicon present.

The range of phosphorus values found, based on dry weight of polysaccharides analysed was:-

(a) for pectin 0.30 - 0.42 mg g^{-1}.

(b) for amylopectin 1.45 - 1.93 mg g^{-1}.

(c) for potato starch 1.30 - 1.95 mg g^{-1}.

Although it is doubtful whether this would place silicon (Si) in the list of essential nutrients, there is nevertheless increasing evidence that silicon can produce beneficial effects on plant growth.

The results obtained in this study show that the influence of silicon (Si), phosphorus and polysaccharide samples for precipitating or reducing aluminium concentration in solution could considerably, silicon (Si) and phosphorus precipitate aluminium from solution. The percentage of precipitated aluminium is of the order of 57.7 and 63.6 respectively. The influence of polysaccharide samples for precipitating or reducing aluminium concentration in solution varied from 5.4 - 57.6%. The highest value was obtained for amylopectin and the lowest value for glycogen. The precipitation process mainly depends upon the contents of phosphorus and silicon in the polysaccharide samples. Another significant result from this study is that the addition of soluble silicon to soil has a

beneficial effect, in increasing the availability of soil phosphate. It now seems clear that this beneficial effect of silicon (Si) is not because the plant utilizes silicon instead of phosphate, but rather because the silicate ion displaces the phosphate ion from the surface of soil or colloidal material, thus increasing the availability and the amount of phosphorus.

The toxic effect of aluminium in acid soils can be overcome by the application of lime, organic matter, phosphate or silicon in rather large amounts or by the presence of mycorrhiza. The beneficial effects of these treatments have been variously attributed to:-

1. Supplying essential elements that are deficient in the plant,
2. Changing the soil reaction to a pH range that is favourable for plant growth,
3. Rendering aluminium inactive because of precipitation in the soil,
4. Eliminating the toxic action of aluminium.

According to the Annual Report of the Forestry Commission on Fiunary Forest, Experimental Plots, the forest site continues to grow better than the pasture site, with a mean height of 2.07 compared to 1.43 m. Survival remains excellent on both sites. Second rotation trees are more successful in the same profile because the seedlings are planted in the fermentation layer, i.e. the soil already contains mycorrhizal fungi.

CHAPTER 1

INTRODUCTION

1.1 PROBLEMS IN FORESTRY PRODUCTION ON BASALT-BROWN SOILS

In studies of relationships between tree growth and soil properties an understanding of soil variability and its effect on the precision of determining these properties is essential. This is particularly the case for assessments of capability of forest sites in which timber production is predicted from known relationships between tree growth and site characteristics. Many of the soils available to the Forestry Commission for planting in Scotland are of poor quality, comprising peaty gleys, humic gleys, peats, and podzols with thin iron pans.

The basalt brown soils are a minor and much sought-after commodity because their rooting depth, good structure and better fertility give rise to expectations of a high yielding crop with resistance to wind throw. Since wetness, high rainfall and altitude make these soils in general unsuited to arable farming, it might be thought they would be among the better soils available to soft-wood forestry. This is not always the case.

It was therefore a great disappointment to find that spruce and sitka spruce in particular, did not do well on certain basalt brown forest soils. Some of these soils have been planted with trees in Morvern and on Mull. These large plantations represent a serious loss of capital in their present state of poor growth.

The trouble was tentatively diagnosed as phosphate deficiency and it was thought it might be due to the fixing powers of the soil's high iron content (G. Pyatt, D. B. Patterson, pers. comm., 1968). A pilot experiment in which phosphate retention was measured on samples of Darleith soils confirmed this prediction (Lindsay, 1969). The pilot survey was directed by D. B. Patterson (1970 - 1971), and its object was to examine the poor and variable growth rates associated with basalt soil types. It was conducted on a part of Fiunary Forest and correlations were made with J. S. Bibby's (1969) soil survey on Mull, where the basalt soils were being mapped as Darleith Association Soils (Mitchell and Jarvis, 1956). Brown forest soils and podzols are similarly affected, but analytical data correlating soil and crop growth was confined to the brown forest soils, or "normal brown earths" as they are designated.

The normal brown earths were dark reddish brown with fine sandy loam to sandy clay loam textures, usually with a very strong subangular blocky structure and friable consistency becoming firm, but not indurated in the C horizon. Slight or moderate gleying in the B and C horizons reflected varying degrees of imperfection in the drainage, but their situation on steep slopes allowed them to be classed as free draining Darleith series (Fullerton, 1972). The soil depths varied from 45 to 100 cm depending on their slope situation. Nevertheless, even in their deep phases the soils all exhibited shallow rooting often with a sharp interface between the top of the B and bottom of the A horizon, where rooting ceased (Fullerton, 1972).

Later it was revealed by foliar analysis that the spruce was indeed deficient in phosphate (D. B. Patterson, pers. comm., 1971). The first discovery that raised doubts about the role of the iron oxides and suggested another interpretation for the behaviour was the identification oflarge amounts of allophanic material, i. e. amorphous alumino-silicates (Fullerton, 1972). This could easily be seen in the field by the fluoride test (Fields and Perrott, 1966).

The B horizon of the peaty podzol and all horizons of the brown forest soils in Morvern, and on Mull and most soil samples from Skye stained the paper red. In the laboratory, the reactive soils suspended in saturated sodium fluoride solution reached pH values between 10. 0 and 11. 5 in 30 minutes. This was not found to be the case with comparable soil samples taken from the Pitmedden forest in Fife. Other suggestions put forward to account for the poor growth included the possibility of nickel or manganese toxicity (D.S. Coutts, pers. comm., 1979), due to the displacement of magenisum present as forsterite (Mg_2 SiO_4) by nickel. Most of the research on the trace element (Ni) has been concerned with its effects on growth and metabolism (Mishra and Kar, 1974). Plants are known to accumulate Ni readily and unlike most non-essential elements (Cataldo et al., 1978), Ni is mobile in plants and tends to accumulate in seeds (Mishra and Kar, 1974). Others thought that the poor growth might be due to nitrogen deficiency (D. S. Coutts, pers. comm., 1979).

Based on this background information, several lines of enquiry were suggested and these are summarised below:-

(i) The high degree of aggregation might be due to allophanic clay rather than the iron oxides. The sand fraction contained high proportions of hematite and pyroxene magnetite (Fullerton, 1972). The argument had practical relevance because if the allophanic material influenced the soil structure (Fullerton, 1972), this might be important in agricultural management. It might be recommended, for example, that organic matter levels should be well maintained, or that a soil which appeared poor because of bad drainage, was potentially fertile and worth an economic outlay.

(ii) If the soils were indeed susceptible to phosphate fixation, it might be the allophanic clay rather than the iron oxide which was primarily responsible. Liming the soil would improve phosphate availability in either case, but addition of organic matter and its preferential fixation on the aluminous sites, would inhibit the retention of phosphate by the soil. In view, however, of the later discovery by workers of the Forestry Commission, that phosphate is available in the soils but deficient in the spruce (D. B. Patterson, pers. comm., 1971), it was postulated that aluminum toxicity might be the cause of the deficiency and poor growth of the trees. a parallel study on spruce shoots, details of which were not available when the present project was set up concluded that the failure of poor growth of sitka spruce was due to a shortage of available phosphate on high soluble aluminium soils (James et al, 1978).

Aluminium is more soluble and available to plant at soil pH values below 5.5. In nature as soils become more acid plants have tended to adapt to the changed conditions (Helyar, 1978).

Acid soils are often low in essential nutrients such as P, Ca, Mg and K as well as being high in the potentially base elements - Al and Mn.

In addition to direct effects on the levels of the soil, acidity alters the populations and activities of the micro-organisms responsible for transformations involving N, P and S in the soil, thus indirectly affecting the availability of these nutrients to higher plants (Jackson, 1967).

1.2 A FIELD INVESTIGATION ON SITKA SPRUCE (CHECK ON BASALT BROWN EARTHS)

1.2.1 BACKGROUND

It is proposed to test the idea that spruce check on brown earths is due to the high content of allophane (amorphous alumino-silicate) in the soil, i.e. to reactive aluminium, and that this in turn has a detrimental effect either on phosphate uptake or on phosphate metabolism. All acid brown earths tested in Britain (H. Fullerton, 1975, unpublished work), particularly those in the strongly leached western areas, contain high amounts of allophane throughout the subsoil and sometimes also in the top soil. There is no ill effect on pasture, and in woodland on most parent materials the podzolising action of conifers and other tree species could be seen as protective, i.e. they remove the allophane to lower horizons. This can happen in less than fourteen years (Fullerton, 1975, unpublished work). On basalt soils, however, the podzolising activity is inhibited and the allophane content remains high throughout the profile.

The aluminium can be immobilised even on basalt soils by chemical combination with organic matter or with silica. The aluminium also fails to be mobilised in situations where the pH is less acid or where the soils are relatively little leached.

The following observations from twelve forest sites prompted

this investigation:-

(a) Spruce check or low yield class on basalt acid brown earths where allophane is retained in upper horizons.

(b) Yield class lower than expected on non-basalt acid brown earths, now podzolised, suggesting a slow "getaway".

(c) Good growth in fertile bottom-lands, where the basalt brown earths are well endowed with mull organic matter.

(d) Very good growth on basalt brown earths in drier eastern areas, and correlating with low allophane content (i. e. Pitmedden Forest, Fife).

(e) Checked spruce trees have very poorly developed mycorrhiza, while vigorous trees have plentiful mycorrhiza.

The hypothesis of H. Fullerton (1975) (unpublished work) which was based on the above points cannot yet distinguish whether the organic matter is too low or of the wrong kind to encourage mycorrhiza to develop and thus allow the humus horizon to sustain the trees, or whether the aluminium inhibits the spruce from developing mycorrhiza.

As mentioned previously, one of the early points established by the Forestry Commission was the low amount of phosphate in the spruce needles which could be caused by the action of the mobile aluminium on phosphate uptake in one of the following ways:-

(i) By fixing the phosphate rather strongly in the soil. This might not be detected by the acetic-soluble test.

(ii) By starving the tree of phosphate by precipitating aluminium phosphate on the surface or in the outer cortex of the root.

(iii) By interfering with phosphate metabolism, e. g. by inhibiting root elongation.

Experimental plots were set up to test some of the above factors.

1.2.2 SUMMARY OF EXPERIMENTS

The experiments were designed to test:-

(i) Whether spruce check is the result of planting in the mineral horizon of basalt brown earths, and whether it can be circumvented by planting in the organic horizon.

(ii) Whether self-sown seedlings with well developed mycorrhiza are better adapted than those raised in nursery soils to combat the conditions of acid brown earths.

(iii) Whether the humus provided by the first rotation may allow a more successful second rotation.

(iv) The effect of adding phosphate.

(v) The effect of adding lime.

Initially, two planting sites were set up:-

(a) Upland unplanted pasture: Fiunary main block compartment (302).

(b) Cleared Norway spruce woodland: Fiunary main block compartment (105). (Recent clear felled site).

Also included in the exercise were studies on the effects of the above on the growth of:-

(i) Nursery transplants, and

(ii) Self-sown two year old spruce seedlings.

1.2.3 BASIC TREATMENTS

Species : Sitka spruce

Spacing : Plant spacing was 1.5 x 1.5 m (5ft. x 5ft.)

Protection: All plants were dipped against Hylobious

1.2.4 EXPERIMENTAL TREATMENTS

A. Pasture plots

		Symbol
1.	1 + 1 plants* in basalt mineral soil	(1 + 1) BM
2.	1 + 1 plants in organic horizon	(1 + 1) BO
3.	As for 1 above with added phosphate	(1 + 1) BMP
4.	As for 2 above with added phosphate	(1 + 1) BOP
5.	As for 1 above with added lime	(1 + 1) BML
6.	Self-regenerated plants in basalt mineral soil	(SR) BM
7.	Self-regenerated plants in organic horizon.	(SR) BO

* See Chapter II for details, Section 2.2.5.

B. Forest plots

1.	1 + 1 plants in basalt mineral soil	(1 + 1) BM
2.	1 + 1 plants in F + L layer	(1 + 1) BF
3.	As for 1 above with added phosphate	(1 + 1) BMP
4.	As for 2 above with added phosphate	(1 + 1) BFP
5.	As for 1 above with added lime	(1 + 1) BML
6.	Self-regenerated plants in basalt mineral soil	(SR) BM
7.	Self-regenerated plants in F + L layer	(SR) BF

See Chapter II for fuller details.

1.2.5 DESIGN

Randomised block experiment.

7 treatments replicated three times on each site.

3 x 3 plots. No buffers between plots.

The details are given in Chapter II, Section 2.2.5.2.

Plants: 378 seedling trees were planted.

1 + 1 transplants ex. nursery stock.

108 self-regenerated seedlings preferably 2 + 0 lifted from the forest.

1.3 THE ROLE OF MYCORRHIZA

The mycorrhiza was originally viewed by Frank (1885) as a beneficial root appendage, one which aided in the absorption of water and nutrients from the soil. Since that time much study has been devoted to its occurrence and effect upon the associated host plant. This concept was challenged by others, amongst them, the Pathologist Hartig, who judged the mycorrhizal state to be purely a condition of parasitism on the part of the fungus. Since then, much effort has been devoted to a search for the significance of mycorrhiza to tree growth, and many theories have been advanced (Harley, 1969; Marks and Kozlowski, 1973).

The prevailing view today, however, is that most forms of mycorrhiza are beneficial to the tree (Harley, 1969; Bowen, 1973). The relationship is viewed as truly symbiotic (Zak, 1964), in which the higher plant gains by improved nutrition (Harley, 1969) and the fungus by receiving a supply of carbohydrates (Harley and Lewis, 1969).

Our understanding of the mycorrhizal relationship is relatively

advanced in the case of the ectotrophic mycorrhiza. The majority of forest trees have ectotrophic mycorrhiza, also called ectomycorrhiza (Trappe, 1962), most non-woody species, including a large number of agricultural plants have endotrophic mycorrhiza, also called endomycorrhiza (Trappe, 1962). The endomycorrhiza are usually of the vesicular-arbuscular type (Gerdemann, 1968; Kelly, 1972; Mosse, 1973).

Went (1974) found a tremendous activity of fungi in the upper soil layers where dead leaves, branches and all other debris from the rain forest produced a litter layer completely pervaded by tree roots, fungal hyphae and rhizomorphs. There was an intimate network of hyphae and rhizomorphs between litter and tree roots, and most of these roots pervading the litter were mycorrhizal. Thus it became clear that mycorrhiza is not just a tree root-fungus association, but that it is part of a tripartite system (Went, 1974).

The fungi digest the litter and pass much of the extracted nutrients back to the tree roots thereby closing a nutrient cycle (Meyer, 1974; Went, 1974).

1.4 IMPORTANCE OF INOCULATION

Early reports on the failure of exotic pines usually came from forest nurseries (Mikola, 1973). Afforestation trials were started by establishing nurseries where seedlings suffered and died (May,1953; Mikola, 1970), but after introduction of appropriate fungi, healthy and vigorous seedlings with mycorrhiza were produced (Mikola, 1973; Zak, 1973). When it was discovered that exotic pines showed a need to form

mycorrhizal associations, an annual inoculation of nursery soil was adopted as a standard routine in several countries (May, 1953; Mikola, 1970).

In soils which have long been in agricultural use, mycorrhizal fungi usually are not completely lacking, but the population density may be low or the existing fungi may belong to less effective species (Mikola, 1973). If a forest nursery is established on such soil, introduction of new fungal species may be beneficial (Mikola, 1970).

Inoculation may be an effective measure of improving the growth of seedlings and development of mycorrhiza (Harley, 1969; Mikola, 1973), but, in addition, soil properties such as acidity, fertility or organic matter content, should be corrected in order to favour the introduced fungi (Dominik, 1961).

At the present time, correction of soil conditions is a more common procedure in forest nurseries on agricultural soils than attempts to introduce new fungi (Sobotka, 1963).

1.5 ANALYTICAL PROBLEMS ASSOCIATED WITH PLANT NUTRITION

1.5.1 PHOSPHORUS

A. Available phosphorus

The chemical technique that has received, and is still receiving, the most attention is that of extraction with one or more solutions. The different extracting solutions that have been recommended are legion.

The purpose of these methods has been to characterize the

phosphorus in the soil system. There are many methods varying in principle and technical detail. The selection of a suitable method requires a clear understanding of the objectives behind the determination. Other considerations to be taken into account include the properties of the soils involved, and the accuracy and reproducibility needed. In some instances suggestions for alternative procedures or modifications to meet special circumstances are given as literature citations in Chapter IV.

Most soil P determinations have two distinct phases:

First, the preparation of a solution containing the soil P, and second, the quantitative determination of the P in this solution. The choice of a colorimetric method for determining P depends on the concentration of P in the solution, the concentration of interfering substances in the solution to be analyzed, and the stability of the reducing agent used. Methods based on molybdenum blue are the most sensitive and as a result, are widely used for soil extracts containing small amounts of P as well as for total P in soils. These methods are based on the principle that in an acid molybdate solution containing phosphate ions, a phosphomolybdate complex forms that can be reduced by ascorbic acid, stannous chloride or other reducing agents to give an amolybdenum blue colour. The intensity of the blue colour varies with the P concentration but is affected also by other factors such as acidity, the presence of silicates and substances which influence the oxidation-reduction conditions of the system. A wide variety of adaptations of this basic method has been found necessary to cope with the conditions encountered in practice.

B. Total phosphorus

The determination of total P in soils involves extraction of solubilized inorganic P and mineralized organic P and subsequent determination of the orthophosphate in the extract (Sommers and Nelson, 1972). Selected procedures for analysis of total P in soil are described by Jackson (1958). Perchloric acid digestion procedures are more amenable to routine estimation of total P in a large number of soil samples, however, these digestions are conducted commonly in either Kjeldahl digestion flasks, or other special apparatus (Jackson, 1958) and thus, require considerable laboratory space and equipment. Therefore, the objectives of this study were to develop a simple procedure for determining P in soils by $HClO_4$ digestion.

1.5.2 SILICON (Si)

Only a few methods are in general use for the determination of silicon-

(i) Gravimetric determination after acidic dehydration,

(ii) colorimetric determination as silico-12-molybdate yellow or blue,

(iii) titrimetric methods involving hydrolysis of the $(SiF)_6^{-2}$ ion,

(iv) analysis for silicon by the atomic absorption method.

However, since silicon is a universally distributed and major constituent of the earth's crust, its variations are very numerous and the literature is vast. The intention here is not to be thorough, but simply to be informative and accurate concerning essentials of the analytical chemistry involved. A wide range of chemical methods and

and procedures is found in the treatise of Kolthoff and Elving (1962). Most of the proposed methods for the photometric determination of silicon are based on the formation of yellow silicomolybdic acid or its reduction product, molybdenum blue. Yellow silicomolybdic acid is formed in acid solution by reaction between silicate ions and molybdate ions.

Silicon in materials not decomposed by the acids normally applied is converted to acid soluble silicates by fusion or heating with an alkali. Since, for a long time many analyses have been carried out for the determination of silicon in several materials employing different crucibles for decomposition of the silicate material.

Generally sodium and potassium hydroxides are used for the decomposition of silicate material. This decomposition occurs at a temperature much less than those required for fusions with sodium carbonate.

Platinum, silver, and nickel crucibles were recommended for decomposition of silicate materials in soils and plant material (Kolthoff and Elving, 1962; Jeffery, 1970).

Hydrofluoric acid was not applied for the decomposition of samples in which silicon is determined, because of the fear of losing silicon as the volatile silicon tetrafluoride. A survey of the extensive literature on the spectrophotometric determination of silicon shows only a limited number of procedures in which hydrofluoric acid is used as decomposing agent (Langmyhr and Graff, 1959). In these cases, hydrofluoric acid is

applied in combination with other acids.

Case (1944) used hydrofluoric acid in addition to the usual acids to increase the rate of dissolution of certain non-ferrous alloys in which silicon was finally determined photometrically as yellow silicomolybdic acid. Case (1944) made the important observation that a given amount of silicon, whether it is present as fluorosilicic acid or as hydrated silica gives a good result when measured photometrically as the yellow silico molybdic acid. Case (1944) used boric acid to complex the excess hydrofluoric acid. The present investigation revealed that hydrofluoric acid and a second mineral acid is a more powerful and effective decomposing agent for decomposition of silicate material in soil and plant samples than hydrofluoric acid alone.

1.5.3 COLORIMETRIC DETERMINATION INVOLVING SILICOMOLYBDIC ACID

An extremely voluminous literature exists concerning the colorimetric determination of silicon as silico-12-molybdate. King et al. (1955) give a lengthy bibliography on the subject. Despite its many variations, however, the method basically depends upon the fact that silicon is present in aqueous solution as the momomeric silicate unit ($Si(OH)_4$).

The determination of small quantities of silicon is made by the formation of silicomolybdic acid and the subsequent measurement of the light absorption of this compound, or its reduction product molybdenum blue.

In all cases, however, the analytical conditions have been

determined empirically and little is known concerning the reactions which take place during the analysis. It is generally recognized that the formation and reduction of silicomolybdic acid is dependent upon time and pH (Strickland, 1952; Ringbom, 1959; Govett, 1961), and most of the investigations of a more fundamental nature have been designed to determine the most suitable values for these variables. Very little agreement has been reached especially with regard to pH.

This unsatisfactory state of affairs makes it very difficult for the analyst to vary conditions or to design new methods without carrying out a fresh series of investigations.

Furthermore, phosphorus and silicon can be determined colorimetrically under similar conditions by the formation of blue heteropolymolybdate complexes, but the use of organic acids such as oxalic acid or tartaric acid (Schwartz, 1942) for masking and destroying the yellow phosphomolybdate complex will allow silicon to be determined in the presence of phosphorus.

1.5.4 ALUMINIUM

Aluminium is determined either photometrically, after extracting with a solution of 8-hydroxyquinoline (oxine) in chloroform (Riley, 1958) or by atomic absorption.

The oxine-chloroform method is one of the most common methods for determining Al in soil extracts or solutions of plant ash, after adjusting the pH to 5, and complexing iron as the ferrous-dipyridyl complex. In the absence of interfering substances, accurate analysis for Al is

relatively simple by this method.

However, in the presence of other ions, some of which are common in soils and clays, the exact determination of aluminium by this method is very difficult. Thus the main requirement for satisfactory analysis is either to separate the interfering substances from the Al, or to complex in a non-interfering form those ions which otherwise would cause the greatest errors in the analysis.

The colorimetric method involves the formation of a strongly coloured lake by interacting Al with 8-hydroxyquinoline in chloroform. In order to obtain the best results, it is important to obey the instructions closely. In particular, it is essential that the pH of the solution before extraction should lie in the range 4.9 - 5.0.

This method was adopted as it stands in this investigation.

1.6 SOIL ACIDITY AND PLANT GROWTH

Where neutral soils are acidified or acid soils are neutralized, many factors of the soil environment are changed simultaneously. Some of these changes may have no significant effect on plants and others may be critical (Black, 1968). Factors that are critical in one soil may have no significant effect in another because of differences between the soils concerned (Russell, 1973).

Although plant species and varieties have much in common in terms of their response, important differences may exist in individual instances (Black, 1968). Thus both the magnitude of the effect and

importance of the various components may vary from one case to another. Occasionally a diagnosis can be made from visual examination of the plants, but usually the evaluation of soil-plant relationships under conditions of differing soil acidity is a research problem. There is no single, simple interpretation of titratable acidity or pH in terms of plant response to differing degrees of soil acidity (Black, 1968).

Consequently in this study on the effect of soil pH on plant growth three areas will be emphasised:

(a) toxic substance

(b) nutrient availability

(c) mycorrhiza and microbial activities

1.7 LEVELS OF CHEMICAL ELEMENTS FOUND IN SOILS AND PLANTS

The bulk of the inorganic material of soils consists of the four elements - oxygen, silicon, aluminium and iron, much as in the earth's crust. At least 90% of the mineral matter of most soils consists of the combined oxides of silicon, aluminium and iron (Bear, 1964).

The average chemical composition of these elements as oxide is: (SiO_2 :59.1%, Al_2O_3 : 15.2%, Fe_2O_3 : 3.2%, FeO : 3.7%). The oxides of aluminium and iron increase markedly when nearly all of the minerals have undergone pedogeochemical transformations (Bear, 1964).

The oxides of calcium, magnesium, sodium and potassium each make up about 1 - 2%, and the total of these oxides constitute about 5 - 7% of many soils (Bear, 1964).

(i) Silicon

Silicon is the second most abundant element of the earth's crust. The silicon content, expressed as percentage of SiO_2, ranges from 40 - 70% of many soils, which average about the same as for the earth's crust 59%. The silicon percentage is decreased by dilution with organic matter in soil with a high organic matter content. The percentage expressed as SiO_2, range from 17.2 - 46.5%. The content of silicon in plant material varies enormously between different species (Iler, 1979). Handreck and Jones (1968) have given a range of silicon contents varying from 0.08 - 4.2% as SiO_2

(ii) Aluminium

After oxygen and silicon, aluminium is the most abundant element in the earth's crust, and in the majority of rocks and soils. The aluminium content of soils, expressed on the basis of Al_2O_3, frequently is in the range of 2 - 13% (Bear, 1964).

The content ranges up to 20 - 60% in highly weathered soils and laterites (Bear, 1964), compositions qualifying such soil as bauxite. Aluminium occurs mainly in the aluminosilicate minerals, feldspars, pyroxenes, amphiboles and layer silicates (Hesse, 1971). As silicon is depleted and aluminium is enriched, the molar ratio, SiO_2/Al_2O_3 in soil colloids falls from over 4 in colloids high in layer silicate to less than 1 in colloids high in allophane (Bear, 1964).

Acetic soluble Al in freely drained soils has been summarized by Mitchell (1971) as follows:-

Depth (in)	Aluminium Extr. (ppm)
0 - 8 S	1060
13 - 19 B_2	2520
22 - 26 B_3	2230
34 - 44 C	1590

Acetic acid extractable Al values in poorly drained soils derived from livine can be summarized as follows:-

Depth (in)	Aluminium Extr. (ppm)
6	550
12	840
17	475
25	420
36	765

Plant species differ greatly in their reaction to high levels of available aluminium. Messing (1971) showed, the content ranges of Al in lettuce tops and roots to vary from 233 - 480 ppm Al in tops of the lettuce, and from 910 - 1685 ppm Al in the roots of mature plants.

(iii) Iron

The iron content, expressed as percentage of Fe_2O_3, makes up 1 - 6% of many soils, which is comparable to 7% in the earth's crust (Bear, 1964), and 1 - 7% in various rocks. Iron is subject to an increase in concentration through soil development processes. This is reflected by contents of 10 - 15% in many soil colloids (Hesse, 1971). Under poor drainage, the iron becomes reduced and in the presence of organic matter is frequently mobilized (Bear, 1964).

The iron contents of plant materials, expressed as Fe (Jackson, 1958) vary from 80 - 1000 ppm in legumes and 30 - 430 ppm in grasses. Pritchett and Llewellyn (1966) gave a range of iron contents expressed as Fe in two year old slash pine on sandy loam soils from 56 - 85 ppm Fe.

(iv) Calcium

The calcium content, expressed as CaO, is generally in the low range of about 1% in soils (Bear, 1964), except where it occurs in carbonate or sulphate form.

The calcium of igneous rocks occurs mainly in the plagioclase series of Feldspars. In soils, the high calcium end of the plagioclase series weathers fairly rapidly (Bear, 1964). Pritchett and Llewellyn (1966) gave a range of percentages for Ca from 0.19 - 0.37% in two year old slash pine.

Jackson (1958) gave a range of Ca contents as follows:-

Legumes	0.2 - 2.3%
Grasses	0.05 - 0.9%
Vegetables	0.07 - 1.8%

Wells (1965) gave a range of percentages for Ca in Loblolly pine, of 0.13 - 0.45%.

Exchangeable calcium as milliequivalents/100 g soil.

High $>$	8.0
Low $<$	3.0

(v) Magnesium

The magnesium content of soils expressed as MgO frequently is less than 1% in non-calcareous soils (Bear, 1964).

Exchangeable Mg as milliequivalents/100 g soil.

High	5.0
Low	0.3

The content of Mg in plant tissue, given by Pritchett and Llewellyn (1966) varies from 0.07 - 0.13% in two year old slash pine. Wells (1965) : 0.05 - 0.16% in loblolly pine.

The data given by Jackson (1958) for Mg level is as follows:-

Legumes	0.1 - 0.6%
Grasses	0.05 - 0.4%
Vegetables	0.02 - 0.5%

(vi) Potassium

The potassium content, expressed as K_2O, ranges between 0.05 - 3.5% for mineral soils (Bear, 1964). Most of the agricultural soils contain amounts ranging from 1 - 2%. The proportion of total potassium in soils held in soluble and exchangeable forms is usually relatively small (Hesse, 1971).

Exchangeable K as meg/100 g soil:-

High	$>$	1.0
Low	$<$	0.1

The content of K in plant material, given by Pritchett and

Llewellyn (1966) varies from 0.21 - 0.40% in slash pine.

Wells (1965) : 0.2 - 0.8% in Loblolly pine.

The data given by Jackson (1958) for K levels is as follows:-

Legumes	0.5 - 4.2%
Grasses	0.2 - 1.9%
Vegetables	0.7 - 4.0%

(vii) Sodium

The content of sodium, expressed as Na_2O, ranges from 0.1 - 1.0% of many soils. This is much smaller than the average of 3.7% in the earth's crust (Bear, 1964).

Sodium does not seem to be an essential element for any crop. The role of sodium in the nutrition of plants that use this element to optimise growth is not fully known, though one of its effects is to increase the succulence of the plant (Russell, 1973).

(viii) Phosphorus

The phosphorus content of most mineral soils falls between 0.02 - 0.5% P, and a general average of 0.05% (0.12% P_2O_5) frequently is representative of soils, compared to an average of 0.12% phosphorus in the earth's crust (Bear, 1964). About half the soil phosphorus or more occurs in combination with organic matter of surface soils, and the remainder occurs in mineral or inorganic combination (Hesse, 1971).

Acetic-soluble P mg/100 g .

High	$>$	4.5 mg
Low	$<$	2.2 mg

Anion-exchange method, P mg/100 g :

High	>	6.6
Low	<	2.8

Total phosphorus in soil (mg/100 g):

High	>	132
Low	<	44

The content of P in plant materials:

Wells (1965) : 0.10 - 0.28% in Loblolly pine needles -

Pritchett and Llewellyn (1966) : 0.06 - 0.12% in two year old slash pine needles

Shoulders and Tiarks (1980) : 0.08% - 0.38% in thirteen year old slash pine both with and without fertilizers.

The data given by Jackson (1958) is summarized as follows:-

Legumes	0.1 - 1.1%
Grasses	0.05 - 0.8%
Vegetables	0.1 - 0.8%
Fruits	0.1 - 0.7%

(ix) Nitrogen

The quantity of nitrogen in surface soils generally ranges from 0.02 - 0.25% and is closely related to the amount of soil organic matter present, of which N makes up approximately 5% (Bear, 1964). The nitrates, nitrites and exchangeable ammonium, which are the forms available for plant nutrition and which can be extracted by neutral salt solution (Brenner, 1965), usually make up less than 1% of the total soil nitrogen content of mineral soils (Bear, 1964). An appreciable fraction of the

nitrogen content of subsoils and rocks occurs as NH_4^+ ions substituting for K^+ ions in micas.

Plants can take up their nitrogen either as ammonium or as nitrate ions, and most plants probably can do either equally easily (Russell, 1973). The main difference between these two ions is that all nitrate in the soil is dissolved in the soil solution, whilst if the soil contains much clay or humus, much of the ammonium will be present as an exchangeable cation and hence not in solution (Russell, 1973).

The content of nitrogen in plant tissue as given by:

Wells (1965) is 0.70 - 1.28% in Loblolly pine.

Pritchett and Llewellyn (1966) is 0.88 - 1.45% in two year old slash pine.

Shoulders and Tiarks (1980) is 1.06 - 2.07% in thirteen year old slash pine without, and with fertilizer.

(x) Nickel

Most rocks of the earth's crust contain nickel, the content varying with the type of rock (Swaine and Mitchell, 1960). Contents are high in basic eruptive rocks (basalt, gabbro) and relatively low in acid eruptive rocks (granite): 150 ppm and 5 - 10 ppm respectively.

Soil total nickel contents vary within wide limits. The upper and lower limits range from unanalyzable traces (in different soil types of diverse climatic regions) to 5000 ppm (B_2 horizon of a brown podzolic soil in Scotland (Swaine and Mitchell, 1960). These variations occur

on the one hand, in relation to the rocks on which the soils were formed and, on the other hand, in relation to the diverse types of soils, and, consequently, to a certain extent, in relation to the major climatic and ecological zones (Mitchell, 1971). The quantity of nickel extracted by 2.5% acetic acid, represents about 2% of total nickel.

In Scotland, concentrations range from 0.1 ppm in an iron pan, hydromorphic podzol on granite, to 5 ppm in brown podzolic soils - soils richest in nickel are often derived from basic rocks and contain high concentration of humus (Swaine and Mitchell, 1960).

(xi) Manganese

Acetic acid soluble contents and total Mn levels of freely drained brown podzolic soils have been summarized by Mitchell (1971) as follows:-

Depth (in)	Manganese (ppm) Total	Extr.
2 - 7 S	1500	10.5
8 - 12 B_2	3000	85
18 - 22 B_2	5000	116
26 - 30 B - C	2000	115
35 - 42 C	3000	126

The effect of gleying is to bring about the release of a considerable proportion of the trace elements present in the minerals which break down in such conditions. These are then held in the soil in a much more readily extractable form (Mitchell, 1971).

The effect of soil drainage conditions on the contents of acetic acid soluble Mn in soil profiles derived from olivine has been summarized

by Mitchell (1971) as follows:-

Approx. Depth (in)	Manganese ppm
6	70
12	42
17	25
25	> 100
38	> 100

The contents of Mn in plant materials has been summarized by Harrod (1971) as a tentative classification of leaf manganese contents:-

Class	Leaf Mn contents (ppm in DM)
Deficient	Below 40
Normal	40 - 200
Very High	1, 000 - 1, 500
Toxicity Symptoms	above 1, 500
Normal for Crops	100 - 400

1.8 METAL TOXICITIES IN SOIL AND REMEDIAL TREATMENTS

The literature on metal toxicity in plants or soils, is vast and cannot be fully cited here. However, some reviews have been published elsewhere (Bollard and Butler, 1966; Brown and Jones, 1975; Foy, 1974; Foy et al., 1978).

Toxic levels of metals in soils may be caused by natural soil properties or by agricultural, manufacturing, mining and waste disposal practices (Brown and Jones, 1975; Foy, 1978: Foy et al., 1978).

(i) Aluminium

Aluminium toxicity is an important growth limiting factor for plants in many acid soils below pH 5.0, but can occur at pH levels as high as 5.5 (Foy, 1974). The problem is particularly serious in very acid soils. Strong subsoil acidity (Al toxicity) reduces plant rooting and increases susceptibility to drought (Foy et al., 1978). Plants grow poorly under such conditions. However, they often have a low content of phosphorus in the tissue. This can lead to the alternatives and phosphorus deficiency (Clarkson, 1966, 1967; Foy, 1974).

(ii) Manganese

Manganese toxicity occurs in some strongly acid soils below pH 5.5 (Foy et al., 1978). Manganese toxicity is an important problem in acid soils, and the element behaves similarly to Al in that its concentration in the soil solution increases as the pH decreases (Black, 1968). Mn generally affects plant tops more severely than roots. In addition, Mn produces more definitive symptoms in plant tops than does Al (Foy et al., 1978), and for a given plant, Mn accumulates in the foliage somewhat in proportion to injury (Foy and Fleming, 1978).

(iii) Nickel

The importance of nickel is mainly to do with its toxic effects on plant growth - some cases of nickel toxicity have been pointed out, particularly in the brown podzolic soils, hydromorphic gley soils on Serpentinite and Schists in Scotland (Ryan et al., 1967). Nickel toxicity occurs naturally in some soils developed from serpentinite rocks, and low pH (Anderson et al., 1973).

It is now well established that excessive availability of manganese and aluminium are a dominant factors in the low productivity of acid soils. Other metals (for example, Ni), present in the soil in smaller amounts and less widespread, occasionally become toxic to plants.

Soil pH is probably the most important factor and where values are low, liming should be recommended, to change the soil reaction to a pH range that is favourable for plant growth. Addition of organic matter could reduce the toxicity by masking metals such as Al by surface absorption or chelation. Attention should be paid to the fertilizer programme in Fiunary Forest (Expt. plots).

1.9 AIMS OF THE PROJECT

The aims of the present work are:-

To devise routine and accurate methods for the determination of P (inorganic and total) and Si in soil and plant material.

To devise methods for overcoming interferences in the above two determinations.

To identify the main inorganic factors limiting the growth of Sitka spruce on basalt brown earths.

The intention is to accomplish these objectives by carrying out accurate soil analysis as well as yield measurements and needle analysis.

The aim of the field work was designed to test:-

1. Whether there is an inhibiting effect on growth due to allophane,

i.e. mobile aluminium, on phosphate uptake by trees.

2. Whether the inhibition effects the tree directly or indirectly by preventing adequate growth of mycorrhiza.

3. Whether a solution may be found either by immobilising the aluminium or creating conditions suitable for the vigorous growth of mycorrhiza and thus bypassing the effect of aluminium in the subsoil.

4. To assess the role of mycorrhiza in overcoming spruce check problems.

5. To assess the possible roles of Si and some polysaccharides in reducing aluminium toxicity

CHAPTER II

FIELD WORK IN CONNECTION WITH FACTORS AFFECTING SPRUCE GROWTH

2.1 EXPERIMENTAL NOTES

2.1.1 SUMMARY OF RELEVANT PROFILE TERMINOLOGY

Horizon nomenclature used in this work is as follows:-

A_o Horizon of organic matter lying on the surface of the mineral soil. It consists of Litter (L), Fermentation (F) containing many mycorrhizal roots, and Humus (H).

A Uppermost mineral horizon, in which the organic matter is intimately mixed with the inorganic matter.

A_e Eluviated layer, which when present, lies below an A or A_o horizon. The minerals are bleached, due to the removal of iron oxides, and may be grey from a coating of organic matter. It is designated A_2 by the Scottish soil survey.

B_1 Iron pan, if present. It is designated B_1 by the Scottish soil survey.

B_2 Usually a brighter brown than either the A or C horizon, due either to relative enrichment in iron oxides derived from A, or more intensive oxidation and weathering of iron oxides than is occurring in C.

B_3 Subdivision of the B horizon. In Scottish soils it is usually an indurated horizon. Induration is signified by X, e. g. B_3X.

C Weathering parent material, which is a hardened layer. This may also be a CX or indurated horizon.

R Rock.

Moderate gleying, as shown by mottled soil colours of red or brown and yellow or grey, is signified by g as in B_2g. Intensive gleying, where all or most of the iron is in ferrous form by G as in CG. Subscripts are used where it is necessary to subdivide a major horizon in which differences in colour, texture etc. occur, as in C_1G, C_2

2.1.2 SAMPLING

Samples were at first collected in plastic bags and stored moist by putting a test tube of water into each bag and sealing it from the atmosphere. While this is not a recommended procedure for the subsequent determination of available nutrients, certain chemical changes in ion availability are said to take place under moist storage (Jackson, 1962). Hence, all soils were subsequently collected in brass sieve holders (2 mm) and where ever possible, sieved and air-dried the same day.

2.1.3 ALLOPHANE TEST

This test was made on all horizons of the forest soils and was used in field work elsewhere as a matter of routine. A small sample of soil from each horizon was placed on filter paper that had been presoaked in phenolphthalein indicator and dried. A drop of saturated sodium fluoride solution was added to the soil and the degree of development of alkaline pink after the elapse of a few minutes gave an indication of the allophane content (Fields and Perrott, 1966). Organic rich soils

tended to be slower in developing colour.

2.1.4 SELECTION OF THE PROFILE-SAMPLING SITE

The profile site for sampling was chosen on the basis of vegetation, micro-climate, surface drainage, proximity to trees, and any other factors which are pertinent to identification of the profile with the soil type. Road cuts are not the best sampling sites because they are likely to have an overburden and a deposition of limestone dust.

2.1.5 DEEP PROFILE SAMPLE RECOMMENDED

Sampling of the profile of soil and subsoil to the full depth of geochemical weathering is recommended in so far as possible. Interesting facts of mineral weathering and soil formation are revealed by analysis of profiles to the full depth of geochemical weathering, whether the deeper horizons are considered apart of the soil profile proper or not. Knowledge thus gained of the course of mineral weathering as a function of depth is useful in the interpretation of soils, their formation and potential fertility.

2.2 SOIL AND SITE DESCRIPTIONS

2.2.1 LOCH EYNORT FOREST (SKYE)

Rainfall - 90 in.

1. Location : Loch Eynort Forest

   Soil type : Brown earth

   Horizon : A_1

   Vegetation : Sitka spruce

   Rock : Basalt

	Depth (in) :	(1 - 3)
	Yield class :	(120) low yield
2.	Location :	Loch Eynort Forest (Allt Dabhoch)
	Soil type :	Brown earth
	Horizon :	B
	Vegetation :	Sitka spruce
	Rock :	Basalt
	Depth (in) :	(3 - 5)
	Yield class :	(120) low yield
	Age :	Planted 1932
3.	Location :	Loch Eynort Forest
	Soil type :	Brown earth
	Horizon :	B_2
	Vegetation :	Sitka spruce
	Rock :	Basalt
	Depth (in) :	(3 - 6) just below main roots
	Yield class :	low yield
	Age :	Planted 1932
4.	Location :	Loch Eynort (1) Forest
	Soil type :	Brown earth
	Horizon :	A_1
	Vegetation :	Sitka spruce
	Rock :	Basalt
	Depth (in) :	(2 - 3)

Yield class : low yield

Age : Planted 1932

5. Location : Loch Eynort (1) Forest

Soil type : Brown earth

Horizon : B_2

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (6 - 8)

Age : Planted 1932

6. Location : Loch Eynort (1) Forest

Soil type : Brown earth

Horizon : B_{22}

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (7 - 9)

Yield class : low yield

Age : Planted 1932

7. Location : Loch Eynort (1) Forest

Soil type : Brown earth

Horizon : C_{15}

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (10 - 14)

Yield class : low yield

Age : Planted 1932

8.	Location	:	Loch Eynort (2) Forest
	Soil type	:	Brown earth
	Horizon	:	A_1
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(0 - 3)
	Yield class	:	low yield
	Age	:	Planted 1932
9.	Location	:	Loch Eynort (2) Forest
	Soil type	:	Brown earth
	Horizon	:	B_2
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(5 - 8)
	Yield class	:	low yield
	Age	:	Planted 1932
10.	Location	:	Loch Eynort (2) Forest
	Soil type	:	Brown earth
	Horizon	:	C
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(12 - 17)
	Yield class	:	low yield
	Age	:	Planted 1932

11. Location : Loch Eynort (2) Forest

Soil type : Brown earth

Horizon : C_2^0

Vegetation : Sitka spruce

Rock : Basalt

Yield class : low yield

Age : Planted 1932

2.2.2 SALEN FOREST (ISLE OF MULL)

Rainfall - 90 in.

1. Location : Salen Forest 6

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (0 - $1\frac{1}{2}$)

Yield class : good yield (220)

Age : Planted 1936

2. Location : Salen Forest 6

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (4 - 6)

Yield class : good yield (220)

Age : Planted 1936

PLATE 1

General view of Salen Forest (Isle of Mull)

3. Location : Salen Forest 6

Soil type : Brown earth

Horizon : B_2

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (7 - 9)

Yield class : good yield

Age : Planted 1936

4. Location : Salen Forest (7)

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (0 - 3)

Yield class : low yield

Age : Planted 1936

5. Location : Salen Forest (7)

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (3 - 5)

Yield class : low yield

Age : Planted 1936

6.	Location	:	Salen Forest (7)
	Soil type	:	Brown earth
	Horizon	:	B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(7 - 9)
	Yield class	:	low yield
	Age	:	Planted 1936
7.	Location	:	Salen Forest (1)
	Soil type	:	Brown earth
	Horizon	:	A_{12}
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(7 -10)
	Yield class	:	good yield
	Age	:	Planted 1936
8.	Location	:	Salen Forest (1)
	Soil type	:	Brown earth
	Horizon	:	B_3H
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(2 - 4)
	Yield class	:	good yield
	Age	:	Planted 1936

9.	Location	:	Salen Forest (6)
	Soil type	:	Brown earth
	Horizon	:	CX
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(14 - 21)
	Yield class	:	good yield
	Age	:	Planted 1932
10.	Location	:	Out bye Land (Isle of Mull)
	Soil type	:	Brown earth
	Horizon	:	A_2
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(1 - 3)
	Yield class	:	low yield
	Age	:	Planted 1936
11.	Location	:	Out bye land
	Soil type	:	Brown earth
	Horizon	:	A_4
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(2 - 4)
	Yield class	:	low yield
	Age	:	Planted 1936

12. Location : Out bye land

Soil type : Brown earth

Horizon : B_{10}

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (7 - 10)

Yield class : low yield

Age : Planted 1932

13. Location : Out bye land

Soil type : Brown earth

Horizon : C_{24}

Vegetation : Sitka spruce

Rock : Basalt

Yield class : low yield

Age : Planted 1932

14. Location : In bye land (Isle of Mull)

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (1 - 3)

Yield class : good yield (220)

Age : Planted 1936

15. Location : In bye land

Soil type : Brown earth

Horizon : B_2

Vegetation : Sitka spruce

Rock : Basalt

Yield class : good yield

Age : Planted 1936

16. Location : In bye land

Soil type : Brown earth

Horizon : B_5

Vegetation : Sitka spruce

Rock : Basalt

Yield class : good yield

Age : Planted 1936

17. Location : In bye land

Soil type : Brown earth

Horizon : C_{23}

Vegetation : Sitka spruce

Rock : Basalt

Yield class : Good yield

Age : Planted 1936

2.2.3 FIUNARY FOREST (MORVERN), NORTH WEST OF ARGYLL

Rainfall - 80 in.

PLATE 2

General view of Fiunary Forest (50 year old)

1. Location : Fiunary Forest 2. Top road
   Soil type : Podzolised brown earth
   Horizon : A_{1e}
   Vegetation : Sitka spruce
   Rock : Basalt
   Yield class : Very low yield (checked)
   Age : Planted 1936

2. Location : Fiunary Forest 2. Top road
   Soil type : Podzolised brown earth
   Horizon : A_H
   Vegetation : Sitka spruce
   Rock : Basalt
   Yield class : very low yield (checked)
   Age : Planted 1936

3. Location : Fiunary Forest 2. Top road
   Soil type : Brown earth
   Horizon : B_2
   Vegetation : Sitka spruce
   Rock : Basalt
   Depth (in) : (6 - 8)
   Yield class : Very low yield
   Age : Planted 1936

4. Location : Fiunary Forest 8. Top road
   Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (1 - 3)

Yield class : Very low yield

Age : Planted 1936

5. Location : Fiunary Forest. Compartment 105

Soil type : Brown earth

Horizon : A_1

Vegetation : Felled sitka spruce

Rock : Basalt

Depth (in) : (1 - 3)

Yield class : 4 (very low yield)

Age : Planted 1936

6. Location : Fiunary Forest. Compartment 105

Soil type : Brown earth

Horizon : A_o (LXF)

Vegetation : Sitka spruce

Rock : Basalt

Yield class : Very low yield (4)

7. Location : Fiunary Forest

Soil type : Brown earth

Horizon : B_2

Vegetation : Sitka spruce, under pasture

	Rock :	Micaschist
	Yield class :	Very low yield
8.	Location :	Fiunary Forest 5. Savary Glen
	Soil type :	Brown earth
	Horizon :	A_1
	Vegetation :	Very checked sitka spruce
	Rock :	Basalt with granite
	Yield class :	Very low yield (2 ft. high)
	Age :	Planted 1936
9.	Location :	Fiunary Forest. Savary Glen
	Soil type :	Brown earth
	Horizon :	A_2
	Vegetation :	Checked sitka spruce
	Rock :	Basalt
	Yield class :	Very low yield ($\sim$2 ft. high)
	Age :	34 years old
10.	Location :	Fiunary Forest. Savary Glen
	Soil type :	Brown earth
	Horizon :	B
	Vegetation :	Checked spruce
	Rock :	Basalt
	Yield class :	Very low yield ($\sim$2 ft. high)
	Age :	34 years old

11. Location : Fiunary Forest. Savary Glen
Soil type : Brown earth
Horizon : B
Vegetation : Sitka spruce
Rock : Basalt
Depth (in) : (9 - 10)
Yield class : Very low yield
Age : Planted 1936

12. Location : Fiunary Forest 5. Savary Glen
Soil type : Brown earth
Horizon : B_1
Vegetation : Checked Sitka spruce
Rock : Basalt and granite
Yield class : Very low yield
Age : Planted 1932

13. Location : Savary glen, Morvern
Soil type : Brown earth
Horizon : A_1
Vegetation : Sitka spruce
Rock : Basalt
Yield class : Very low yield
Age : Planted 1934

14. Location : Savary Glen, Morvern
Soil type : Brown earth

Horizon : B_2

Vegetation : Sitka spruce

Rock : Basalt

Yield class : Very low yield

Age : Planted 1934

15. Location : Savary Glen, Morvern

Soil type : Brown earth

Horizon : B_3

Vegetation : Sitka spruce

Rock : Basalt

Yield class : Very low yield

Age : Planted 1934

16. Location : Savary Glen, Morvern

Soil type : Brown earth

Horizon : C

Vegetation : Sitka spruce

Rock : Basalt

Yield class : Very low yield

Age : Planted 1934

17. Location : Morvern

Soil type : Brown earth

Horizon : A

Vegetation : Beech, Hard Wood

Rock : Basalt

18.	Location	:	Morvern
	Soil type	:	Brown earth
	Horizon	:	B
	Vegetation	:	Beech, Hard Wood
	Rock	:	Basalt

2.2.4 PITMEDDEN FOREST, FIFE (EAST COAST OF SCOTLAND)

Rainfall - 25 in.

Soil samples were taken from the 'main line thinning' strips, and needles from the lower branches of the brashed trees surrounding the pits.

1.	Location	:	Pitmedden Forest 1. Compartment 7
	Soil type	:	Brown earth with very slight gleying in B, i.e. imperfectly drained brown earth
	Horizon	:	A_1
	Vegetation	:	Under Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(1 - 18)
	Yield class		Very good yield (244)
2.	Location	:	Pitmedden Forest. Compartment 7
	Soil type	:	Brown earth with very slight gleying in B. Small pale rusty mottles
	Horizon	:	B
	Vegetation		Sitka spruce
	Rock	:	Basalt
	Depth (in)	:	18+, sampled at (4 - 7)
	Yield class	:	Very good yield

3.	Location	:	Pitmedden Forest 1. Compartment 7
	Soil type	:	Brown earth
	Horizon	:	A_o (LXF)
	Vegetation	:	Sitka spruce
	Depth (in)	:	$1\frac{1}{2}$ deep. No H layer
4.	Location	:	Pitmedden Forest 2. Compartment 7
	Soil type	:	Brown earth
	Horizon	:	A_o (LXF)
	Depth (in)	:	$1\frac{1}{2}$ inches depth. No H horizon. Many mycorrhizal roots
5.	Location	:	Pitmedden Forest 2. Compartment 7
	Soil type	:	Brown earth, imperfectly drained, since B horizon was slightly gleyed. Silt loam texture
	Horizon	:	A
	Vegetation	:	Under Sitka spruce. Some chickweed, bracken, rose bay, willow herb and stinging nettle, indicate a soil of high base status and adequate phosphate
	Rock	:	Basalt
	Depth (in)	:	(0 - 14), sampled at (5 - 7)
	Yield class	:	Very good
6.	Location	:	Pitmedden Forest 2. Compartment 7
	Soil type	:	Yellow brown earth, silt loam, very slightly indurated yellow brown colour with vesicles and slight rusty mottling.
	Horizon	:	B
	Vegetation	:	Under sitka spruce

	Rock	:	Basalt
	Depth (in)	:	14+
	Yield class	:	Very good yield
7.	Location	:	Pitmedden Forest 3. Compartment 7
	Soil type	:	Brown earth
	Horizon	:	A_o (LXF)
	Depth (in)	:	$1\frac{1}{2}$ inches depth. No horizon. Many mycorrhizal roots
8.	Location	:	Pitmedden Forest 3. Compartment 7
	Soil type	:	Brown earth with gleyed lower B horizon clay loam texture. No induration
	Horizon	:	A
	Vegetation	:	Under sitka spruce. Some chickweed, bracken, willow herb and stinging nettle, indicate a soil of high base status and adequate phosphate
	Rock	:	Basalt
	Depth (in)	:	(1 - 7)
	Yield class	:	Very good yield
9.	Location	:	Pitmedden Forest 3. Compartment 7
	Soil type	:	Brown earth with gleyed, clay loam texture. No induration
	Horizon	:	B_2
	Vegetation	:	Under sitka spruce
	Rock	:	Basalt
	Depth (in)	:	(7 - 30)
	Yield class	:	Very good

10. Location : Pitmedden Forest 3. Compartment 7

Soil type : Loam, strong rusty mottles

Horizon : B_3g

Vegetation : Under sitka spruce

Rock : Basalt

Depth (in) : 30+

Yield class : Very good

11. Location : Pitmedden Forest 4. Compartment 7

Soil type : Brown earth

Horizon : A_o (LXF)

Depth (in) : $1\frac{1}{2}$ inches depth. No H horizon, many mycorrhizal roots

12. Location : Pitmedden Forest 4. Compartment 7

Soil type : Brown earth with gleyed lower B

Horizon : A

Vegetation : Under sitka spruce. Some chickweed, bracken, willow herb and stinging nettle, indicate a soil of high base status and adequate phosphate

Rock : Basalt

Depth (in) : (1 - 7)

Yield class : Very good

13. Location : Pitmedden Forest 4. Compartment 7

Soil type : Brown earth, with slight colour change. Loam to sandy loam.

Horizon : B_2

Vegetation : Under sitka spruce

	Rock	:	Basalt
	Depth (in)	:	(7 - 10)
	Yield class	:	Very good
14.	Location	:	Pitmedden Forest 4. Compartment 7
	Soil type	:	Loamy sand, fairly mottled
	Horizon	:	B_3
	Vegetation	:	Under sitka spruce
	Rock	:	Basalt
	Depth (in)	:	10+
	Yield class	:	Very good
15.	Location	:	Pitmedden Forest 4. Compartment 7
	Soil type	:	Brown earth, food deep mull brown soil with gleyed B
	Horizon	:	A_1
	Vegetation	:	Grass land
	Rock	:	Basalt
	Depth (in)	:	(5 - 10)
16.	Location	:	Pitmedden Forest 5. Compartment 7
	Soil type	:	Surface water gley. Silty to clay loam
	Horizon	:	A_1
	Vegetation	:	Species of grass, barley, chick weed
	Rock	:	Basalt
	Depth (in)	:	(0 - 4)

17. Location : Pitmedden Forest 5. Compartment 7

Soil type : Large rusty mottles

Horizon : Bg

Rock : Basalt

Vegetation : Under grass species, barley

Depth (in) : (4 - 16)

18. Location : Pitmedden Forest 5. Compartment 7

Soil type : Strongly gleyed with blue grey patches and rusty mottles

Horizon : CG

Vegetation : Grassland

Rock : Basalt

Depth (in) : 16+

19. Location : Pitmedden Forest 5. Half-way of grassy slope alongside, compartment 7

Soil type : Deep mull brown forest soil

Horizon : A_1

Vegetation : Grassland

Rock : Basalt

Depth (in) : (10 - 12)

20. Location : Pitmedden Forest 6. Top of grass slope alongside, Compartment 7

Soil type : Brown soil

Horizon : A_1

Vegetation : Grassland

Rock : Basalt

Depth (in) : (3 - 6)

21. Location : Pitmedden Forest 6. Top of grass slope alongside

Soil type : Brown soil

Horizon : B_2

Vegetation : Under grassland

Depth (in) : (10 - 13)

22. Location : Pitmedden Forest 7. Compartment 7

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (3 - 6)

Yield class : Very good

23. Location : Pitmedden Forest 7. Compartment 7

Soil type : Brown earth

Horizon : B_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (6 - 10)

Yield class : Very good

24. Location : Pitmedden Forest 8. Compartment 7

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (2 - 5)

Yield class : Very good

25. Location : Pitmedden Forest 9. Compartment 8

Soil type : Brown earth

Horizon : A_1

Vegetation : Sitka spruce

Rock : Basalt

Depth (in) : (4 - 7)

Yield class : Good

26. Location : Pitmedden Forest 11. Compartment 8

Soil type : Brown earth

Horizon : A_1

Vegetation : Under Norway spruce

Rock : Basalt

Depth (in) : (2 - 5)

Yield class : Good

2.2.5 FIUNARY FOREST (EXPERIMENTAL PLOTS)

(Grid reference: 686482, 672491)

2.2.5.1 Experimental Notes

B : Basalt

M : Mineral soil (i.e. organic layer removed and seedling planted in the mineral subsoil)

F : Fermentation layer, which consists of many mycorrhizal roots (forest site only)

O : Organic turf layer (Mull soil, humic rich). Pasture site only

P : Phosphate fertilizer

L : Lime

SR : Self regeneration, dug up seedlings self-grown by the roadside

1 + 1 : Two year old seedlings, first year in a pot, second year planted in a nursery

1 + 0 : One year old seedlings, because the deer eat them self regeneration only)

Important: Nursery seedlings have no mycorrhiza, when planted out (NPK suppresses them), whereas SR seedlings have fully developed mycorrhiza.

Fertilizer: Unground rock phosphate (URP) scattered at 85 g /tree = 378 kg/ha = 49 kg phosphorus/ha. Lime at 10, 000 kg/ha = 30 kg/plot = 2. 2 kg/plant. Every plot consists of nine trees, triplicate treatments, i. e. every treatment consists of twenty-seven individual trees as shown in Table 2. 01 (for forest site).

Needles were taken from the branches of the trees surrounding the soil pits.

2. 2. 5. 2 Location and Site Description: NM 686482

1. Location : Fiunary Forest. Compartment 105

Plot : 1

Treatment : Lime, mineral soil

Symbol : BML

Soil type : Brown earth

PLATE 3

General view of the forest site (compartment 105), 4 - 5 years old

PLATE 4

Bottom left BML Treatment in Forest Site

(4 - 5 years old)

PLATE 5

BF Treatment in Forest Site (4 - 5 years old)

PLATE 6

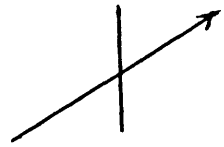
Bottom left BMP Treatment in Forest Site

(4 - 5 years old)

	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
2.	Location	:	Fiunary Forest. Compartment 105
	Plot	:	2
	Treatment	:	Fermentation and phosphate
	Symbol	:	BFP
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
3.	Location	:	Fiunary Forest. Compartment 105
	Plot	:	5
	Treatment	:	Fermentation layer
	Symbol	:	BF
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975

4.	Location	:	Fiunary Forest. Compartment 105
	Plot	:	6
	Treatment	:	Self regeneration, fermentation layer
	Symbol	:	SR BF
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
5.	Location	:	Fiunary Forest. Compartment 105
	Plot	:	7
	Treatment	:	Mineral soil
	Symbol	:	BM
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
6.	Location	:	Fiunary Forest. Compartment 105
	Plot	:	9
	Treatment	:	Phosphate, mineral soil
	Symbol	:	BMP
	Soil type	:	Brown earth

Diagram of Experimental Plots

Forest Site NM 686482  MN

21 BM	20 BMP	19 BFP
16 SR BF	17 BF	18 SR BM
15 SR BM	14 BF	13 BMP
10 BM	11 BFP	12 SR BM
9 BMP	8 SR BF	7 BM
4 BML	5 BF	6 SR BF
3 BML	2 BFP	1 BML

TABLE 2.01

Experiment Record from Forestry Commission. Characteristics Assessed : Height "4 year" ..... Forest or Felled Site. Method and Percentage of Sampling : 100%. Unit of Measurement : Cm.

Unit No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Treatment	BML	BFP	BML	BML	BF	SR-BF	BM	SR-BF	BMP	BM	BFP	SR-BM	BMP	BF	SR-BM	SR-BF	BF	SR-BM	BFP	BMP	BM
Assessment Headings																					
Height classes or Serial Number of plants 1	153	97	111	119	133	51	181	39	115	101	129	53	123	151	115	27	129	09	97	185	107
2	141	115	143	195	137	27	129	71	145	147	155	77	77	101	79	87	171	35	107	157	93
3	125	159	103	165	157	35	103	59	135	149	163	99	119	121	113	-	129	21	133	143	43
4	141	125	141	147	175	93	145	35	151	147	125	39	109	113	49	35	143	55	113	153	107
5	111	161	151	163	149	27	115	31	159	197	165	47	153	145	79	53	111	39	113	131	125
6	113	117	173	185	199	-	145	85	151	159	141	41	139	175	85	51	193	17	-	137	95
7	105	75	125	133	169	61	173	55	137	101	103	67	135	141	71	57	89	61	143	115	105
8	107	143	123	167	193	95	135	25	139	173	185	49	139	157	77	55	141	55	75	111	99
9	117	137	127	139	121	95	89	35	145	99	149	83	127	185	71	-	97	47	141	123	159
TOTALS	1113	1129	1197	1413	1433	484	1215	435	1277	1273	1317	555	1121	1289	739	365	1203	339	922	1255	933
No. of plants	9	9	9	9	9	8	9	9	9	9	9	9	9	9	9	7	9	9	8	9	9
Mean	123.7**	125.4	133.0**	157.2**	159.2*	60.5	135.0	48.3	141.9	141.4	146.3	61.7	124.6	143.2*	82.1	52.1	133.7*	37.7	115.3	139.4	103.7

* BF ranks first, average: 145.37

** BML ranks second, average: 137.9

	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
7.	Location	:	Fiunary Forest. Compartment 105
	Plot	:	12
	Treatment	:	Self regeneration, mineral soil
	Symbol	:	SR BM
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975

(ii) Pasture Site : NM 672491

1.	Location	:	Pasture site. Compartment 302
	Plot	:	1
	Treatment	:	Mineral soil
	Soil type	:	Brown earth
	Symbol	:	BM
	Horizons	:	A and B
	Vegetation	:	Under Sitka spruce
	Rock	:	Basalt

	Yield class	:	Checked
	Age	:	Planted 1975
2.	Location	:	Pasture Site. Compartment 302
	Plot	:	2
	Treatment	:	Organic matter
	Symbol	:	BO
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Under Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
3.	Location	:	Pasture Site. Compartment 302
	Plot	:	3
	Treatment	:	Phosphate, mineral soil
	Symbol	:	BMP
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Under Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
4.	Location	:	Pasture Site. Compartment 302
	Plot	:	4

	Treatment	:	Lime
	Symbol	:	BML
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Under Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975
5.	Location	:	Pasture Site. Compartment 302
	Plot	:	5
	Treatment	:	Self regeneration, mineral soil
	Soil type	:	Brown earth
	Symbol	:	SR BM
	Horizons	:	A and B
	Vegetation	:	Under Sitka spruce
	Yield class	:	Checked
	Age	:	Planted 1975
6.	Location	:	Pasture Site. Compartment 302
	Plot	:	6
	Treatment	:	Self regeneration, organic matter
	Symbol	:	SR BO
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Under Sitka spruce
	Rock	:	Basalt

PLATE 7

Top right SR BM Treatment

Bottom left BM Treatment in Pasture Site

(4 - 5 years old)

PLATE 8

BOP Treatment in Pasture Site

(4 - 5 years old)

PLATE 9

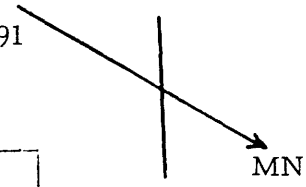
BMP Treatment in Pasture Site

(4 - 5 years old)

Diagram of Experimental Plots

Pasture Site

NM 672491



1 BM	5 BML	2 BO	
3 BMP	4 BOP	7 SR BO	REP III
6 SR BM	5 BML	4 BOP	
2 BO	3 BMP	7 SR BO	REP II
6 SR BM	1 BM	4 BOP	
5 BML	6 SR BM	7 SR BO	
3 BMP	2 BO	1 BM	REP I

* Gate

To Forest Road through larch and sitka spruce

TABLE 2.02

Experiment Record from Forestry Commission. Characteristics Assessed : Height "4 year" ..... Pasture Site. Method and Percentage of Sampling : 100%. Unit of Measurement : Cm.

Unit No.		1	2	3	REP I 4	5	6	7	8	9	REP II 10	11	12	13	14	15	REP III 16	17	18	19	20	21
Treatment		BM	BO	BMP	BML	SR-BM	SR-BO	BOP	BM	SR-BM	BO	BMP	SR-BO	BOP	BML	SR-BM	BMP	BOP	SR-BO	BO	BML	BM
Assessment Headings																						
Height classes or Serial Number of plants	1	85	99	103	79	47	41	89	79	35	75	111	43	123	109	75	87	79	77	93	85	87
	2	71	95	109	125	21	13	137	57	49	71	111	21	87	85	49	93	103	23	61	99	61
	3	87	95	123	103	31	15	83	75	15	67	87	-	105	99	33	71	93	37	57	91	61
	4	69	93	97	79	11	29	79	79	-	59	109	23	87	93	39	85	99	31	83	67	69
	5	81	85	99	87	15	47	101	57	25	73	87	39	101	101	23	81	81	-	69	91	79
	6	81	77	113	101	39	33	95	65	21	71	81	57	115	107	45	77	103	31	97	87	65
	7	77	89	97	103	15	41	113	101	17	67	69	21	85	115	47	97	123	19	67	91	85
	8	109	77	99	91	31	49	79	83	19	77	103	81	109	85	11	95	87	65	79	71	73
	9	113	65	135	93	37	51	89	69	23	81	93	37	89	95	37	105	83	21	61	67	53
TOTALS		773	765	975	861	247	319	865	665	204	641	851	322	901	889	359	791	851	304	667	749	633
No. of Plants		9	9	9	9	9	9	9	9	8	9	9	8	9	9	9	9	9	8	9	9	9
Mean		85.9	85.0	108.3*	96.7***	27.4	35.4	96.1**	73.9	25.5	71.2	94.6*	40.3	100.1**	98.8***	39.9	87.9*	94.6**	38.0	74.1	83.2***	70.3

* BMP rank first, average 96.93

** BOP rank first, average 96.93

*** BML rank second, average 92.57

	Yield class	:	Checked
	Age	:	Planted 1975
7.	Location	:	Pasture Site. Compartment 302
	Plot	:	7
	Treatment	:	Phosphate, organic matter
	Symbol	:	BOP
	Soil type	:	Brown earth
	Horizons	:	A and B
	Vegetation	:	Sitka spruce
	Rock	:	Basalt
	Yield class	:	Checked
	Age	:	Planted 1975

Every plot consists of nine trees, triplicate treatments, i.e. every treatment consists of twenty-seven trees as shown in Table 2 (pasture site).

2.3 BASALT ROCKS

Igneous rocks, which are mineralogically defined as composed essentially of calcic plagioclase ($> An_{50}$) and ferromagnesian minerals usually.

2.3.1 MINERALOGY OF BASALTIC ROCKS

In the more general sense, the composition of basaltic rocks can be expressed in terms of only two rock-forming minerals a plagioclase feldspar of labradorite composition and an augitic pyroxene. Such

minerals constitute the bulk of gabbros, dolerites and basalts whereas certain rare gabbroic rocks of accumulative origin may lack one of these essential minerals, no such possibility exists for basalts, and the melting temperatures of basalts are a close approximation to those of mixtures of these two minerals. However, further minerals are invariably present in different proportions and can be classed as essential to the majority of basaltic variants. The more calcic plagioclases and members of the pyroxene group such as the ortho-pyroxenes, pigeonites and subcalcic augites. The olivines and opaque-oxide minerals are another two major minerals.

These four mineral groups, the plagioclase feldspars, pyroxenes, olivines and opaque oxides, have been described at length because of extensive studies, particularly within the last two decades (Brown, 1967) on their structural and chemical varieties.

The rock in hand specimen was dark, fine grained with phenocrysts.

2.3.1.1 Plagioclase Feldspars

All the plagioclase structures are based on a framework of (Si, Al) - 0 tetrahedra. The composition of which can be expressed chiefly in terms of the anorthite ($Ca\ Al_2\ Si_2\ 0_8$) and albite ($Na\ Al\ Si_3\ 0_8$) intermediate and components of an isomorphous series. The compositional range is generally between about An_{85} and An_{50}.

2.3.1.2 Pyroxenes

Composition, the general formula of the pyroxenes can be

written: $X_{1-p}Y_{1+p}Z_2O_6$ ($0 \leq p \leq 1$) where X = Ca, Na, Y = Mg, Fe^{2+}, Mn, Ni, Al, Fe^{3+}, Z = Si, Al, . The accepted nomenclature in the system Ca Mg Si_2O_6, Ca Fe Si_2O_6, Mg Si O_3, Fe Si O_3 is according to Poldervaart and Hess (1951) for the clinopyroxenes and orthopyroxenes.

2.3.1.3 Olivines

The olivines belong to the orthosilicate structural group of the silicate minerals. Individual (Si O_4) tetrahedra are linked by divalent atoms, such as Mg or Fe^{2+}, in six fold co-ordination with the oxygen atoms, the end members of the series being forsterite (Mg_2 Si O_4) and fayalite (Fe_2 Si O_4).

2.3.1.4 Opaque Oxides

The more common non-silicate minerals of mafic and ultramafic igneous rocks are either iron-titanium oxides or chrome spinels ($Fe_2Ti\ O_4$), (Fe Ti O_3).

2.3.1.5 Minor constituents

In addition to the four mineral groups already considered basaltic rocks may contain a varied assemblage of other minerals. The more important essential minerals are the silica minerals, the feldspathoids, amphiboles and micas.

2.3.2 SILICATE SYSTEMS RELATED TO BASALTIC ROCKS

The main non-volatile chemical constituents of basalts are expressed by the following eight oxides: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, and some times TiO_2.

2.4 BROWN EARTHS

A uniformly coloured B horizon is a characteristic feature of the normal brown earth. There are no sharp horizon boundaries and they do not show any pronounced translocation of sesquioxides.

Normal brown earths

These are dark reddish brown with fine sandy loam to sandy clay loam textures. Slight or moderate gleying in the B and C horizon, reflected varying degrees of imperfection in the drainage but their situation on steep slopes allowed them to be classed as free draining.

Podzolised brown earths

Where there are basalts on brown earths, highly leached soils, and podzols would normally develop. The high base and Al content in the basalt means that weathering is keeping pace with leaching.

2.5 HALLBARNS FARM SOILS

MN 42, ME 41, South West of Scotland

Rainfall (35 - 45 in).

These soils from an arable farm (top soils) near Kilmarnock, are a part of Kilmarnock association (Mitchell and Jarvis, 1956), a short generalised profile description as follows:-

Slope	:	Very gentle
Aspect	:	South West
Vegetation	:	Wheat and Barley; Trifolium repens; Bellis perennis, Ranunculas repens; Grassland
Rock	:	Mixed till derived from igneous and sedimentary rocks mainly of carboniferous age.

Drainage class	:	Imperfect
Soil type	:	Brown to yellowish brown clay loam (10 YR 4/3, 10 YR 5/4, Mitchell and Jarvis, 1956). Medium sub-angular blocky, slightly plastic, organic matter moderate, root frequent, few fine faint ochreous and grey mottles. Sharp change into.
Horizon	:	S (plough layer)
Depth (in)	:	(0 - 9)

These soil samples are:-

1.	Arran	9.	How Thora
2.	Byre	10.	Frost
3.	Barley field (1)	11.	Mid Arran
4.	Barley field (2)	12.	Meadow
5.	Carmel Bank	13.	Rose
6.	Craig	14.	Spinery
7.	Holm	15.	White Hiedi
8.	Home field		

2.6 ANNUAL PROGRESS REPORTS BY FORESTRY COMMISSION PERSONNEL

(i) General report on experiment

(Condition, growth, form and colour of plants and particulars of all factors effecting the growth of sitka spruce.

Survival still very good on both pasture and forest sites. Overall growth has been much better on both sites in 1978 from growth in 1977. The seedlings at last, would appear to be getting away although mean height is still well behind transplants. Pasture sites trees tend to be a

darker green but are well behind in mean height. There is no sign as yet of check. No further hylobius damage was observed and previous damage has healed.

(ii) Provisional summary of obvious results of any assessment for which data is available (Tables 2.01 - 2.03).

* 1st year height summary show:

Forest site	BML ranks first, followed closely by BMP (Fig. 2.06).
Pasture site	BML ranks first, followed closely by BOP (Fig. 2.07).

* 2nd year height summary show:

Forest site	BML ranks first, followed by BMP (Fig. 2.06)
Pasture site	BML ranks first, followed closely by BOP.

* 3rd year height summary show:

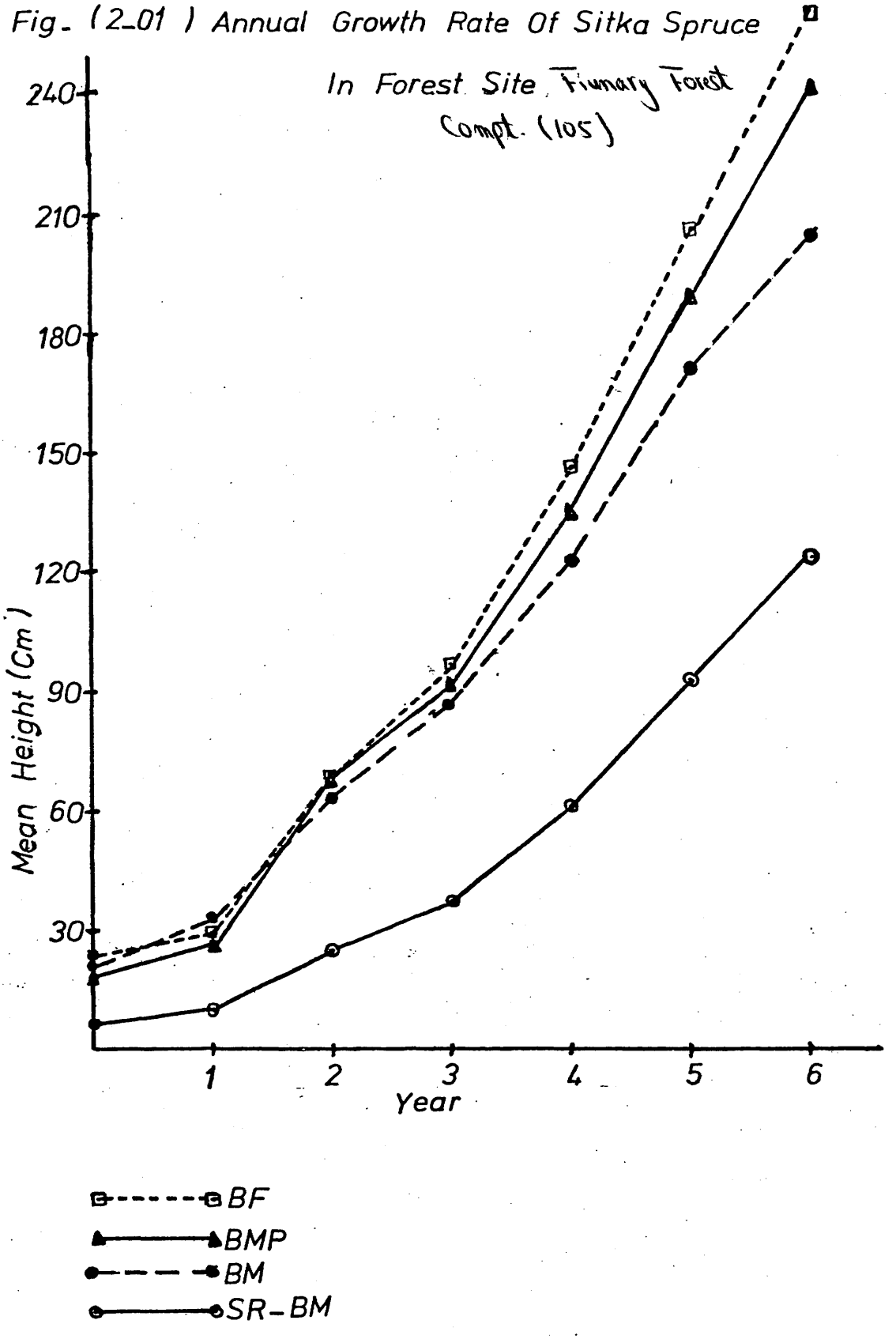
Forest site	BML ranks first, followed by BF (Fig. 2.06)
Pasture site	BOP ranks first, followed closely by BML (Fig. 2.07).

* 4th year height summary show:

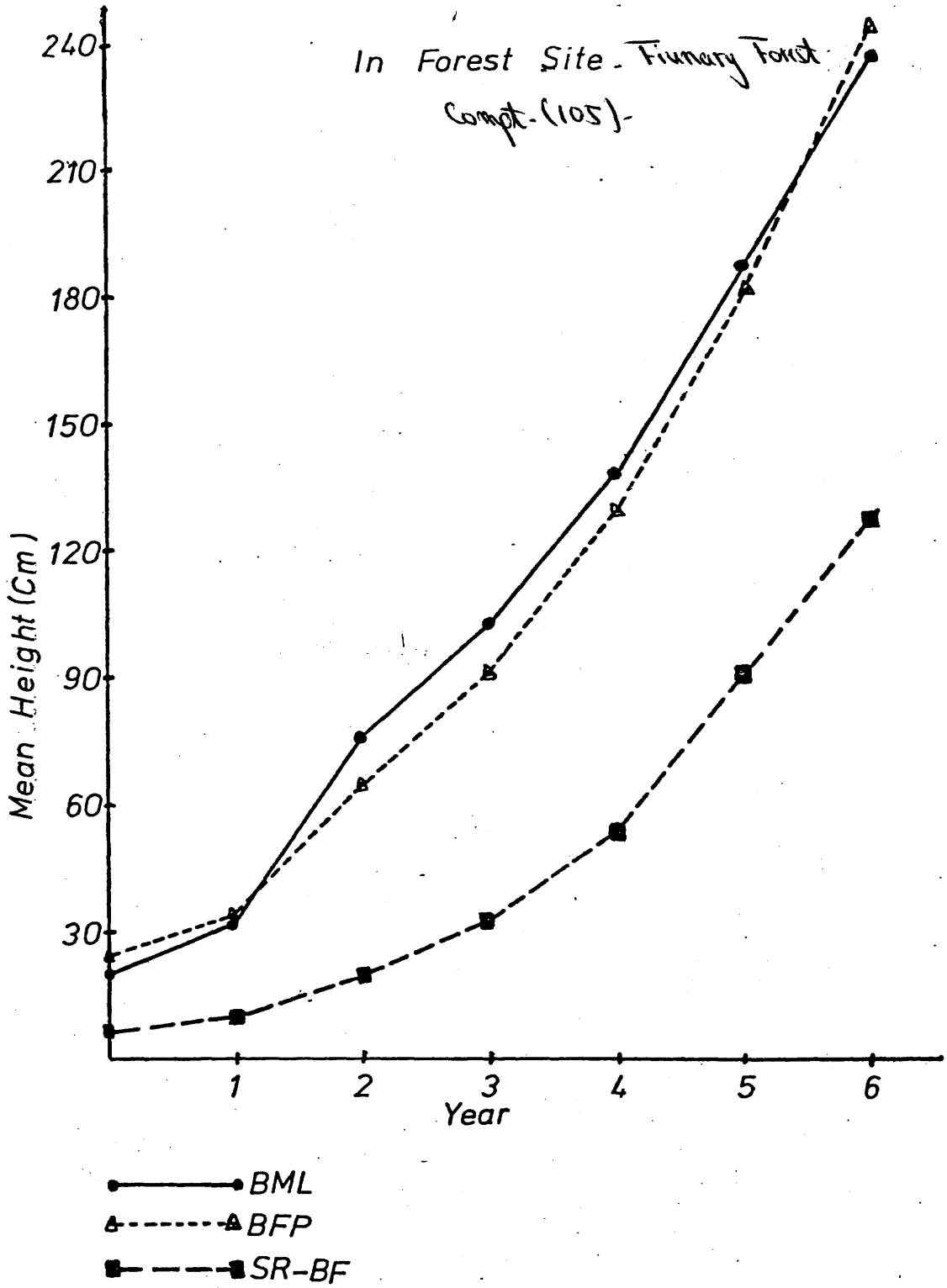
Forest site	BF ranks first, followed by BML secondly. (Fig. 2.01, 2.06)
Pasture site	BMP and BOP, which is normal FC treatment, rank first equal followed closely by BML (Fig. 2.07), (Table 2.04).

Other treatments are probably significantly less. Although lime treatments proved to be somewhat better initially, they have this year been overtaken by other treatments on both sites.

Fig. (2_01) Annual Growth Rate Of Sitka Spruce



Fig_(2.02) Annual Growth Rate Of Sitka Spruce



Eig _(2_03) Annual Growth Rate Of Sitka Spruce In Pasture Site. Fiumary Forest Compt. (302).

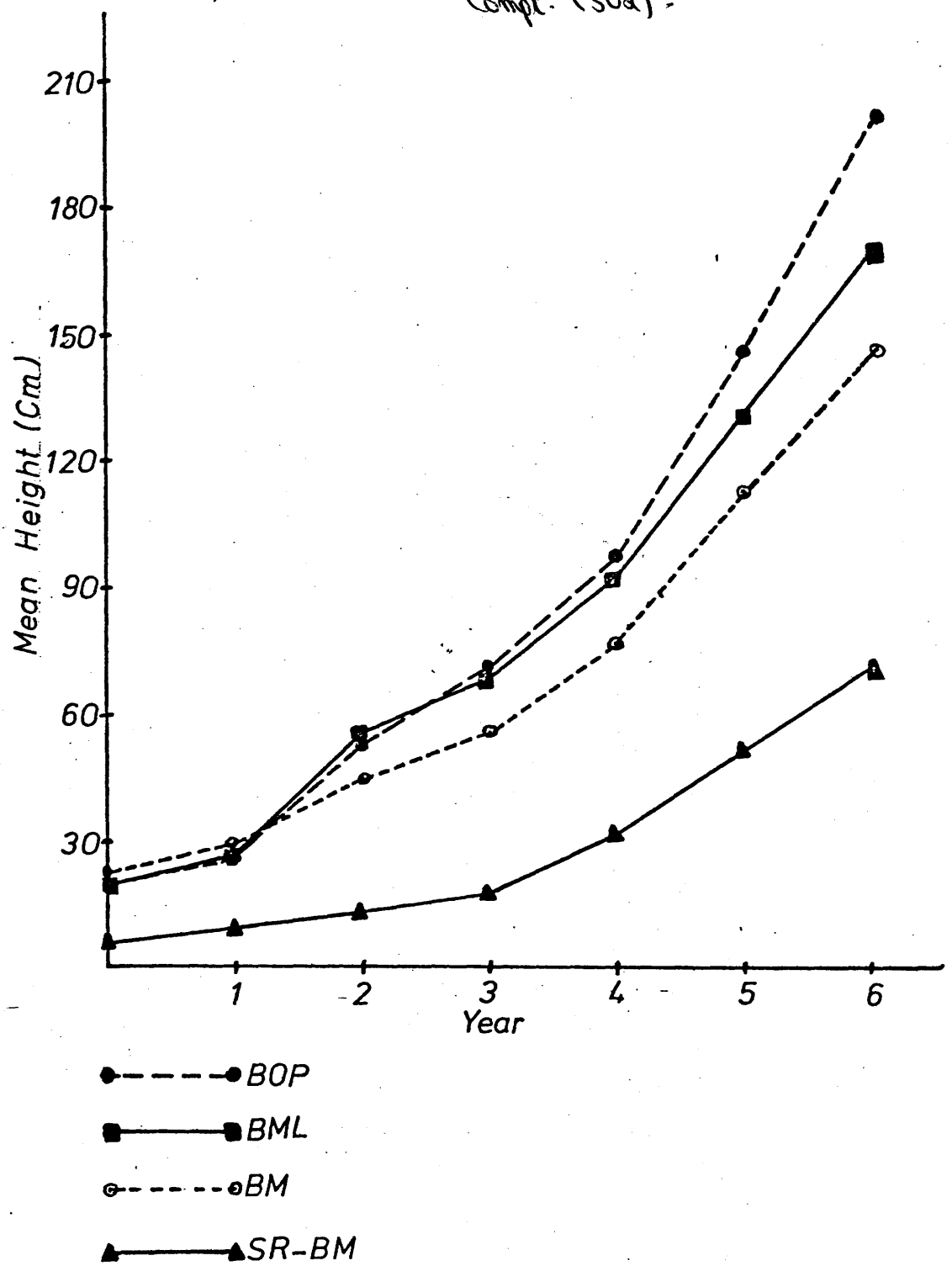


Fig.(2_04) Annual Growth Rate Of Sitka Spruce In Pasture Site. Tumary Forest Compt-(302).

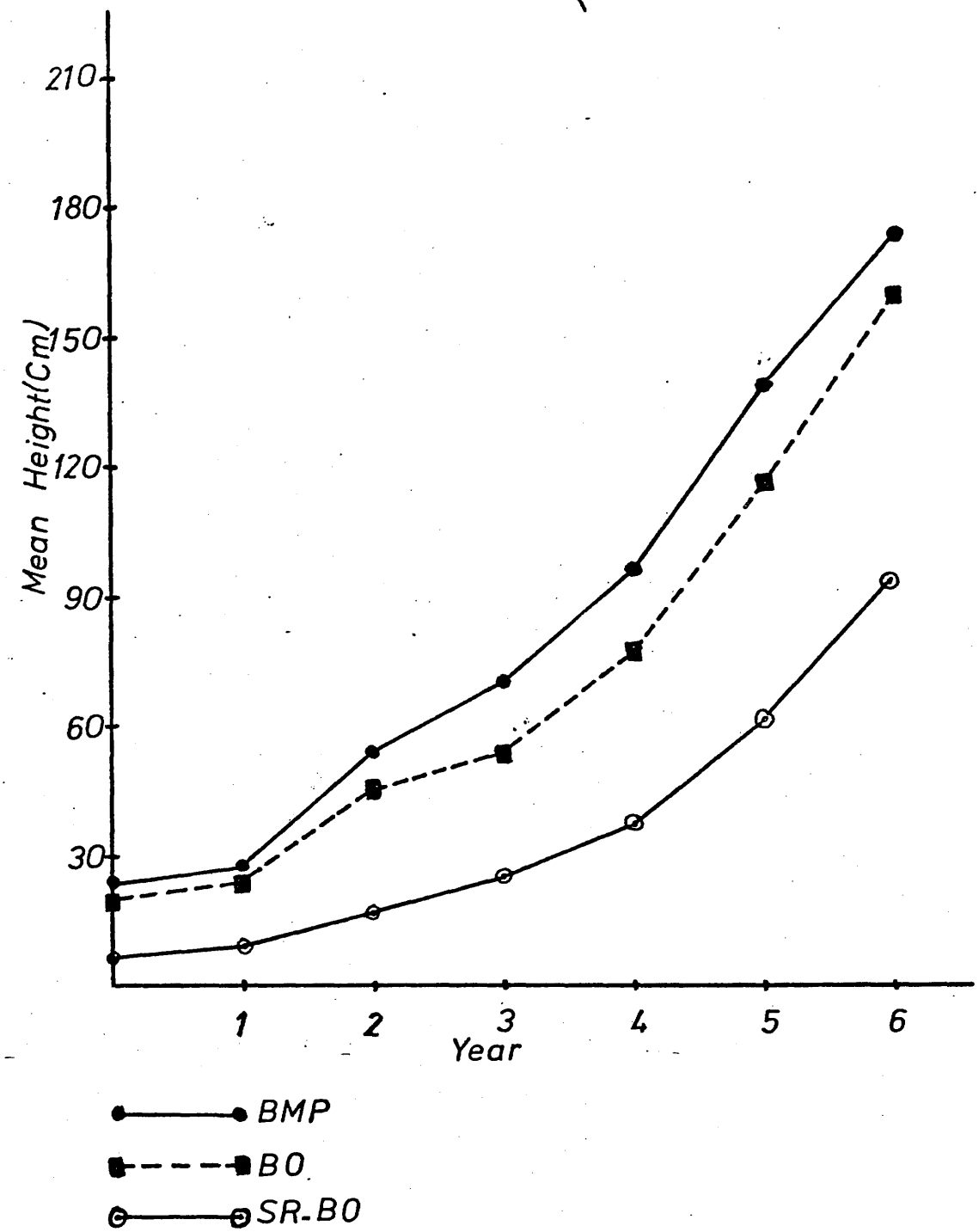


Fig. (2_0.5) Annual Growth Rate Increment Of Sitka Spruce

In Forest Site . Fiumary Forest . Compt. (105)

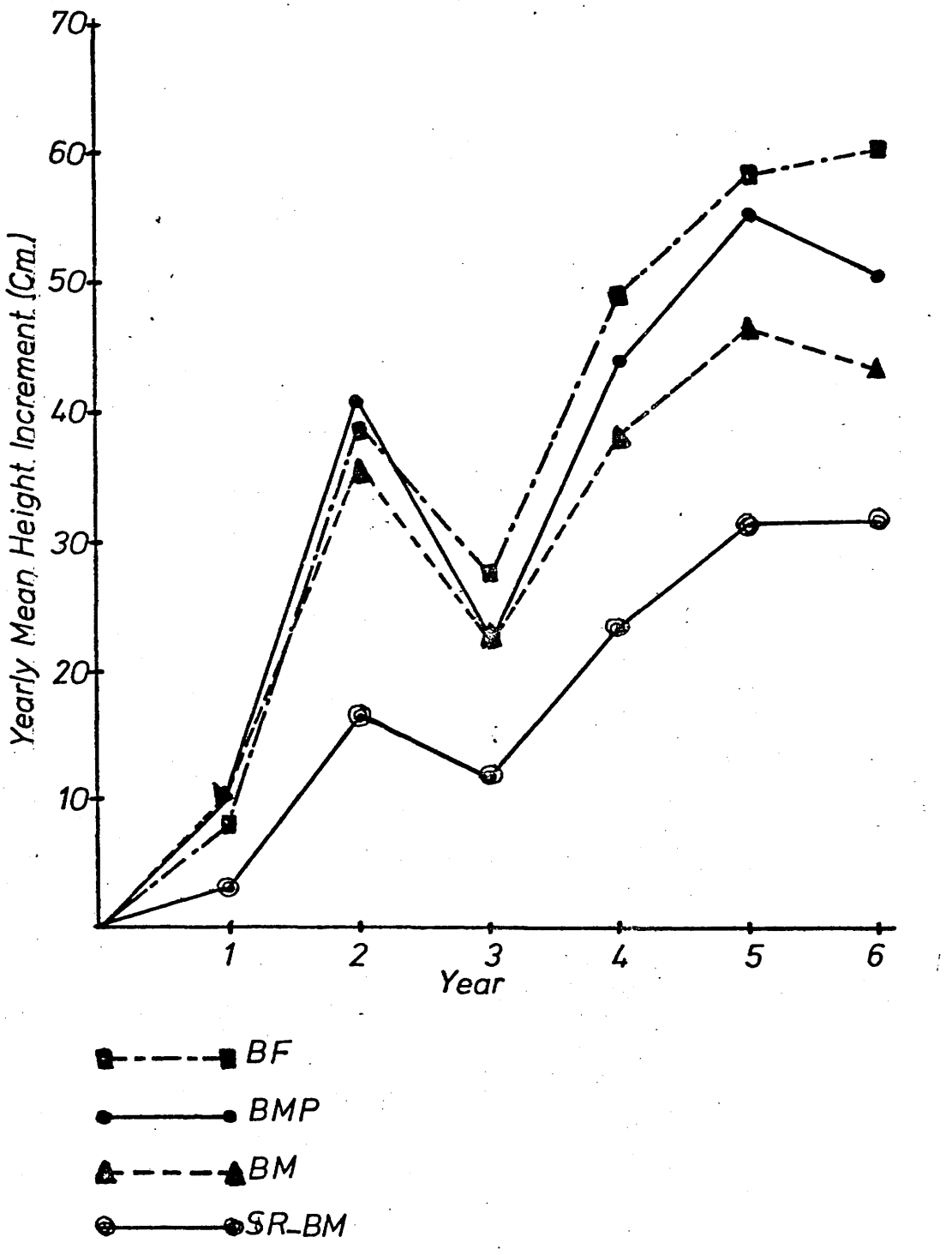


Fig. (2.06) Annual Growth Rate Increment Of Sitka Spruce In Forest Site, Fiunary Forest. Compt. (105).

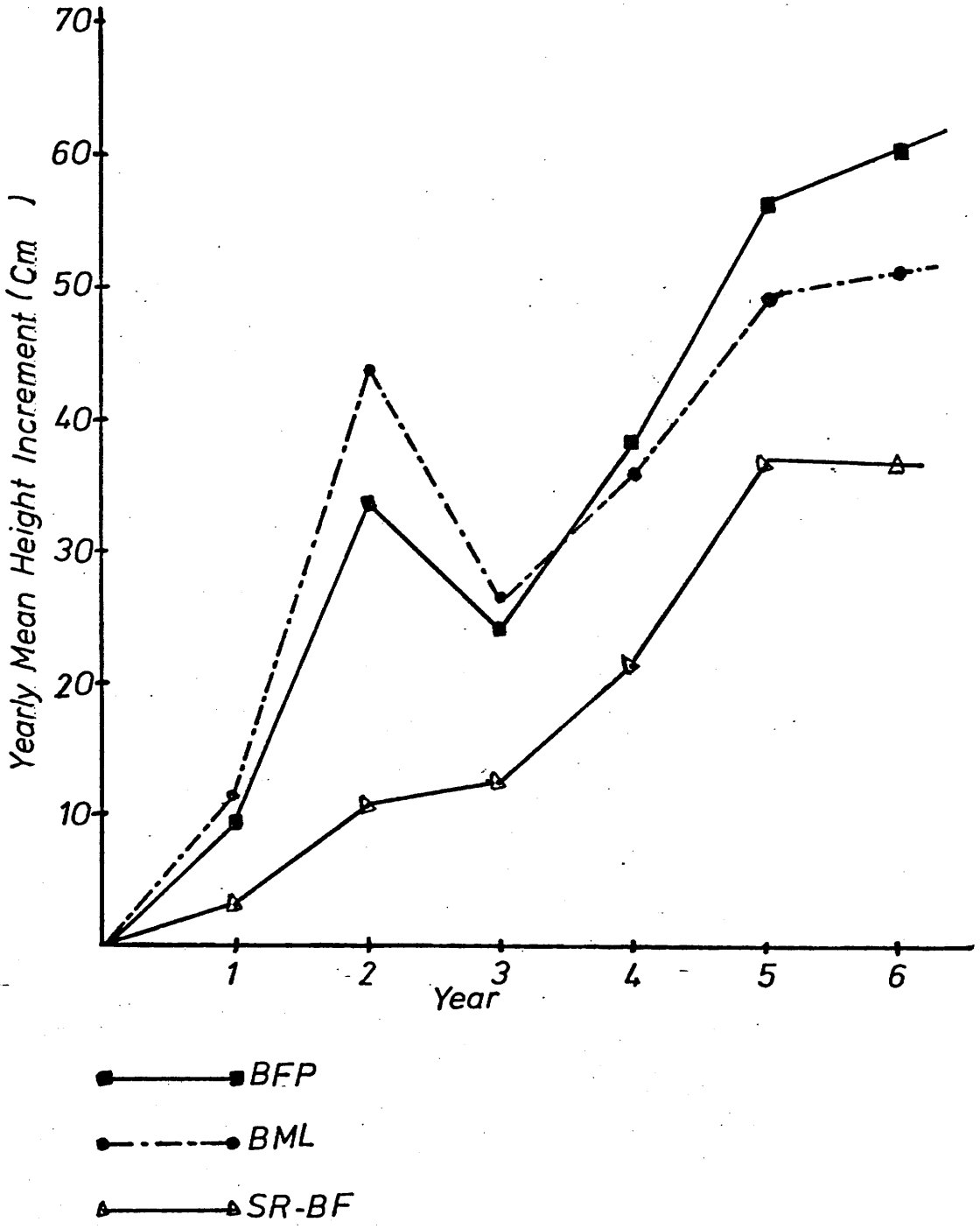


Fig.(2-07) Annual Growth Rate Increment Of Sitka Spruce

In Pasture Site, Fiunary Forest - Compt. (303)

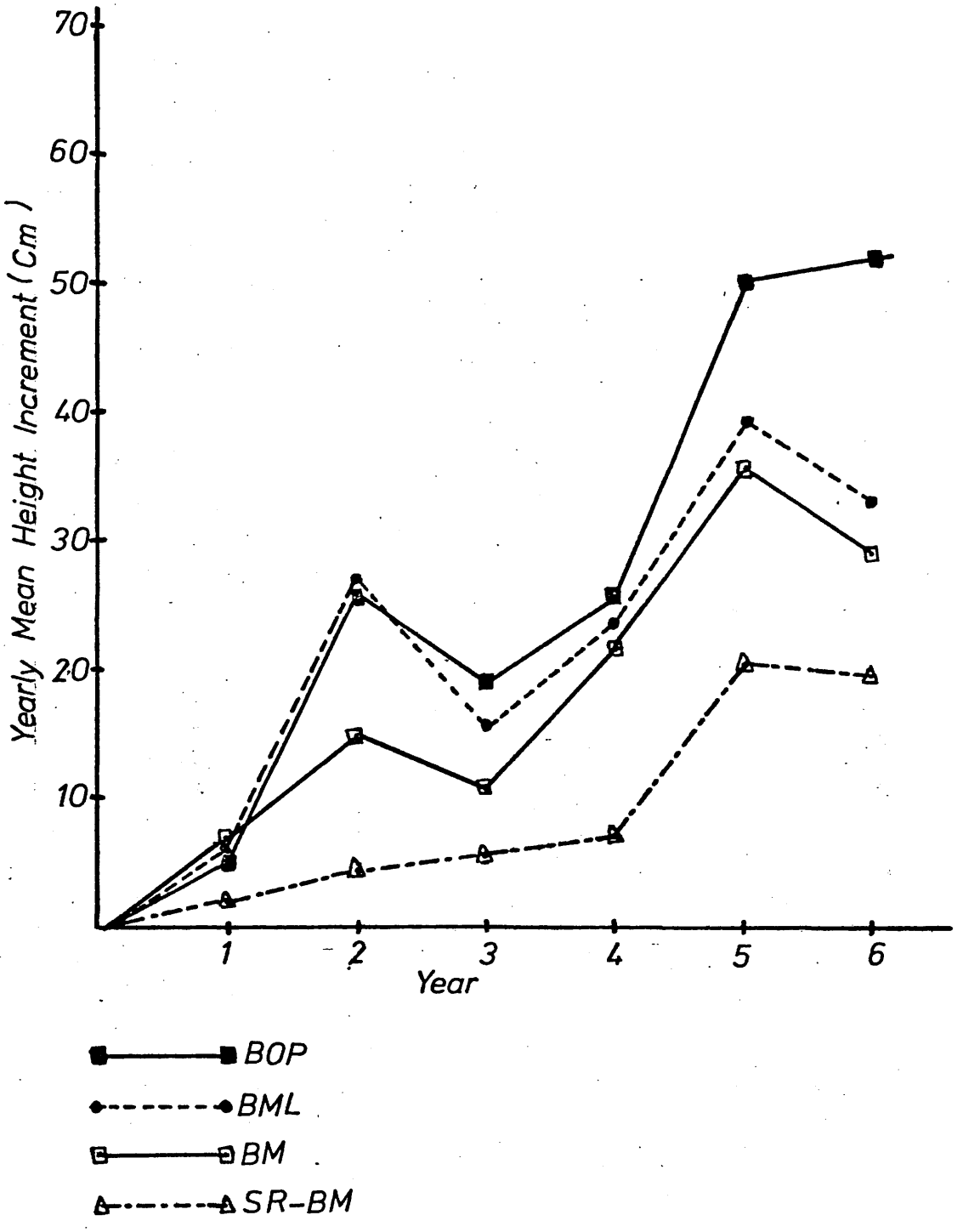


Fig (2_08_) Annual Growth Rate Increment Of Sitka Spruce

In Pasture Site . Fiumary Forest - Compt. (302).

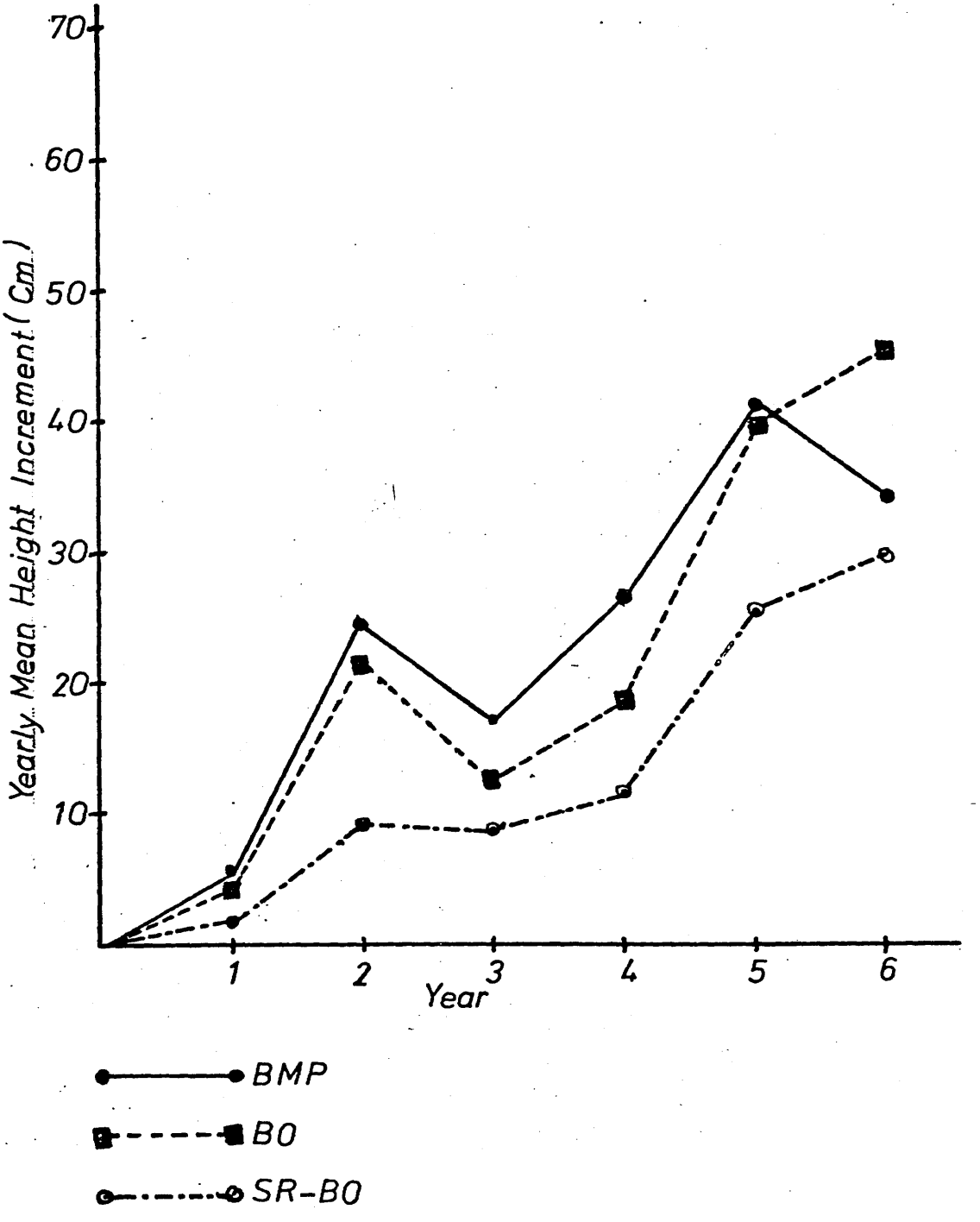


TABLE 2.03

Experiment Record from Forestry Commission. Assessment of Fiunary Forest. Characteristics Assessed : Mean Heights. Unit of Measurement : Cm. Age: 0 - 6 years.

Treatments			Mean Height (cm)						
			Year						
			0	1	2	3	4	5	6
Pasture Site									
1.	1 + 1	BM	22.43	29.40	44.23	54.93	76.70	112.33	141.09
2.	1 + 1	BO	19.73	24.00	45.67	58.10	76.77	116.60	161.00
3.	1 + 1	BMP	23.20	28.43	53.23	70.40	96.93	138.03	170.47
4.	1 + 1	BOP	20.77	26.40	52.43	71.43	96.93	147.20	199.17
5.	1 + 1	BML	20.47	26.83	53.67	69.07	92.57	131.87	165.57
6.	SR	BM	6.83	8.60	13.23	18.77	30.93	51.50	70.97
7.	SR	BO	7.17	8.63	17.60	26.33	37.90	63.60	92.73
Forest/Felled Site									
1.	1 + 1	BM	20.25	30.27	66.47	88.57	126.70	173.23	216.40
2.	1 + 1	BF	21.97	29.80	68.80	96.10	145.37	203.57	260.87
3.	1 + 1	BMP	18.47	28.50	69.00	91.13	135.30	190.57	240.63
4.	1 + 1	BFP	23.30	32.37	66.03	90.83	129.00	184.13	243.13
5.	SR	BM	6.03	9.20	25.57	37.13	60.50	91.83	123.40
6.	SR	BF	6.10	9.17	19.80	32.13	53.63	90.60	126.50
7.	1 + 1	BML	20.60	32.10	75.77	101.97	137.90	186.87	236.73

TABLE 2.04

Assessment of Fiunary Forest. Characteristics Assessed : Yearly mean height increment. Unit of Measurement : Cm. Age: 1 - 6 years.

Treatments			Blocks						Total	Mean
			Mean Height Increment							
			Year							
			1	2	3	4	5	6		
Pasture site										
1.	1 + 1	BM	6.79	14.83	10.70	21.71	35.63	28.74	118.64	19.77
2.	1 + 1	BO	4.27	21.67	12.43	18.67	39.83	44.40	141.27	23.55
3.	1 + 1	BMP	5.23	24.80	17.17	26.53	41.10	32.44	147.27	24.55
4.	1 + 1	BOP	5.63	26.03	19.00	25.50	50.27	51.97	178.40	29.73
5.	1 + 1	BML	6.36	26.84	15.40	23.50	39.30	33.70	145.10	24.18
6.	SR	BM	1.77	4.63	5.54	12.16	20.57	19.47	64.14	10.69
7.	SR	BO	1.46	8.97	8.73	11.57	25.70	29.13	85.56	14.26
Forest/Felled site										
1.	1 + 1	BM	10.04	36.20	22.10	38.13	46.53	43.17	196.17	32.70
2.	1 + 1	BF	7.83	39.00	27.30	49.27	58.20	59.50	238.90	39.85
3.	1 + 1	BMP	10.03	40.50	22.13	44.17	55.27	50.06	222.16	37.03
4.	1 + 1	BFP	9.07	33.66	24.80	38.17	55.13	59.00	219.83	36.64
5.	SR	BM	3.17	16.37	11.56	23.37	31.33	31.57	117.37	19.56
6.	SR	BF	3.07	10.63	12.33	21.50	36.97	35.90	120.40	20.07
7.	1 + 1	BML	11.47	43.70	26.20	35.93	48.97	49.86	216.13	36.02

It, therefore, appears that liming on its own has no real benefit for normal forest practice and most certainly is out, due to cost of application.

* 5th year height summary show:

The forest site is growing better than the pasture site (1.66 mean height compared to 1.08 m), with many trees now over 2 metres. Survival excellent on both sites.

Forest site — BF ranks first, which is the equivalent of BO on the pasture site, which was not so good (Fig. 2.01 and 2.05).

BMP treatment is next, followed by the lime treatment (BML) and closely behind by BFP.

Both phosphate treatments are quite good, BM treatment is quite a bit poorer as it had been in the pasture site (see Figs. 2.01, 2.02, 2.05 and 2.06).

The SR plants are again a failure and of poor colour.

Effects of lime treatments on both sites are now dropping after having given better results for the first three years (Tables 2.03 and 2.04).

Pasture site — Treatment BOP is well ahead of all the others (Figs. 2.03 and 2.07) followed by BMP and BML (Figs. 2.04, 2.07 and 2.08) (with little between these). Therefore, direct notch with phosphate is now giving better results than planting into the mineral soil with phosphate. The BO and BM treatments which did not get P are both significantly behind the P treatments. The self generated plants are a failure and though showing good survival, are very pale in colour now.

The summary of 6th year heights shows that the forest site continues to grow better than the pasture sites with a mean height of 2.07 m compared to 1.43 m. Survival remains excellent on both sites.

Forest site — Colour and growth are better here. Trees are glaucous and have much better branch spread and needle size. There is strong intermingling of branches now. The height trend is again fairly similar to last year. BF is well ahead followed by the two treatments BFP and BMP (Table 2.03), with little between these two. The lime treatment is also fairly close to the P treatments. BM falls well behind and the two SR treatments are a failure (Figs. 2.05 and 2.06).

Pasture site — The height trend is the same as last year. The P treatments are well ahead, especially BOP (Fig. 2.03), showing the direct notch with P to mineral soil planting with P. BO and BM are well behind (Figs. 2.03 and 2.04), BM more so. The lime treatment is also trailing but not quite so much as the P treatments (Tables 2.03 and 2.04). The SR treatments are a failure. Colour throughout is quite good with little difference between treatments.

The lime plots have fallen behind now, so there seems to be no advantage in using it, although BF (no P) has given the best result.

2.7 THE ALLOPHANE TEST ON SOILS

(i) Definition of Allophane

Allophane materials are amorphous alumino-silicate or non-crystalline alumino-silicate. These materials are characterised by structural randomness but otherwise they show a gradation of properties in their response to Na F.

(ii) Modes of Formation of Allophane

Allophane is found in rocks and soils. In rocks it occurs as linings to fissures and this suggests precipitation at low pressure and temperature from solutions containing hydrous alumina and silica.

They were synthesised artificially under similar conditions by Mattson (1928 , 1930), in a series of studies on the co-precipitation of alumina and silica. In the soil they are found (a) as the weathering products of rocks produced by volcanic activity, and (b) in the subsoils of podzols. This suggests two possible modes of origin, the first determined by the disordered structure of the rock mineral and the second controlled by a leaching process (Helen Fullerton, 1972).

(iii) Dissolution of Allophane by Fluoride

Fluoride reacts slowly with clay minerals with release of hydroxyl ions into the solution (Fields and Perrott, 1966). In the following experiment, the allophane content was assessed by noting the rise in pH in a given time:-

Experiment

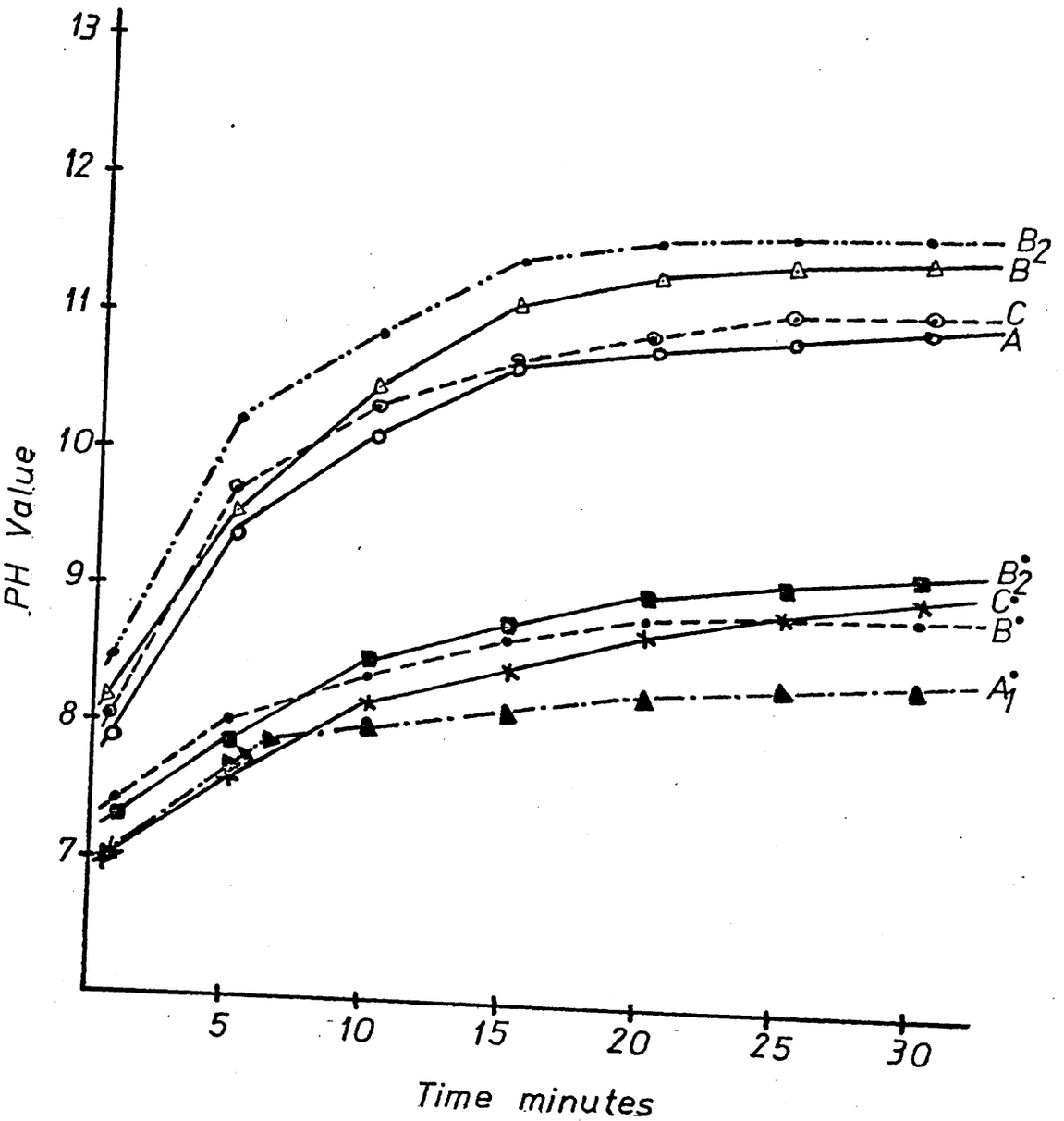
The rise in pH for forest soils treated with NaF solution. 50 ml saturated NaF solution was added to 1 g air-dry soil and the rise in pH with time was recorded. The pH of the NaF solution was previously adjusted from 6.8 to 7.0. It was found to be important to make the NaF solution up fresh each day, because the pH rose as it reacted with the glass. The results are shown in Figures 2.09 and 2.10, where pH values for a period of 30 minutes (Table 2.05) gives the pH after 30 minutes. Very high values were obtained for the B horizons of the Fiunary, Savary Glen and Salen Forests (strong reaction). The pH rose to between 11.0 and 11.6 after 30 minutes treatment. Lower values were recorded in their respective C horizons from between 10.4 - 10.6. In the case of Pitmedden Forest, the A horizon showed negligible reactivity (pH 8.4), and slight reaction in B horizon (see Figs. 2.09 and 2.10).

TABLE 2.05

Average of pH values obtained after 30 min., when 1 gm air dry-soil was treated with 50 ml saturated Na F solution.

Basalt Brown Forest Soils							
Pitmedden forest		Fiunary forest		Savary Glen		Salen forest	
Horizon	pH	Horizon	pH	Horizon	pH	Horizon	pH
A_1	8.3	A	10.5	A	10.6	A	10.2
A_2	8.5	B	11.2	B	11.1	B	10.8
B	8.9						
B_2	9.2	B_2	11.5	B_2	11.6	B_2	11.2
B_2g	9.1	C	10.6	B_3	11.5	C	10.4
B_3	9.2						
				C	10.5	C_x	10.2
C	8.8						

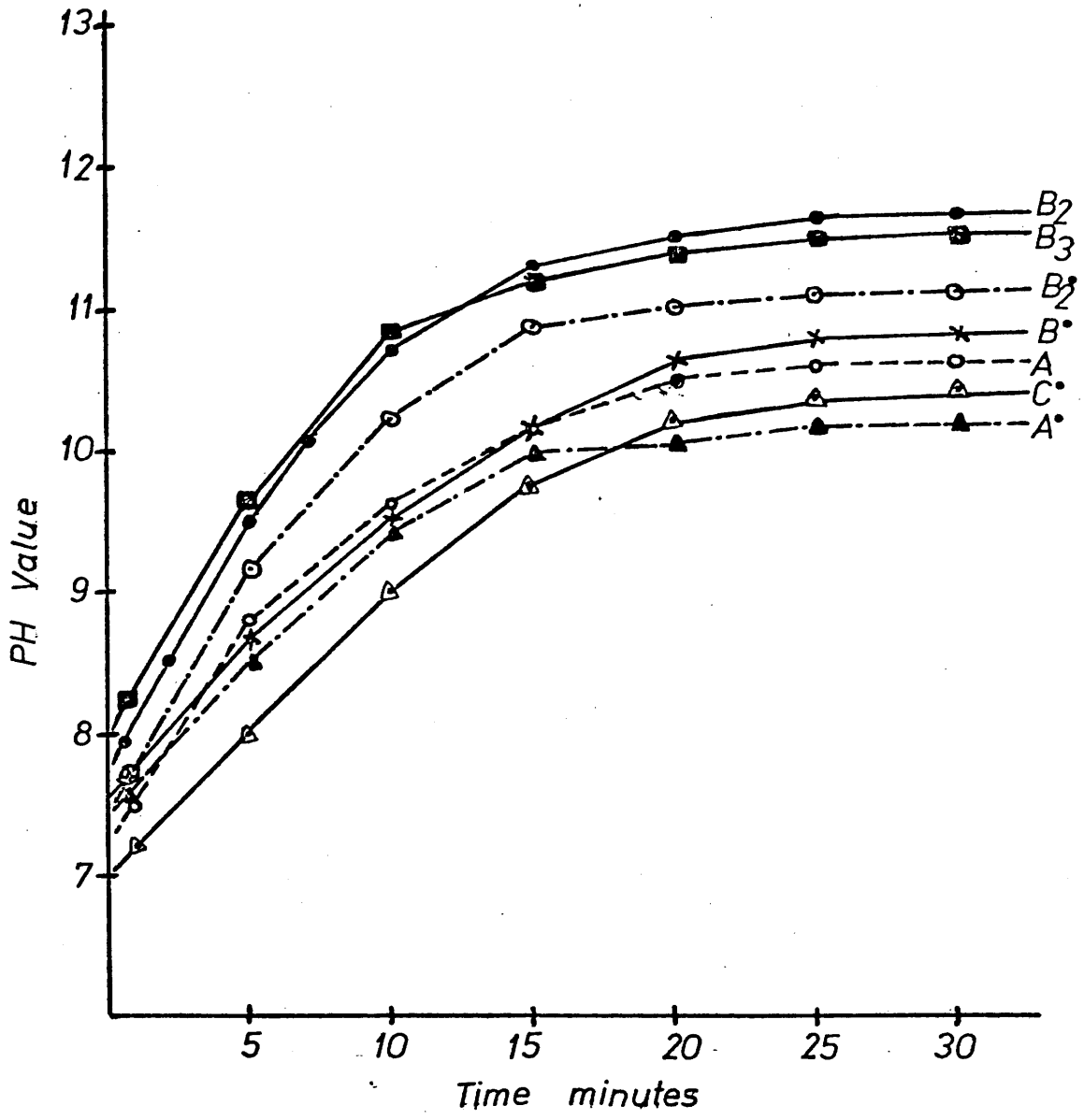
Fig-(2-09) Rise In PH With Time On Addition Of Satuated NaF Solution To 1g: Air-Dry Soil



(A, B, B_2, C) Fiunary Forest

($A_1^•$, $B^•$, $B_2^•$, $C^•$) Pitmedden Forest

Fig.(2_10) Rise In PH With Time On Addition Of Saturated NaF Solution To 1 g Air_Dry Soil



(A, B_2, B_3) Savary Glen Forest

($A^\bullet$, $B^\bullet$, $B_2^\bullet$, $C^\bullet$) Salen Forest

CHAPTER III

ANALYTICAL METHODS AND SOIL PLANT NUTRIENT CORRELATIONS

3.1 THE NUTRIENT REQUIREMENTS OF PLANTS

Apart from carbon, oxygen and hydrogen, which are obtained from carbon dioxide and water, plants must extract their nutrients from the growth medium in which they are situated. These nutrients are taken up by the roots as ions and transported within the vascular system of the plant. The amounts of different elements required by a plant vary and it is usual to divide these into two distinct groups, the macro and micro nutrients.

In the following discussion a brief account will be given of the effects of the various nutrients on crop growth.

3.1.1 MACRONUTRIENTS

(a) Nitrogen

Nitrogen is without doubt the most important plant nutrient as it is a constituent of protein and nucleic acid, and therefore essential for healthy plant growth and reproduction. Both nitrate and ammonium ions are absorbed by plant roots, although once inside the plant the nitrate ions are reduced to ammonium ions which are used in amino acid synthesis. Nitrogen has two main effects on plants:-

It leads to increased protein production and hence to an increase in size and surface area which allows more photosynthesis to occur, and it causes the production of larger cells with thinner cell walls, thus

making plants more succulent.

A deficiency of nitrogen is evidenced by poor growth and leaves which are yellow or have a red tinge. Low levels of protein production cause a stunted plant with a poor chance of survival.

(b) Phosphorus

Phosphorus is one of the major nutrients required by a plant for healthy growth, but its content in plants is considerably less than that of nitrogen, calcium and potassium. As a limiting factor in growth, however, phosphorus is more important than calcium and probably more important than potassium.

The determination of plant available phosphorus in soils is one of the most important analyses performed in relation to predicting plant growth and a considerable amount of time has been devoted to this particular subject to ensure that the results are reliable. This element is dealt with in a separate chapter, the next one (Chapter IV).

(c) Potassium

Potassium is the third most important element which is commonly added to the soil as fertilizer in order to raise the amount available to the plants, and hence the yield of a crop. Arnold (1960) has listed four forms which occur in soil:-

1. Potassium dissolved in the soil solution which is the immediate source for plant roots.
2. Exchangeable potassium which is held on the negatively charged soil colloids, and which readily replenishes the

soluble potassium.

3. Non-exchangeable, but available potassium which is found near the surface of the clay mineral lattices, and which can replace exchangeable potassium as it is removed from the exchange sites.

4. Inert potassium held well inside the clay mineral lattices or in coarse mineral particles, and which can be released only by weathering.

(d) Calcium

The requirement of plants for calcium is considerably less than for any of the three previous nutrients. Sufficient is taken up, however, to classify it as a macronutrient. Its role in a plant appears to be an involvement with the growth and functioning of meristems, especially in the root tip, it is also found as a constituent of cell walls. In this country, calcium is the dominant cation in soil held on the exchange complex. In acid soils the level of exchangeable calcium falls, although it may still be the most abundant cation. Liming of soils tends to ensure that calcium is seldom deficient in this country. Other forms of calcium commonly found are in minerals such as feldspars, hornblende, calcite and gypsum.

(e) Magnesium

Magnesium is essential for all green plants as it is incorporated into the chlorophyll molecule, and so is necessary for photosynthesis. Most of the magnesium in British soils is found in the silicate mineral fraction in such forms as mica, hornblende, olivine, serpentine and isomorphously substituted for aluminium in clay minerals. Other elements

needed in moderate quantities include:-

(f) Sulphur

Sulphur is an essential constituent of many proteins, and is also a constituent of the oils produced by certain plants. Organic sulphates also appear to be essential constituents in the plant. A lack of sulphur frequently shows in a yellowing of the leaf.

(g) Sodium

It would generally be agreed that sodium is beneficial to the growth of certain plants although not necessarily essential. The role of sodium in the nutrition of plants that need this element for optimum growth is not fully known (Russell, 1973), though one of its effects is to increase the succulence of the plant, i. e. the amount of water held by unit dry weight of leaf tissue. This may be the reason why it appears to increase the drought resistance of these plants. Breakdown of minerals such as plagioclase feldspar releases sodium in a plant available form.

(h) Silicon

Even though silicon is one of the most abundant elements, it has been considered to be non-essential for most living organisms, whereas carbon which is far less plentiful, is the primary element upon which all life depends. Although it is doubtful whether any plant physiologist today would place silicon in the list of essential nutrient elements, there is nevertheless increasing evidence that it can produce beneficial effects on plant growth.

For the most part these effects have been observed amongst

gramineous species and the best examples are seen where silica decreases aluminium toxicity (see Chapter VII), alleviates manganese toxicity (Jones and Handreck, 1967), and improves resistance to fungal and insect attack. However, it is important to study this element very carefully, see Chapters V and VII).

3.1.2 MICRONUTRIENTS AND OTHER TRACE ELEMENTS

Plants need very small quantities of certain elements, the trace or minor elements, for their nutrition, and these include iron, manganese, zinc and copper (Russell, 1973).

3.2 CHEMICAL ANALYSIS

3.2.1. (a) All laboratory analyses were performed in duplicate or triplicate on soils and needles of sitka spruce and Mycorrhiza. Soil samples were collected from different forest sites as explained in Chapter II. These samples were selected to represent a range of values and to represent as much variation as possible within the soil and needle samples. Soil samples were air-dried, sieved and passed through a 2 mm sieve, or ground and passed through a 100 mesh sieve for total determination of needle samples of sitka spruce were oven-dried and ground to give a fine powder. The pH of the soil samples was measured using the standard 1 : 2.5 soil : water ratio.

The organic matter was determined by a wet combustion method (Walkley and Black, 1947), which uses a mixture of dichromate and concentrated sulphuric acid. The acid is used to acidify and to supply heat. The amount of dichromate reduced is measured by back titration using

ferrous iron.

(b) Loss on ignition

A soil ignited at 700°C will lose weight due to loss of organic matter and loss of combined water. Calcareous soils will also lose carbonate.

Procedure

The vitreosil basin containing the oven-dry sample was placed in a muffle furnace set at 700°C until ignition was completed. The basin was then removed and held at 110°C for 1.5 hr., after which it was cooled in a desiccator and re-weighed. The percentage loss on ignition was calculated:-

$$\% \text{ loss of ignition} = \frac{\text{wt. of oven-dry soil-wt. of ignited}}{\text{wt. of oven-dry soil}} \times 100$$

3.2.2 THE MEASUREMENT OF CATION-EXCHANGE CAPACITY OF SOILS

Cation-exchange capacity (CEC) is extensively used in characterising soils for survey purposes and in assessing their ability to supply cations to plants.

Many methods have been and continue to be proposed for the determination of cation-exchange capacity, and while most of them will indicate the order of magnitude of exchange capacity, the values may vary widely, depending upon the particular technique employed. This can be partly accounted for by the variations which exist in the composition of the minerals and organic materials possessing replaceable cations vary

widely in soils, as do the kinds and proportions of exchangeable cations held by soils.

3.2.2.1 Method (Bache, 1976)

Unbuffered salt was used (e.g. M NH_4 Cl or K Cl). It is usual to determine Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, Na^+ and perhaps also Mn^{2+} in the extract, and the sum of their charges is taken as the exchange capacity at the natural pH of the soil.

3.2.2.2 Procedure

The soil was leached with isopropyl alcohol (2-propanol) to remove soluble salts and then saturated with ammonium ions by leaching with ammonium chloride. The displaced cations were collected in the leachate.

10 g air-dry soil were weighed accurately and thoroughly mixed, with an equal volume of acid-washed sand to assist percolation. The column was leached with 100 ml 2-propanol and the leachate discarded. M NH_4 Cl was passed through the column, the leachate collected in a 250 ml volumetric flask and made up to the mark with M NH_4 Cl.

3.2.3 SOIL PH AND LIME REQUIREMENT

The lime requirement of a soil is the amount of pure Ca CO_3 or CaO required to raise the pH of an acid soil to some value between 6 and 7, depending on the crop requirement. It is not enough, however, simply to take the soil pH, since different soils have different responses to the addition of lime.

3.2.3.1 Buffer Curve Method

5 g soil were weighed into 6, 100 ml conical flasks. The following additions of lime water and deionised water were made.

Lime water (ml)	0	10	20	30	40	50
Water (ml)	50	40	30	20	10	0

The flasks were stoppered and shaken on wrist-shaker for 30 mins. The lime water provided was standardised to approximately 0.01 M by titrating 10 ml with 0.1 M H Cl using methyl orange indicator. The pH of each suspension was determined and a graph drawn of pH against lime water (ml) added. The amount of lime water needed to raise the pH of the soil to 6.2 and 6.5 was determined.

3.3 THE EXTRACTION AND ANALYSIS OF NUTRIENTS AND TRACE METALS

3.3.1 NITROGEN DETERMINATION FOR SOIL AND PLANT TISSUE

(a) Principles

The Kjeldahl procedure generally employed for the determination of total nitrogen involves two steps:-

(i) Digestion of the sample to convert the organic nitrogen to ammonium.

(ii) Determination of the ammonium in the digest.

The digestion is usually performed by heating the sample with $H_2 SO_4$ containing a catalyst to promote oxidation of organic matter and conversion of organic nitrogen to ammonium such as $K_2 SO_4$, or $Na_2 SO_4$ are added to increase the temperature of digestion. The catalysts generally found are Hg, Cu or Se, which increase the rate of oxidation of organic

matter by $H_2 SO_4$. The ammonium in the digest is usually determined by titration of the ammonia liberated by distillation of the digest after having been made alkaline.

(b) The Kjeldahl Method for Nitrogen Determination (Bremner, 1965)

5 g. of ground soil samples were weighed in duplicate, transferred to Kjeldahl flasks, 50 ml Analar sulphuric acid added plus one Kjeldahl copper catalyst tablet (BDH Chemicals Ltd., each tablet contained 1 g. $Na_2 SO_4$ and 0.1 g. $Cu SO_4 5H_2O$).

The sodium sulphate raises the temperature of the digestion, while the copper sulphate acts as a catalyst, both help to decrease the digestion time. Initially, the flame was kept low to prevent frothing and loss of ammonia, once all the water had boiled off, the heat was increased and the flask boiled until the digest cleared. Further additions of sulphuric acid were made if necessary to prevent the flask drying out. When the digest had cleared the flask was allowed to cool and the contents were then diluted with 200 ml deionised water. The flask was then clamped into a distillation unit and 125 ml 50% sodium hydroxide were added. The ammonia released was collected in 50 ml 2% boric acid to which 3 drops of alcoholic methyl red/methylene blue indicator (1.2 g. methyl red and 0.8 g. methylene blue in 11 ml 95% ethanol) had been added.

The first ammonia to distil over caused the colour change purple to green. Distillation was continued for 30 minutes after this colour change occurred. The borate anion formed by the reaction:

$$NH_3 + H_3BO_3 \longrightarrow NH_4^+ + H_2BO_3^-$$

Can be titrated with standard acid.

$$H_2BO_3^- + H^+ \longrightarrow H_3BO_3$$

The colour reverting to purple. The standard acid used was

$$\frac{M}{35} \quad HCl \simeq 0.028\ M$$

1 ml M/35 H Cl = 0.4 mg Nitrogen

3.3.2 ESTIMATES OF PLANT AVAILABLE NUTRIENTS BY 0.5 M ACETIC ACID

Estimates of plant available nutrients are made by extracting the soil with a suitable reagent. 0.5 M acetic acid is commonly used by the Advisory Service in Scotland.

Plant roots take up nutrients from the solution. Some nutrients are found only in solution, e.g. NO_3^-, but most exist in a state of equilibrium with exchangeable or readily soluble ions, which are in turn in equilibrium with fixed or unavailable forms. These unavailable nutrients act as buffers which can maintain the levels of available and soluble nutrients. Plant growth is dependent on a continuing supply of "readily available" nutrients. Phosphorus and potassium are examples of nutrients which are required by plants in high amounts.

3.3.2.1 Procedures

10 g. soil samples were weighed out accurately in triplicate into a 4 oz screw cap bottle and 100 ml 0.5 M acetic acid added. The bottles were shaken for 16 h. (overnight). The extracts were filtered

into polythene storage bottles through a Whatman filter paper (No. 42). Standard solutions were prepared with 0. 5 M acetic acid solution.

3. 3. 3 USE OF DILUTE CALCIUM CHLORIDE FOR THE EXTRACTION OF PLANT AVAILABLE, SILICON, ALUMINIUM AND IRON

It was suggested that 0. 01 M Ca Cl_2 had promise for diagnostic extraction of plant available aluminium and manganese from acid soils (Hoyt and Nyborg 1971 a, b).

McKeague and Cline (1963 a, b) studied the forms and concentration of dissolved silica in water extracts of soils. They concluded that shaking techniques were not always suitable for obtaining equilibrium measurements. They reported that monosilicic acid, presumably $Si(OH)_4$, was the form of dissolved silica in soil extracts. Concentrations of dissolved silica in water extracts of the soils increased with temperature and with soil solution ratio, and decreased with increasing pH (McKeague and Cline, 1963 a). Aluminium is present in solution in aqueous extracts as gibbsite-like $Al(OH)_3$ (Hoyt and Nyborg, 1971 a).

The objective of the present study was to compare several soil extraction methods in order to find a measure of soil aluminium that would best predict the aluminium taken up by plants and its adverse effect on yields when the plots were grown on acid soils.

3. 3. 3. 1 Procedure

The same procedure was used as described above (Section 3. 3. 2. 1). Polyethylene bottles were used in preparing the extracts in

case of silica.

3.3.4 DETERMINATION OF NA-DITHIONITE AND NH_4-OXALATE EXTRACTABLE IRON, ALUMINIUM, MANGANESE AND SILICON IN SOILS

Aluminium, iron, manganese and silicon were determined in acid ammonium oxalate extracts and in dithionite extracts from a wide range of brown forest soils, several oxide and silicate minerals, and some amorphous preparations of iron or aluminium and silica. The oxalate extraction dissolved much of the iron and aluminium from the amorphous materials but very little from crystalline oxides, whereas the dithionite extraction dissolved a large proportion of the crystalline iron oxides as well as much of the amorphous materials (McKeague and Day, 1966; Raad et al., 1969).

3.3.4.1 Procedure

The method of McKeague and Day (1966) was adopted:-

(i) Tamm's acid oxalate:

24.9 g ammonium oxalate + 12.6 g oxalic acid were made up to 1 litre. The pH was adjusted to 3.5.

(ii) Dithionite method:

Acetate Buffer: 68.05 g Na OAC. $3H_2O$ in 1 litre + 390 ml glacial acetic acid were made up to 2.5 litre.

The pH was adjusted to 3.8.

The contents were shaken for 16 hr.

3.3.5 DETERMINATION OF TOTAL CONCENTRATION OF ELEMENTS IN SOILS

Acid digestions and $Na_2 CO_3$ fusion are the most commonly used techniques for extracting total concentration elements from soils. The fusion with alkali gave low and erratic values in all samples (Jeffery, 1970). The results of present investigation confirm that. The other methods were more reliable. The acids recommended for digestion are perchloric or hydrofluoric acid. Perchloric acid is to be preferred as silica is removed by filtration. However, these digestions best carried out in conical flasks on a sand-bath at temperatures of 180 - 200°C.

3.3.5.1 Procedure

See Chapter IV, Section 2.3.2.6.

3.3.6 PLANT MATERIAL ANALYSIS MINERAL CONSTITUENTS

3.3.6.1 The extraction of mineral nutrients from soil by growing crops is a selective type of soil chemical analysis. Plant tissue analysis aids in the characterisation of soil chemical properties in terms of soil fertility and mineral nutrition of plants. Mineral is employed here for present purposes to cover the mineral elements in plants. A wet-oxidation procedure is given which results in the conversion of the elements - phosphorus, potassium, calcium, sodium, magnesium, manganese, iron, aluminium, nickel and others to a suitable form for analytical determination.

3.3.6.2 Preparation of Plant Tissue Sample

Freshly sampled plant tissue was dried in air or in an oven at

60^{o} to 80^{o}C, protected in both cases from fumes etc. that could lead to contamination. Speed in drying helps to avoid the growth of moulds or to minimise loss of weight by enzymatic action in the tissue. The size of plant tissue sample needed for analysis is determined by fineness of grinding. Contamination in the case of the major elements is generally considered to be negligible.

3.3.6.3 Wet oxidation of Plant Tissue (Tri-acid mixture)

3.3.6.3.1 Oxidation of the organic matter of plant tissue and release of the mineral elements such as potassium, magnesium, phosphorus, calcium and aluminium may be accomplished either by a wet ternary acid mixture as employed in the procedure to be described here, or by dry ashing (considered in the alternative procedure). Wet oxidation with $H\,Cl\,O_4$ avoids the loss of elements through volatilization and gives a clear solution of all constituents except Si, which is quantitatively dehydrated and precipitated and is removable by filteration. The resultant solution is ideal for analysis of both the major and minor elements.

3.3.6.3.2 Reagents

Reagents required include Aristar $H\,NO_3$ and a ternary solution of three Aristar acids prepared by mixing 100 ml of concentrated $H\,NO_3$, 10 ml of concentrated $H_2\,SO_4$ and 40 ml of $H\,Cl\,O_4$ (any quantity in volume ratio of (10 : 1 : 4) and then allowing to cool before use.

3.3.6.3.3 Precaution

Predigestion of plant tissue in $H\,NO_3$ prior to addition of $H\,Cl\,O_4$

is highly important to preclude danger of explosion and fire. Sixty or more percent $H Cl O_4$ is never added directly to plant tissue without predigestion in $H NO_3$.

3.3.6.3.4 Procedure (Jackson, 1958)

To 1 g of dried and powdered plant tissue sample in a 500 ml conical flask, 5 ml of Aristar $H NO_3$ was added. The flask was swirled to moisten the entire mass of tissue and then placed on a steam plate (bath) for 30 min. and then on the electric hot plate at 180°C to 200°C as measured in a flask of glycerol with thermometer standing on the hot plate. A funnel was placed at the top of the flask to exhaust the oxides of nitrogen and to condense unreacted acid fumes. The suspension was boiled until taken nearly to dryness. The predigestion with $H NO_3$ required about 45 min.

The digestion flask and contents were cooled slightly, then an appropriate amount of the ternary mixture of acids ($H NO_3$ - $H_2 SO_4$-$H Cl O_4$) was added, consisting of 5 ml. Digestion was carried out at 180°C to 200°C until dense white fumes of $H_2 SO_4$ and $H Cl O_4$ were evolved. The digestion was continued at the same temperature until the acid liquid was largely volatilized. When the digestion was complete, the flask was removed. Once cooled sufficiently, 50 ml of deionised water was added and the solution transferred through a filter into a 100 ml volumetric flask. The conical flask was washed to bring the volume of the solution to the mark. Blank digestions (in duplicate) were run on the reagents, added in the same amounts as employed in the determinations. All steps were carried out in parallel with the sample.

3.3.7 DIGESTION WITH HYDROFLUORIC ACID FOR TOTAL SILICON

Rapid decomposition of silicates is achieved in a specially designed decomposition vessel made of teflon without volatilization or loss of silica by hydrofluoric at 240°C. All the reaction steps and decomposition are carried out in the fume cupboard.

3.3.7.1 Reagents

Reagents required include Aristar H NO_3, and Aristar H_2 SO_4 and HF, Analar Boric Acid.

3.3.7.2 Procedure

150 mg ± 50 of the sample (100 mesh size sample portions) were transferred into the teflon decomposition vessel. 4 ml Aristar H_2 SO_4 and 5 ml Aristar H NO_3 acid were added and the vessel closed and sealed, and the contents heated at 240 ± 10°C for 3 hr. on a sand bath. The vessel was thoroughly cooled and 5 ml Aristar hydrofluoric acid added to the clear solution, and the vessel closed and resealed. Heating was continued for a further two hr. The teflon vessel bomb was again cooled to ambient temperature, then placed in the freezer (at -18°C) for 2 hr to prevent loss of silicon as silicon tetrafluoride (Si F_4) which is volatile (it vaporizes at about 35°C). The contents were transferred to a 100 ml polyethylene flask containing 2.8 g of 99.9% boric acid. The boric acid was added to suppress Si interference during analysis, by reacting with the excess of HF.

A two-step exothermic reaction is involved in the formation of fluoro boric from hydrofluoric and boric acids (Sharpe, 1954).

$$H_3BO_3 + 3\,HF \rightleftharpoons H\,BF_3OH + 2\,H_2O$$

$$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O$$

The best way of getting the boric acid into solution was found to be to add the boric acid to about 50 ml deionised water in the standard flask and on frequent shaking most of the boric acid dissolved. The sample was then added.

A blank solution containing all reagents was made up and analysed together with the samples. Standard solutions of silicon were prepared (50 ppm).

3.4 METHODS OF ANALYSIS

3.4.1 ATOMIC ABSORPTION SPECTROSCOPY

This is probably the most widely used method of metal analysis because of the ease of handling of the equipment, the sensitivity and the range of elements which can be detected. The principles have been well discussed (Kirkbright and Sargent, 1974; Elwell and Gidley, 1966).

In brief, in atomic absorption analysis the element being determined must be reduced to the elemental state, vaporized and introduced into the beam of radiation from the source. This process is most frequently accomplished by drawing a solution of the sample, as a fine mist, into a suitable flame. The flame thus serves a function analogous to that of the cell and solution in conventional absorption spectroscopy, therefore, the method can be simply defined as the absorption of radiant energy by atoms. This absorption and its quantitative correlation with

the concentration of metal ions originally present in a sample solution serves as the basis of analytical atomic absorption.

3.4.1.1 Atomic Absorption Spectra

The absorption spectrum of an element in its gaseous, atomic form consists of a series of well-defined, narrow lines arising from electronic transitions of the outermost electrons. For metals, the energies of many of these transitions correspond to wavelengths in the ultraviolet and visible regions. The energy-level diagram for the outer electrons of an element provides a convenient means of showing the types of transitions responsible for atomic absorption.

3.4.1.2 Production of Free Atoms

There are two main methods of producing free atoms:-

(i) Flame

Here a combination of gases is burned in the light path. The sample solution is aspirated into the flame where the solvent is dried off to form a clotlet. The clotlet is thermally dissociated into free atoms and finally the free atoms absorb radiant energy. The whole process takes a matter of seconds. The main types of flames used are:-

(a) Air/acetylene with a temperature of approximately 2200°C and is the preferred flame for about thirty-five elements.

(b) Nitrous oxide/acetylene with a maximum temperature of 2900°C and is used for determination of aluminium and silicon.

(c) Argon/hydrogen with an extremely low temperature of 300° to 800°C using diffused air as an oxidant shows considerably less absorption in the far UV (190 - 220 nm).

(d) Air/hydrogen with a temperature of about 2000°C is useful for the determination of alkali metals (K, Na, Rb) as the lower temperature considerably reduces ionization.

(ii) Flameless Atomisation

The flame is replaced either by a carbon furnace or a tantalum filament with maximum temperatures of about 2600°C and 3200°C respectively. In the flameless system the stages which the sample goes through - drying etc., can be controlled electrically. The solution is first dried at a temperature just below boiling point to prevent spluttering and then the temperature is increased to a value at which the accompanying material will be thermally destroyed without causing a loss of the element of interest. Finally the temperature is very rapidly increased so that the element will be thermally dissociated into its atoms.

3.4.1.3 Interferences

There are many types of interference. The main ones are:-

(i) Chemical Interferences

These occur when the element of interest combines with some other cation or anion in solution to form a compound which influences the degree of reduction to free atoms, i.e. reducing the number of atoms capable of absorbing radiation at resonant energy.

Chemical interferences can be overcome or controlled in two ways:-

(a) Use of a higher temperature flame which produces additional energy to break down the compound formed.

(b) By addition of a releasing agent, i. e. a chemical species which when added to the sample solution will preferentially react with the element of interest or the interferant.

(ii) Matrix Interferences

These occur when the physical characteristics of the sample vary considerably, e. g. when the sample solution contains high concentrations of dissolved salts or acid, or a different viscosity which alters the aspiration rate.

Matrix effects can be controlled by:-

(a) Dilution of the sample until the effect of dissolved salts or acid become negligible.

(b) Running or matching sample and standard solutions for major constituents.

(c) Use of the method of standard additions. Aliquots of the sample are taken. One is diluted to a known volume with solvent. To the other, aliquots are diluted to the same volume with suitable quantities of known standards added so that the final solutions contain different additions of the metal to be determined. The absorbance is measured for each solution and plotted against the added concentration. The resulting straight line is passing through zero absorbance, the working curve must be linear over the concentration range covered by the sample.

(iii) Ionisation Interferences

These occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom giving a positively

charged ion and reducing the number of metal atoms in the flame.

These can be controlled by:-

Using a cooler flame which has less energy available to produce ionisation and the addition to both samples and standard of an excess of an easily ionised element (e.g. alkali metals).

(iv) Spectral Interferences

Spectral interferences can occur when an absorbing wavelength of an element present in the sample but not being detected falls within the width of the absorption line of the element of interest giving an erroneously high result. It can be overcome by using a smaller spectral slit width, and using an alternative wavelength for the element.

3.4.2 FLAME PHOTOMETRY

Flame tests for sodium and potassium have been used for many years in quantitative analysis. The temperature of a flame can be kept more nearly constant than is the case for any electric source. This makes flame spectroscopy particularly attractive for the quantitative determination of those elements for which its sensitivity is adequate. In practice, quantitative work usually is carried out with aqueous solutions. The solution is introduced into the flame as a fine spray or mist by means of an nebulizer operated at constant air pressure. The temperature of the flame is constant over long periods of time when the rate of consumption of the flame gases and the rate of entry of spray are kept constant. The intensities of the emitted spectrum lines may be determined in the photographed spectrum or may be measured directly by isolating the desired spectrum line by means of a spectroscope

equipped with a suitably narrow exit slit and a photometer. A comprehensive discussion of the principles and applications of flame photometry should be consulted for further details (Herrmann and Alke made, 1963).

3.4.3 SPECTROPHOTOMETRIC ANALYSIS : COLORIMETRIC METHOD

This method of analysis is based upon the fact that different substances absorb radiation of a given frequency to different extents, that each substance has a characteristic absorption spectrum.

The existence of a colour is due to absorption in the visible region of the spectrum. The transmittance of a solution at a certain wavelength, or at any other wavelength where absorption occurs, is related to the concentration of a particular component have been well explained by Kolthoff et al. (1969). For many practical procedures involving visible and ultraviolet measurements, refer to comprehensive works on colorimetric determination of metals by Sandell, (1959). A collection of colorimetric procedures by Allport and Brocksopp (1963) are valuable for many analytical applications.

3.4.3.1 Aluminium

Oxine-chloroform method (Riley, 1958).

Aluminium is determined photometrically in solution. It is extracted with a solution of 8-hydroxyquinoline in chloroform, after adjusting the pH to 5 and complexing iron as the ferrous- pyridyl complex. The absorption of the aluminium complex is measured at 410 mμ

3.4.3.1.1 Reagents

Complexing solution:

(a) 25% w/v hydroxyl amine hydrochloride : 25 g NH_2 OH. H Cl was dissolved in 100 ml water.

(b) Sodium acetate (0.5 M) : 17.0 g hydrated Na OAC was dissolved in water and diluted to 250 ml.

(c) Bipyridyl solution : 0.2 g 2,2'-bipyridyl was dissolved in 100 ml 0.2 M H Cl.

4 ml hydroxyl amine hydrochloride, 50 ml. 0.5 M sodium acetate, and 20 ml bipyridyl solution was mixed and made to 100 ml. The solution was stable for one month.

8-hydroxyquinoline reagent (oxine):

1.25 g of 8-hydroxyquinoline (AR) was dissolved in 250 ml chloroform. It was filtered and stored in an amber glass bottle in a refrigerator. It was rejected if it became coloured on standing.

Standard aluminium solution (20 µg Al_2O_3/ml):

0.9302 g Al K $(SO_4)_2$ $12H_2O$ was dissolved in water and made to 500 ml in a volumetric flask. This was Standard I containing 200 µg Al_2O_3/ml.

10 ml of this solution was diluted to 100 ml. This was Standard II, containing 20 µg Al_2O_3/ml.

3.4.3.1.2 Procedure

Standard curve: x ml standard II solution was pipetted into a stoppered 50 ml separating funnel and 10-x ml H_2O was added, where x = 0 to 10 ml. 10 ml complexing reagent was added, taking care to keep

the stem of the funnel dry. The pH was checked and found to be 5.0. After 5 min., 20 ml 8-hydroxyquinoline was added. The funnel was stoppered and shaken by hand, the stopper being loosened to allow $CH\ Cl_3$ vapour to escape after the first two or three shakes. After 2 min. shaking, the yellow chloroform layer was run through a small plug of filter paper, held in the stem of a funnel into a perfectly dry 25 ml volumetric flask. 2 - 3 ml $CH\ Cl_3$ were added to the separating funnel which was rinsed by rotating it gently and the chloroform washing was passed into the flask. The solutions were made up to 25 ml with $CH\ Cl_3$ and stored in a cupboard until ready to be measured, because aluminium-oxinate solutions are somewhat light sensitive. Optical densities were read on a Unicam 600 Spectrophotometer at 410 mμ in a 1 cm cell against a chloroform blank and the value of the reagent blank was subtracted.

A standard curve was constructed from 0 -10 μg $Al_2\ O_3$/ml. Sample solutions require to be buffered by the complexing reagent within the narrow limits 4.9 - 5.0 in order to remove iron interference. Aliquots of sample solution containing 10 ml complexing reagent were brought to pH 4.9 - 5.0 with 30% acetic acid or solid hydrated sodium acetate as required. After 5 min. 20 ml. 8-hydroxyquinoline was added. The above process was repeated.

3.4.3.2 Silicon Analysis

Molybdenum blue method:

A vast number of colorimetric methods based on the production of yellow molybdisilicic acid and its reduction product, molybdenum blue

have been published.

The method used here is essentially a modification of the method of Mullin and Riley (1955). If molybdate is added to the acid solutions which are preferably in the pH range of 1.8 - 2.0, a reaction forms giving silico-12-molybdate (see Chapter V).

3.4.3.2.1 Equipment and Reagents

Polyethylene ware, rather than glassware, was employed whenever possible in order to minimize silicon contamination. Glassware might be used as in the case of pipettes, volumetric flasks etc. However, the glassware must be steeped in nitric-sulphuric acid mixture (ratio 1 : 1) overnight to dehydrate the silica. The glassware was rinsed thoroughly in water and filled with water until ready for use.

1. Ammonium molybdate solution

20 g of Ammonium molybdate tetrahydrate was dissolved in water containing 60 ml of 12 M hydrochloric acid and diluted to one litre. It was prepared fresh weekly.

2. Metol solution

10 g of metol (P-methyl amino-phenol sulphate) was dissolved in water containing 6 g. sodium sulphite and diluted to 500 ml. After filtration through Whatman No. 1 filter paper, the contents were stored at room temperature in a polyethylene bottle. The reagent was discarded when discoloured.

3. Oxalic acid solution

15% m/v, 15 g of dihydrogen oxalic acid were dissolved in 100 ml and stored in a plastic bottle.

4. Reducing solution

100 ml of metol solution, 60 ml oxalic acid solution, 120 ml 9N sulphuric acid and 20 ml of deionised water were mixed in a 500 ml polyethylene bottle and stored under refrigeration. The reducing solution was allowed to attain room temperature prior to use.

The fresh reducing solution should be prepared fortnightly.

3.4.3.2.2 Experimental

Standard curve, standard solutions were prepared in duplicate by pipetting x ml standard silica solution into a 50 ml volumetric flask, where x = 0 to 10 ml (up to 50 μg Si). The pH of this solution was adjusted to 1.9. The reagents were added with the help of a stopclock, 3 ml of ammonium molybdate was added with mixing, giving the pale yellow colour of silico-12-molybdate. After exactly 10 min., 15 ml of reducing solution was added, the solutions were made up to 50 ml with deionised water and allowed to stand for 3 hr. The optical density of the solution was measured at 810 mμ in 1 cm cells on a Unicam SP600 Spectrophotometer against the reagent blank. Absorbence was plotted against silicon concentration.

Sample solutions are required to contain monomeric silicic acid and to be free of organic or other reducing agents. In the presence of sulphuric acid, the maximum value for the colour development of yellow silico-12-molybdate is obtained between pH 1 and 2.5 (Govett, 1961). It was found best to maintain the sample pH at the same pH as the standard solutions, i.e. 1.9 before molybdate addition. Conditions were also critical in other respects such as in the degree of polymerisation

of the molybdate (Govett, 1961), hence the need to renew it weekly.

Interferences from phosphate and iron were removed by the addition of oxalic acid and hydroxylamine hydrochloride (see Chapter V).

3.5 RESULTS

TABLE 3.01

Estimation of Plant-available Nutrients by 0.5 M CH_3 COOH for Pitmedden Forest

No.	Sample Pitmedden Forest	mg/100 g , air-dry sample, ± standard deviation					
		Al	K	Ca	Mg	Na	Ni
1.	Pit. 1A	112.4 ± 10.2	75.1 ± 2.2	168.6 ± 10.5	72.5 ± 3.5	62.5 ± 2.4	1.0 ± 0.4
2.	Pit. 1B	37.2 ± 3.1	46.5 ± 2.5	250.2 ± 8.2	70.6 ± 2.5	40.8 ± 2.5	1.3 ± 0.5
3.	Pit. 2A	152.2 ± 12.2	69.6 ± 3.4	180.2 ± 5.2	80.3 ± 5.2	61.2 ± 2.2	0.4 ± 0.1
4.	Pit. 2B	32.8 ± 3.8	45.1 ± 1.4	360.8 ± 8.8	63.6 ± 3.8	35.6 ± 3.4	0.8 ± 0.2
5.	Pit. 3A	115.4 ± 4.4	68.8 ± 2.8	172.6 ± 4.6	68.4 ± 3.4	64.4 ± 4.2	0.6 ± 0.2
6.	Pit. 3B	123.3 ± 13.3	44.3 ± 4.2	265.2 ± 10.2	51.2 ± 2.2	38.2 ± 4.2	0.9 ± 0.3
7.	Pit. $3B_3$	118.2 ± 12.1	36.2 ± 2.1	271.3 ± 7.2	46.3 ± 4.3	33.9 ± 2.2	0.6 ± 0.2
8.	Pit. 4A	182.5 ± 10.4	70.5 ± 6.2	195.4 ± 6.4	68.7 ± 4.5	62.8 ± 8.5	1.2 ± 0.5
9.	Pit. $4B_2$	145.6 ± 8.4	52.4 ± 4.2	215.6 ± 10.4	57.8 ± 3.2	50.8 ± 5.4	1.5 ± 0.6
10.	Pit. $4B_3$	58.4 ± 4.2	44.5 ± 3.5	280.4 ± 8.4	53.8 ± 4.2	36.2 ± 2.4	0.8 ± 0.2
11.	Pit. 5A	152.4 ± 8.2	91.5 ± 6.4	158.2 ± 6.4	66.7 ± 4.5	70.8 ± 4.5	0.7 ± 0.3
12.	Pit. 5B	120.5 ± 10.4	106.4 ± 6.2	188.2 ± 6.2	46.3 ± 4.2	81.5 ± 6.2	0.8 ± 0.2
13.	Pit. 5Bg	110.2 ± 8.2	103.2 ± 7.1	190.1 ± 8.1	42.4 ± 2.8	52.8 ± 4.5	0.2 ± 0.0
14.	Pit. 6A	154.4 ± 6.2	86.6 ± 4.2	160.2 ± 8.0	60.2 ± 5.1	66.2 ± 4.1	0.8 ± 0.3
15.	Pit. 6B	178.6 ± 6.4	80.5 ± 5.5	174.6 ± 6.2	42.8 ± 8.4	46.2 ± 4.0	1.0 ± 0.4
16.	Pit. $7A_1$	106.6 ± 8.5	76.5 ± 5.2	185.2 ± 5.0	67.8 ± 3.6	65.6 ± 5.5	0.7 ± 0.3
17.	Pit. 7B	115.6 ± 5.4	66.2 ± 4.2	226.5 ± 8.4	52.6 ± 3.5	60.1 ± 3.0	0.9 ± 0.3
18.	Pit. 8A	110.4 ± 8.2	78.3 ± 2.1	180.6 ± 5.4	68.2 ± 4.2	66.8 ± 4.4	0.8 ± 0.2
19.	Pit. 9A	95.6 ± 5.4	80.2 ± 4.4	178.2 ± 4.2	62.4 ± 3.2	68.5 ± 3.5	0.6 ± 0.2
20.	Pit. 9B	108.4 ± 6.2	84.5 ± 6.2	240.6 ± 6.2	65.6 ± 5.5	60.2 ± 4.1	0.9 ± 0.3
	Average	106.2 ± 7.4	69.8 ± 4.2	210.4 ± 8.2	59.8 ± 4.1	60.1 ± 4.2	0.8 ± 0.3
	Minimum	32.8 ± 3.8	36.2 ± 2.1	158.2 ± 6.4	42.4 ± 2.8	33.2 ± 2.2	0.2 ± 0.0
	Maximum	182.5 ± 10.4	106.4 ± 6.2	360.8 ± 8.8	80.3 ± 5.2	84.5 ± 6.2	1.5 ± 0.6

TABLE 3.02

Estimation of plant-available nutrients by 0.5 M CH_3 COOH for Fiunary, Savary Glen Forests

No.	Sample	mg/100 g					
		Al	K	Ca	Mg	Na	Ni
1.	Fiunary 2A (top road)	1210.8 ± 120.4	72.6 ± 4.2	148.2 ± 6.2	65.2 ± 5.1	36.4 ± 4.2	1.8 ± 0.5
2.	Fiunary 2B	1456.2 ± 144.2	70.3 ± 3.8	160.2 ± 5.1	66.8 ± 4.2	68.2 ± 4.1	2.1 ± 0.4
3.	Fiunary 2C	1285.8 ± 135.4	53.8 ± 3.7	153.2 ± 6.3	56.2 ± 4.1	36.9 ± 3.5	1.8 ± 0.6
4.	Fiunary $1A_1$	1240.6 ± 166.2	69.2 ± 4.1	145.8 ± 4.5	66.8 ± 2.8	39.2 ± 2.2	2.0 ± 0.4
5.	Fiunary 2A ie	638.6 ± 42.8	33.2 ± 2.8	80.2 ± 4.1	29.4 ± 3.1	19.5 ± 2.5	0.5 ± 0.2
6.	Fiunary B_2 (micachist)	1495.2 ± 115.2	66.5 ± 4.2	165.9 ± 5.6	60.8 ± 2.8	60.8 ± 3.4	0.8 ± 0.3
7.	Fiunary, Savary Glen $5A_1$	1550.2 ± 244.1	56.3 ± 4.5	150.6 ± 4.5	52.6 ± 4.5	49.8 ± 3.6	0.9 ± 0.3
8.	Fiunary 5, Savary Glen A (granite)	1575.6 ± 165.4	59.2 ± 3.2	146.4 ± 4.2	55.8 ± 3.5	52.4 ± 4.4	1.2 ± 0.5
9.	Fiunary, Savary Glen B	1648.4 ± 252.2	63.8 ± 3.5	165.6 ± 5.2	48.9 ± 2.8	60.5 ± 3.5	1.3 ± 0.5
10.	Fiunary, Savary Glen C	1536.8 ± 182.4	48.4 ± 2.4	146.4 ± 4.4	39.2 ± 3.5	49.2 ± 3.1	0.8 ± 0.2
11.	Fiunary, Savary Glen A_2	1225.4 ± 125.2	56.2 ± 2.6	118.6 ± 6.2	48.2 ± 2.4	35.6 ± 2.5	0.6 ± 0.2
12.	Fiunary, Savary Glen $5B_2$	1597.6 ± 113.5	63.2 ± 3.1	158.7 ± 5.2	53.6 ± 3.5	59.6 ± 3.5	1.0 ± 0.3
13.	Savary Glen A_1	1588.3 ± 222.1	54.7 ± 3.2	120.6 ± 4.4	51.4 ± 2.2	45.2 ± 3.2	1.5 ± 0.6
14.	Savary Glen B_2	1678.2 ± 128.4	62.6 ± 2.5	148.5 ± 2.8	64.2 ± 4.2	64.4 ± 4.2	1.4 ± 0.5
15.	Savary Glen B_3	1670.4 ± 130.2	60.2 ± 2.2	129.5 ± 3.2	55.8 ± 2.8	58.6 ± 2.6	1.3 ± 0.6
16.	Savary Glen C	1590.3 ± 110.2	53.6 ± 1.8	118.2 ± 2.2	46.6 ± 2.4	46.3 ± 4.2	0.8 ± 0.2
	Average	1150.2 ± 182.1	51.2 ± 3.2	140.8 ± 4.9	46.4 ± 3.6	42.6 ± 3.3	0.9 ± 0.3
	Minimum	638.6 ± 42.8	33.2 ± 2.8	80.2 ± 4.1	29.4 ± 3.1	19.5 ± 2.5	0.5 ± 0.2
	Maximum	1678.2 ± 128.4	72.6 ± 4.2	165.9 ± 5.6	64.2 ± 4.2	68.2 ± 4.1	2.1 ± 0.4

TABLE 3.03

The Extraction of Plant-available Silica, Aluminium and Iron by 0.01 M Ca Cl_2 for Pitmedden Forest

No.	Sample	mg/100 g											
		Al			Fe			Si			Si 0.01 M Mg SO_4		
1.	Pitmedden 1A	9.8	±	2.2	0.60	±	0.08	14.5	±	4.2	13.1	±	2.3
2.	Pitmedden 1B	3.7	±	1.5	0.78	±	0.12	11.8	±	2.8	12.1	±	2.5
3.	Pitmedden 2A	11.7	±	2.6	0.58	±	0.06	10.2	±	2.5	11.4	±	2.1
4.	Pitmedden 2B	4.4	±	1.2	0.86	±	0.14	8.5	±	1.4	7.2	±	1.3
5.	Pitmedden 3A	10.6	±	2.5	0.64	±	0.08	18.2	±	4.2	16.8	±	2.6
6.	Pitmedden 3B	10.8	±	2.2	0.90	±	0.12	11.2	±	2.2	13.7	±	2.1
7.	Pitmedden $3B_3$	8.4	±	1.6	0.92	±	0.10	9.5	±	1.4	10.8	±	2.5
8.	Pitmedden 4A	11.8	±	2.6	0.58	±	0.07	16.5	±	2.5	14.6	±	2.2
9.	Pitmedden $4B_2$	10.4	±	2.4	0.76	±	0.14	9.6	±	1.4	13.2	±	2.1
10.	Pitmedden $4B_3$	7.8	±	1.5	0.52	±	0.08	7.5	±	0.9	9.2	±	1.2
11.	Pitmedden 5A	11.4	±	2.2	0.60	±	0.06	13.5	±	2.5	10.6	±	1.5
12.	Pitmedden 5B	9.2	±	1.8	0.76	±	0.10	8.2	±	1.2	9.8	±	1.2
13.	Pitmedden 5Bg	5.4	±	0.8	0.36	±	0.03	5.3	±	0.8	4.2	±	0.6
14.	Pitmedden 6A	12.2	±	2.2	0.45	±	0.05	12.0	±	1.2	14.6	±	1.8
15.	Pitmedden 6B	14.2	±	3.5	0.65	±	0.08	8.3	±	1.1	10.1	±	2.1
16.	Pitmedden 7A	10.6	±	2.2	0.55	±	0.05	11.6	±	2.2	16.0	±	3.0
17.	Pitmedden 7B	10.9	±	1.6	0.75	±	0.09	13.2	±	1.5	15.2	±	2.6
18.	Pitmedden $8A_1$	9.2	±	1.5	0.57	±	0.03	16.2	±	1.6	18.2	±	2.2
19.	Pitmedden 9A	9.8	±	1.4	0.72	±	0.08	14.6	±	2.2	16.8	±	2.6
20.	Pitmedden 9B	10.8	±	1.5	0.93	±	0.10	12.4	±	2.1	14.2	±	1.2
	Average	9.4	±	2.4	0.65	±	0.08	11.2	±	2.5	12.4	±	2.4
	Minimum	3.7	±	1.5	0.36	±	0.03	5.3	±	0.8	4.2	±	0.6
	Maximum	14.2	±	3.5	0.93	±	0.10	18.2	±	4.2	18.2	±	2.2

TABLE 3.04

The Extraction of Plant-available Silica, Aluminium and Iron by 0.01 M Ca Cl_2, for Fiunary and Savary Glen Forests

No.	Sample	mg/100 g air-dry		
		Al	Fe	Si	Si 0.01 M Mg SO_4
1.	Fiunary 2A (top road)	21.5 ± 3.5	0.80 ± 0.06	12.8 ± 2.6	15.6 ± 3.6
2.	Fiunary 2B	29.8 ± 4.4	0.76 ± 0.05	16.5 ± 2.2	17.2 ± 3.2
3.	Fiunary 2C	13.5 ± 2.2	0.52 ± 0.02	10.7 ± 1.7	8.9 ± 1.2
4.	Fiunary $1A_1$	28.8 ± 4.2	0.88 ± 0.08	16.8 ± 3.5	14.8 ± 1.6
5.	Fiunary 2 Aie	40.6 ± 6.2	1.26 ± 0.42	5.2 ± 1.6	4.6 ± 1.4
6.	Fiunary B_2 (micachist)	22.8 ± 4.5	4.54 ± 0.82	14.5 ± 2.5	8.6 ± 4.8
7.	Fiunary, Savary Glen $5A_1$	26.8 ± 4.6	1.26 ± 0.32	18.6 ± 3.5	15.6 ± 2.5
8.	Fiunary 5, Savary Glen A_1 granite	30.2 ± 4.8	1.30 ± 0.28	16.2 ± 2.2	12.4 ± 3.2
9.	Fiunary, Savary Glen B	39.5 ± 3.6	1.80 ± 0.40	12.5 ± 2.1	11.8 ± 2.6
10.	Fiunary, Savary Glen C	20.2 ± 2.6	1.10 ± 0.20	10.8 ± 1.6	9.7 ± 1.2
11.	Fiunary, Savary Glen A_2	28.2 ± 3.2	1.55 ± 0.45	8.5 ± 2.0	6.8 ± 2.2
12.	Fiunary, Savary Glen $5B_2$	35.2 ± 4.1	2.15 ± 0.35	18.2 ± 3.1	15.8 ± 2.2
13.	Savary Glen A_1	23.2 ± 3.4	1.26 ± 0.22	17.5 ± 2.2	17.0 ± 2.0
14.	Savary Glen B_2	30.6 ± 3.5	1.75 ± 0.35	18.4 ± 2.8	13.6 ± 3.6
15.	Savary Glen B_3	28.5 ± 2.2	1.56 ± 0.45	14.5 ± 2.5	11.8 ± 3.2
16.	Savary Glen C	16.8 ± 1.6	0.82 ± 0.28	8.2 ± 1.2	9.1 ± 1.1
	Average	22.8 ± 4.3	2.43 ± 0.28	12.4 ± 2.3	11.8 ± 2.4
	Minimum	13.5 ± 2.2	0.52 ± 0.02	5.2 ± 1.6	4.6 ± 1.4
	Maximum	40.6 ± 6.2	4.54 ± 0.82	18.6 ± 3.5	17.2 ± 3.2

TABLE 3.05

The Extraction of of Aluminium, Iron and Manganese and other metals by NH_4-oxalate

No.	Sample Pitmedden Forest	Tamm's Acid oxalate (mg/100 g)					
		Al	Fe	Mn	Si	Mg	Ni
1.	Pit. 1A	550 ± 38	1360 ± 120	60.6 ± 3.5	88.6 ± 6.5	98.6 ± 4.5	2.1 ± 0.6
2.	Pit. 1B	620 ± 62	1220 ± 160	28.5 ± 2.5	176.2 ± 16.2	87.2 ± 3.6	2.9 ± 0.8
3.	Pit. 2A	600 ± 50	1540 ± 118	49.3 ± 2.8	82.6 ± 8.5	90.2 ± 4.2	2.2 ± 0.7
4.	Pit. 2B	662 ± 55	1320 ± 120	31.6 ± 3.5	128.5 ± 10.2	81.8 ± 4.2	2.8 ± 0.8
5.	Pit. 3A	625 ± 35	1550 ± 145	52.6 ± 3.4	86.6 ± 6.2	78.3 ± 4.8	1.8 ± 0.7
6.	Pit. 3B	780 ± 40	1360 ± 120	40.2 ± 2.2	152.8 ± 8.5	68.2 ± 3.8	2.1 ± 0.9
7.	Pit. $3B_3$	792 ± 28	1380 ± 128	54.6 ± 2.5	146.6 ± 10.5	65.6 ± 4.5	1.6 ± 0.6
8.	Pit. $4A^3$	685 ± 35	1525 ± 155	31.8 ± 2.2	95.8 ± 10.2	79.8 ± 3.6	1.7 ± 0.5
9.	Pit. 4B	810 ± 60	1380 ± 120	24.6 ± 3.2	166.2 ± 14.2	86.9 ± 4.5	2.5 ± 0.9
10.	Pit. $4B_3$	795 ± 35	1266 ± 134	50.5 ± 2.5	169.1 ± 11.3	65.3 ± 3.2	1.8 ± 0.7
11.	Pit. $5A^3$	735 ± 45	1680 ± 120	34.8 ± 3.5	96.1 ± 8.1	75.8 ± 5.4	1.5 ± 0.6
12.	Pit. 5B	840 ± 45	1500 ± 150	26.5 ± 2.2	168.2 ± 12.2	82.6 ± 4.2	2.1 ± 0.8
13.	Pit. 5Bg	650 ± 32	1212 ± 118	58.4 ± 2.2	58.2 ± 8.1	56.8 ± 2.6	0.8 ± 0.2
14.	Pit. 6A	810 ± 30	1775 ± 125	41.6 ± 2.6	92.2 ± 8.2	63.2 ± 2.2	1.2 ± 0.6
15.	Pit. 6B	989 ± 40	1850 ± 150	48.5 ± 3.5	132.6 ± 10.4	50.6 ± 2.5	2.0 ± 0.8
16.	Pit. 7A	665 ± 35	1532 ± 128	32.3 ± 2.2	83.6 ± 7.5	80.4 ± 4.2	1.8 ± 0.6
17.	Pit. 7B	729 ± 41	1390 ± 110	47.6 ± 2.2	152.5 ± 8.5	93.5 ± 2.5	2.5 ± 0.8
18.	Pit. $8A_1$	640 ± 30	1460 ± 120	47.2 ± 1.6	90.8 ± 6.5	82.8 ± 2.8	2.1 ± 0.7
19.	Pit. $9A_1$	760 ± 38	1506 ± 166	46.8 ± 2.5	86.6 ± 6.2	86.1 ± 2.6	2.0 ± 0.6
20.	Pit. 9B	840 ± 40	1665 ± 125	32.7 ± 2.5	162.5 ± 8.5	90.2 ± 4.5	1.5 ± 0.5
	Average	755 ± 45	1395 ± 135	41.2 ± 2.8	122.8 ± 12.2	78.8 ± 3.5	2.0 ± 0.6
	Minimum	550 ± 38	1212 ± 118	24.6 ± 3.2	58.2 ± 8.1	50.6 ± 2.5	0.8 ± 0.2
	Maximum	989 ± 40	1850 ± 150	60.6 ± 3.5	176.2 ± 16.2	98.6 ± 4.5	2.9 ± 0.8

TABLE 3.06

The extraction of aluminium, iron and manganese and other metals by NH_4-oxalate for Fiunary Forest

No.	Sample Fiunary Savary Glen	Tamm's Acid Oxalate (mg/100 g)											
		Al		Fe		Mn		Si		Mg		Ni	
1.	Fiunary 2A (top road)	3370	± 160	3820	± 146	60.6	± 4.5	95.5	± 8.5	73.6	± 7.5	2.1	± 0.8
2.	Fiunary 2B	3595	± 178	3980	± 150	67.5	± 3.5	103.6	± 7.5	62.5	± 4.5	3.0	± 1.2
3.	Fiunary 2C	3200	± 110	3580	± 120	45.6	± 5.2	85.6	± 5.4	56.8	± 4.2	1.0	± 0.4
4.	Fiunary 2Aie	1269	± 131	1890	± 110	40.5	± 2.5	36.6	± 4.2	45.6	± 3.2	0.7	± 0.2
5.	Fiunary B_2 (micashist)	3578	± 122	4035	± 125	68.6	± 2.6	130.2	± 8.1	75.2	± 3.2	2.8	± 1.1
6.	Fiunary $1A_1$	3286	± 124	4060	± 120	62.2	± 4.5	102.3	± 4.2	63.6	± 3.5	2.3	± 1.1
7.	Fiunary, Savary Glen 5Al	3365	± 135	4075	± 125	63.5	± 3.5	96.2	± 4.2	66.8	± 4.2	2.5	± 1.0
8.	Fiunary, Savary Glen $5A_1$ (granite)	3288	± 122	3895	± 115	59.5	± 2.5	92.6	± 4.5	63.6	± 2.6	1.8	± 0.9
9.	Fiunary, Savary Glen B	3576	± 124	4080	± 120	70.6	± 2.6	118.2	± 4.6	75.6	± 4.5	3.1	± 1.2
10.	Fiunary, Savary Glen C	3206	± 114	3085	± 125	42.6	± 3.5	90.6	± 4.5	50.6	± 4.2	1.1	± 0.8
11.	Fiunary, Savary Glen A_2	3185	± 115	3386	± 124	58.6	± 2.6	75.5	± 3.5	56.2	± 3.2	2.2	± 0.8
12.	Fiunary, Savary Glen $5B_2$	3515	± 125	4085	± 142	72.6	± 4.5	116.6	± 10.2	80.2	± 4.2	2.8	± 0.7
13.	Savary Glen A_1	3342	± 138	3960	± 140	61.6	± 3.3	88.6	± 4.5	62.8	± 2.6	2.1	± 0.8
14.	Savary Glen B_2	3595	± 115	4175	± 125	75.3	± 3.2	106.8	± 8.2	74.9	± 4.5	3.3	± 1.2
15.	Savary Glen B_3	3410	± 150	3680	± 120	70.2	± 2.2	105.2	± 4.2	68.2	± 3.2	2.6	± 1.0
16.	Savary Glen C	3280	± 120	3210	± 115	58.6	± 4.5	96.8	± 2.8	60.8	± 2.6	1.8	± 0.8
	Average	3253	± 137	3780	± 120	56.1	± 2.9	96.8	± 4.9	69.8	± 3.8	2.2	± 0.8
	Minimum	1269	± 131	1890	± 110	40.5	± 2.5	36.6	± 4.2	45.6	± 3.2	0.7	± 0.2
	Maximum	3595	± 150	4175	± 125	75.3	± 3.2	118.2	± 4.6	80.2	± 4.2	3.3	± 1.2

TABLE 3.07

The Extraction of Aluminium, Iron and Manganese and other metals by NH_4-oxalate for Fiunary Forest

No.	Sample Experimental Plots	Tamm's Acid Oxalate (mg/100 g)					
		Al	Fe	Mn	Si	Mg	Ni
1	1 BML A	1960 ± 140	2866 ± 134	48.6 ± 3.5	84.2 ± 4.5	89.2 ± 3.2	1.7 ± 0.6
2	1 BML B	2160 ± 136	3155 ± 145	56.7 ± 4.5	93.6 ± 3.5	84.8 ± 4.5	2.1 ± 0.8
3	3 BML A	1845 ± 125	2786 ± 124	64.5 ± 3.2	83.9 ± 3.8	90.6 ± 2.6	1.5 ± 0.7
4	3 BML B	2075 ± 135	3055 ± 145	57.8 ± 3.5	102.6 ± 8.5	85.4 ± 3.2	1.9 ± 0.8
5	4 BML A	1820 ± 130	3080 ± 120	66.2 ± 4.2	85.6 ± 5.2	108.2 ± 4.2	1.6 ± 0.5
6	4 BML B	2280 ± 120	3282 ± 118	68.6 ± 2.6	101.2 ± 3.6	92.6 ± 4.5	2.1 ± 0.9
7	5 BF A	1910 ± 120	3280 ± 126	60.1 ± 3.1	94.8 ± 2.8	80.5 ± 3.5	1.3 ± 0.6
8	5 BF B	2020 ± 110	3682 ± 118	53.6 ± 3.2	108.6 ± 4.5	92.6 ± 3.6	1.8 ± 0.8
9	14 BF A	1929 ± 112	3368 ± 122	52.6 ± 3.5	110.6 ± 5.2	76.8 ± 4.4	1.5 ± 0.7
10.	14 BF B	2165 ± 135	3760 ± 140	50.6 ± 2.6	112.8 ± 4.4	82.7 ± 3.5	2.0 ± 0.8
11.	17 BF A	1860 ± 126	3320 ± 180	48.5 ± 2.5	98.5 ± 4.5	71.8 ± 3.5	2.2 ± 0.8
12.	17 BF B	2066 ± 134	3780 ± 120	55.6 ± 2.4	110.6 ± 5.2	80.7 ± 4.5	2.6 ± 0.9
13.	2 BFP A	1780 ± 120	3450 ± 140	50.8 ± 2.5	91.8 ± 3.6	70.6 ± 3.6	1.6 ± 0.6
14.	2 BFP B	1960 ± 140	3675 ± 120	58.6 ± 2.6	98.6 ± 2.4	75.4 ± 3.2	2.0 ± 0.7
15.	11 BFP A	1818 ± 122	3640 ± 160	56.2 ± 3.1	128.6 ± 6.2	66.8 ± 4.2	1.8 ± 0.6
16.	11 BFP B	1986 ± 124	3810 ± 140	48.6 ± 3.5	120.6 ± 10.4	72.6 ± 4.6	2.2 ± 0.8
17.	19 BFP A	1910 ± 126	3320 ± 180	58.6 ± 2.6	115.6 ± 5.6	67.3 ± 3.5	1.7 ± 0.6
18.	19 BFP B	2080 ± 120	3680 ± 140	60.3 ± 2.8	126.4 ± 4.2	61.8 ± 2.6	2.4 ± 0.8
19.	9 BMP A	2280 ± 124	3320 ± 110	62.6 ± 3.5	96.2 ± 4.2	81.8 ± 4.6	2.1 ± 0.7
20.	9 BMP B	2628 ± 112	3658 ± 122	71.3 ± 3.3	108.6 ± 4.8	73.8 ± 4.5	2.4 ± 0.6
21.	13 BMP A	2483 ± 137	3436 ± 144	62.8 ± 4.5	103.4 ± 7.2	63.7 ± 3.6	1.7 ± 0.5
22.	13 BMP B	2650 ± 140	3628 ± 127	66.7 ± 3.6	112.8 ± 8.4	75.6 ± 4.5	1.8 ± 0.7
23.	20 BMP A	2680 ± 120	3250 ± 140	70.6 ± 3.5	108.6 ± 4.5	66.7 ± 4.5	1.8 ± 0.6
24.	20 BMP B	3010 ± 118	3520 ± 182	73.5 ± 2.6	116.2 ± 4.2	70.3 ± 3.3	2.1 ± 0.7
25.	7 BM A	3275 ± 135	3748 ± 152	72.3 ± 4.2	92.6 ± 4.5	62.6 ± 2.8	2.1 ± 0.5
26.	10 BM B	3486 ± 164	3986 ± 168	75.8 ± 4.5	118.2 ± 6.2	68.3 ± 3.1	2.3 ± 0.7

continued ...

TABLE 3.07

continued

No.	Sample Experimental Plots	Tamm's Acid Oxalate (mg/100 g)											
		Al		Fe		Mn		Si		Mg		Ni	
27.	10 BM A	3295	± 126	3898	± 162	66.2	± 3.2	98.8	± 4.5	60.8	± 2.8	1.9	± 0.6
28.	10 BM B	3526	± 144	4080	± 140	71.2	± 2.8	120.6	± 4.3	71.3	± 3.1	2.5	± 0.8
29.	21 BM A	3186	± 184	3986	± 134	65.3	± 3.3	88.3	± 4.8	62.6	± 3.4	1.9	± 0.7
30.	21 BM B	3560	± 195	4080	± 128	70.6	± 3.5	106.8	± 6.6	68.9	± 4.5	3.0	± 1.2
31.	15 SR BM A	3488	± 168	3995	± 193	65.6	± 3.5	80.7	± 5.2	64.6	± 3.3	1.8	± 0.6
32.	15 SR BM B	3610	± 175	4128	± 142	70.2	± 2.2	93.4	± 4.2	68.7	± 4.5	2.4	± 0.9
33.	1 BM A	3268	± 122	4060	± 145	64.8	± 3.5	90.8	± 3.8	63.8	± 2.5	2.0	± 0.5
34.	1 BM B	3450	± 150	4186	± 128	70.2	± 3.1	96.9	± 4.2	71.2	± 3.1	2.3	± 0.8
35.	2 BML A	2510	± 120	3210	± 140	58.6	± 2.5	93.6	± 3.2	70.8	± 2.7	1.9	± 0.6
36.	3 BMP B	2680	± 140	3689	± 131	62.3	± 3.3	88.7	± 3.4	66.7	± 4.2	1.7	± 0.7
	Average	2521	± 155	3578	± 142	60.2	± 3.2	102.4	± 4.8	74.7	± 3.6	2.2	± 0.8
	Minimum	1780	± 120	2786	± 124	48.5	± 2.5	80.7	± 5.2	60.8	± 2.8	1.3	± 0.6
	Maximum	3610	± 175	4186	± 128	75.8	± 4.5	128.6	± 6.2	108.2	± 4.2	3.0	± 1.2

TABLE 3.08

The Extraction of Aluminium, Iron and Manganese and other metals by NH_4-oxalate for Salen and Loch Eynort Forests

No.	Sample	Tamm's Acid Oxalate (mg/100 g.)					
		Al	Fe	Mn	Si	Mg	Ni
1.	Salen 1 A_1(0 - 3)	2280 ± 233	1855 ± 145	62.6 ± 4.5	26.3 ± 9.3	42.5 ± 2.2	0.8 ± 0.2
2.	Salen 1 A_1(7 - 9)	3250 ± 145	3510 ± 168	58.5 ± 3.7	88.6 ± 6.5	110.3 ± 4.8	3.0 ± 1.2
3.	Salen 1 A_{12}(7 - 10)	3150 ± 231	3710 ± 185	66.7 ± 4.5	94.3 ± 14.3	116.3 ± 4.9	2.5 ± 0.8
4.	Salen 6 A_1(4 - 6)	2850 ± 148	3850 ± 155	63.8 ± 3.6	97.3 ± 3.2	95.7 ± 5.5	2.1 ± 0.6
5.	Salen 6 C_x(C14-21)	1997 ± 137	1240 ± 160	55.7 ± 4.5	124.3 ± 6.2	97.6 ± 3.4	1.0 ± 0.4
6.	Mull, Out Bye A_2	2060 ± 125	2550 ± 140	33.9 ± 3.5	38.2 ± 2.2	61.8 ± 3.2	2.1 ± 0.7
7.	Mull, Out Bye A_4	3320 ± 180	3670 ± 130	63.5 ± 4.2	29.8 ± 3.5	78.6 ± 4.5	2.0 ± 0.8
8.	Mull, Out Bye B_5	3630 ± 170	4085 ± 126	73.2 ± 5.2	96.8 ± 4.4	102.6 ± 4.0	2.5 ± 0.7
9.	Mull, Out Bye B_{10}	3692 ± 158	4056 ± 154	54.8 ± 4.5	97.9 ± 4.5	86.2 ± 4.2	1.8 ± 0.6
10.	Mull, Out Bye C_{23}	3120 ± 164	1969 ± 121	33.6 ± 2.6	86.9 ± 4.6	70.6 ± 3.5	1.2 ± 0.7
11.	Mull, Out Bye C_{24}	2680 ± 146	1798 ± 114	31.4 ± 2.2	93.4 ± 3.2	64.7 ± 2.6	1.9 ± 0.5
12.	Loch Eynort 1 A_1	2470 ± 130	3380 ± 140	62.7 ± 3.6	65.8 ± 5.6	91.2 ± 4.9	1.8 ± 0.6
13.	Loch Eynort2 A (2 - 3)	2685 ± 125	3789 ± 136	65.8 ± 4.5	86.7 ± 4.5	88.6 ± 4.2	1.9 ± 0.8
14.	Loch Eynort B_2 (6 - 8)	2812 ± 184	4080 ± 120	80.9 ± 2.8	98.6 ± 4.4	92.9 ± 3.5	2.2 ± 0.7
15.	Loch Eynort 2A	2780 ± 128	3586 ± 124	64.2 ± 4.1	89.9 ± 4.8	78.7 ± 3.6	2.0 ± 0.5
16.	Loch Eynort 2 B_2 (5 - 9)	3136 ± 144	4025 ± 165	70.3 ± 3.2	110.3 ± 6.2	96.4 ± 4.1	2.8 ± 0.7
17.	Loch Eynort C12-17	2780 ± 126	3667 ± 133	58.6 ± 3.4	128.6 ± 4.5	78.6 ± 3.5	1.2 ± 0.6
18.	Loch Eynort C_{15}	2642 ± 118	3250 ± 150	52.4 ± 2.2	116.3 ± 3.2	70.7 ± 4.4	1.0 ± 0.4
19.	Loch Eynort C_{20}	2580 ± 120	1836 ± 144	38.7 ± 2.5	107.6 ± 3.5	64.6 ± 3.3	0.7 ± 0.2
	Average	2918 ± 154	3165 ± 136	54.8 ± 3.6	82.5 ± 6.4	78.9 ± 3.8	1.8 ± 0.7
	Minimum	1997 ± 137	1836 ± 144	31.4 ± 2.2	26.3 ± 9.3	42.5 ± 2.2	0.7 ± 0.2
	Maximum	3692 ± 158	4085 ± 126	80.9 ± 2.8	128.6 ± 11.5	116.3 ± 4.9	3.0 ± 1.2

TABLE 3.09

The Extraction of Aluminium, Iron, Manganese and Silica by Na-Dithionite for Pitmedden Forest.

No.	Sample	Dithionite (mg/100 g)			
		Al	Fe	Mn	Si
1.	Pitmedden 1 A	610 ± 25	2528 ± 132	58.2 ± 3.1	98.2 ± 10.2
2.	Pitmedden 1 B	530 ± 18	2410 ± 120	31.6 ± 3.5	182.9 ± 12.7
3.	Pitmedden 2 A	708 ± 28	2280 ± 162	48.3 ± 5.2	88.7 ± 8.6
4.	Pitmedden 2 B	460 ± 40	2120 ± 118	28.7 ± 4.5	177.8 ± 13.7
5.	Pitmedden 3 A	710 ± 38	2335 ± 125	51.8 ± 4.6	103.7 ± 13.4
6.	Pitmedden 3 B	800 ± 45	2440 ± 160	39.7 ± 2.5	170.6 ± 10.5
7.	Pitmedden 3 B_3	603 ± 42	2126 ± 124	31.8 ± 2.2	173.8 ± 9.8
8.	Pitmedden 4 A	620 ± 38	2780 ± 120	59.2 ± 4.2	95.9 ± 10.5
9.	Pitmedden 4 B_2	750 ± 45	2895 ± 105	38.7 ± 4.4	180.4 ± 12.6
10.	Pitmedden 4 B_3	580 ± 62	2560 ± 112	35.5 ± 3.2	163.8 ± 14.5
11.	Pitmedden 5 A	630 ± 40	2450 ± 150	52.4 ± 5.6	95.7 ± 12.3
12.	Pitmedden 5 B	440 ± 20	2270 ± 160	40.3 ± 4.8	162.8 ± 10.4
13.	Pitmedden 5 Bg	356 ± 24	1890 ± 118	30.6 ± 3.5	80.3 ± 7.2
14.	Pitmedden 6 A	760 ± 30	2650 ± 140	62.7 ± 4.5	93.4 ± 7.3
15.	Pitmedden 6 B	810 ± 36	2785 ± 135	55.8 ± 5.4	126.8 ± 10.6
16.	Pitmedden 7 A	620 ± 40	2250 ± 125	52.7 ± 3.3	93.8 ± 12.4
17.	Pitmedden 7 B	668 ± 34	2365 ± 134	43.8 ± 3.5	102.6 ± 12.3
18.	Pitmedden 8 A_1	585 ± 35	2145 ± 140	56.4 ± 4.4	86.3 ± 6.2
19.	Pitmedden 9 A_1	600 ± 28	2262 ± 138	48.7 ± 2.6	97.3 ± 8.7
20.	Pitmedden 9 B^1	695 ± 25	2450 ± 120	37.6 ± 3.5	126.6 ± 10.4
	Average	625 ± 42	2390 ± 130	44.5 ± 4.1	124.8 ± 11.2
	Minimum	356 ± 24	1890 ± 118	28.7 ± 4.5	80.3 ± 7.2
	Maximum	810 ± 36	2895 ± 105	62.7 ± 4.5	182.9 ± 12.7

TABLE 3.10

The Extraction of Aluminium, Iron and Manganese by Na-Dithionite, Fiunary Forest.

No.	Sample	mg/100 g								
		Al			Fe			Mn		
1.	1 BML A	1920	±	160	3280	±	182	60.8	±	4.6
2.	1 BML B	2060	±	142	3620	±	166	66.7	±	3.5
3.	3 BML A	1780	±	180	3720	±	130	62.6	±	3.4
4.	3 BML B	1995	±	162	3456	±	110	67.4	±	4.1
5.	4 BML A	1680	±	140	3560	±	165	62.6	±	2.8
6.	4 BML B	2080	±	201	3310	±	135	68.6	±	3.5
7.	5 BF A	1780	±	128	3560	±	142	59.6	±	3.4
8.	5 BF B	1860	±	150	3640	±	172	56.7	±	3.5
9.	14 BF A	1826	±	142	3560	±	214	62.6	±	4.4
10.	14 BF B	1943	±	135	3785	±	210	56.8	±	4.6
11.	17 BF A	1710	±	126	3380	±	110	60.2	±	3.1
12.	17 BF B	1790	±	110	3688	±	122	55.6	±	4.4
13.	2 BFP A	1680	±	126	3283	±	103	62.5	±	3.5
14.	2 BFP B	1820	±	147	3595	±	115	60.3	±	2.2
15.	11 BFP A	1678	±	122	3398	±	152	58.2	±	2.1
16.	11 BFP B	1760	±	145	3580	±	120	61.8	±	3.2
17.	19 BFP A	1710	±	122	3460	±	140	55.7	±	3.3
18.	19 BFP B	1860	±	120	3610	±	120	62.7	±	3.6
19.	9 BMP A	1860	±	140	3360	±	118	65.2	±	4.1
20.	9 BMP B	1986	±	134	3570	±	120	71.8	±	4.5
21.	13 BMP A	1920	±	138	3416	±	124	78.6	±	3.4
22.	13 BMP B	2095	±	125	3680	±	122	80.3	±	5.2
23.	20 BMP A	1986	±	140	3480	±	108	74.2	±	3.5
24.	20 BMP B	2183	±	133	3690	±	110	81.4	±	3.2
25.	7 BM A	2480	±	120	3600	±	120	101.8	±	4.6
26.	7 BM B	2720	±	140	3780	±	110	90.6	±	3.5

continued ...

TABLE 3.10

continued

No.	Sample	mg/100 g								
		Al			Fe			Mn		
27.	10 BM A	2495	±	218	3580	±	120	108.6	±	4.8
28.	10 BM B	2889	±	215	3810	±	140	96.2	±	3.5
29.	21 BM A	2588	±	221	3640	±	160	102.8	±	4.4
30.	21 BM A	2975	±	185	3875	±	120	90.3	±	5.3
	Compartment 302									
31.	1 BM A	2660	±	180	3780	±	130	101.8	±	5.6
32.	1 BM B	2840	±	120	3989	±	141	82.6	±	4.5
33.	2 BML A	1950	±	150	3460	±	120	68.6	±	4.2
34.	2 BML B	2180	±	118	3600	±	98	72.5	±	3.4
35.	3 BMP A	2088	±	122	3695	±	105	75.2	±	2.8
36.	3 BMP B	2400	±	110	3810	±	95	80.3	±	4.1
	Average	2110	±	144	3492	±	152	68.2	±	4.2
	Minimum	1680	±	126	3280	±	182	55.6	±	4.4
	Maximum	2975	±	185	3989	±	141	108.6	±	4.8

TABLE 3.11

Soil Characteristics for Pitmedden Forest

No.	Sample	pH	% Carbon	% Nitrogen	The measurement of EC (mg/100 g)					
					Al	Mn	Mg	Ca	K	Na
1.	Pitmedden 1A	5.9	3.1	1.4	23.5	5.7	30.7	335	20.6	19.5
2.	Pitmedden 1B	6.1	0.7	0.4	12.0	2.4	26.3	378	16.8	22.7
3.	Pitmedden 2A	5.8	3.1	1.3	20.4	1.7	24.5	375	19.6	18.0
4.	Pitmedden 2B	6.2	0.5	0.3	4.8	0.3	37.6	490	21.8	20.5
5.	Pitmedden 3A	5.9	2.1	1.2	8.2	0.9	38.4	350	16.2	21.0
6.	Pitmedden 3B	6.1	1.6	0.6	3.8	Nil	27.5	385	18.3	20.2
7.	Pitmedden $3B_3$	6.3	0.5	0.4	3.5	Nil	44.2	390	22.0	19.2
8.	Pitmedden $4A^3$	6.0	3.4	1.4	10.5	0.5	17.8	386	14.8	24.2
9.	Pitmedden $4B_2$	6.1	1.8	0.7	6.8	0.2	27.2	456	16.3	25.1
10.	Pitmedden $4B_3$	6.4	0.5	0.3	5.6	Nil	35.8	547	18.1	16.0
11.	Pitmedden $5A^3$	5.9	3.5	1.3	10.1	0.5	18.5	262	22.1	14.5
12.	Pitmedden 5B	6.0	2.2	0.7	4.1	0.6	21.3	290	14.3	21.3
13.	Pitmedden 5Bg	6.2	1.4	0.6	4.0	1.1	17.8	282	11.0	21.5
14.	Pitmedden 6A	5.6	3.0	0.9	22.5	0.7	18.3	245	18.5	15.5
15.	Pitmedden 6B	5.9	1.9	0.6	9.8	0.3	16.1	145	11.8	9.7
16.	Pitmedden 7A	6.1	3.9	1.4	12.8	0.8	28.2	360	20.3	15.2
17.	Pitmedden 7B	6.3	1.8	0.6	6.6	0.5	24.4	398	18.6	16.4
18.	Pitmedden $8A_1$	6.0	3.8	1.4	11.5	1.6	31.2	382	20.2	16.7
19.	Pitmedden $9A^1$	6.0	4.8	1.5	10.8	1.8	28.5	375	22.3	14.3
20.	Pitmedden $9B^1$	6.2	2.3	0.7	5.3	0.8	33.5	450	13.8	15.8
	Average	6.0	2.3	0.9	10.2	1.0	26.0	388	18.5	17.8
	Minimum	5.6	0.5	0.3	3.5	Nil	16.1	145	11.0	9.7
	Maximum	6.4	4.9	1.5	23.5	5.7	44.2	547	22.3	25.1

TABLE 3.12

Soil Characteristics for Fiunary and Savary Glen Forests

No.	Sample	pH	% Carbon	% Nitrogen	The measurement of EC (mg/100 g.)					
					Al	Mn	Mg	Ca	K	Na
1.	Fiunary $2A_4$	3.8	32.1	3.0	150.6	4.2	12.8	60.0	9.5	9.2
2.	Fiunary $2B_2$	4.4	6.6	1.4	98.5	7.1	16.3	93.8	14.1	9.5
3.	Fiunary $2C^2$	4.6	3.8	0.9	37.5	3.9	5.2	141.5	12.5	6.1
4.	Fiunary $1A_1$	4.2	15.6	2.2	76.2	6.7	15.8	168.8	16.2	9.7
5.	Fiunary $2A^1$	4.2	15.2	2.0	78.1	5.1	15.8	145.3	17.3	9.5
6.	Fiunary B_2 (micashist)	4.5	31.2	3.3	88.2	5.5	16.2	29.8	6.5	9.8
7.	Fiunary, Savary Glen $5A_1$	4.4	24.2	2.7	128.2	2.2	28.0	141.5	16.5	11.5
8.	Fiunary, Savary Glen $5A^1$ (granite)	4.3	23.8	2.5	131.6	2.8	20.3	133.8	17.0	12.6
9.	Fiunary, Savary Glen B	4.7	19.5	1.8	142.2	4.1	18.2	128.2	13.5	12.0
10.	Fiunary, Savary Glen C	5.1	3.9	0.8	28.5	12.5	22.1	190.2	13.0	20.2
11.	Fiunary, Savary Glen A 2	4.4	30.8	3.0	108.5	14.2	17.5	149.5	20.2	19.5
12.	Fiunary, Savary Glen $5B_2$	4.6	8.3	1.2	88.5	6.1	18.8	135.6	20.3	11.5
13.	Savary Glen A_1	4.2	12.5	1.4	105.5	15.0	16.2	123.4	17.0	16.2
14.	Savary Glen B_2	4.6	8.8	1.0	125.1	9.7	18.6	168.5	21.3	19.3
15.	Savary Glen B_3	4.9	7.0	0.7	72.5	3.8	20.8	180.6	17.8	13.2
16.	Savary Glen C^3	5.2	4.2	0.5	28.5	1.8	25.6	87.5	13.5	11.0
	Average	4.5	14.6	1.7	92.9	6.5	16.6	121.8	15.6	11.4
	Minimum	3.8	4.2	0.5	28.5	1.8	5.2	29.8	6.5	6.1
	Maximum	5.2	32.1	3.3	150.6	15.0	28.0	190.2	21.3	20.2

TABLE 3.13

Soil Characteristics for Kilmarnock Association

No.	Sample Kilmarnock Association Hallborn's Farms	pH	% Carbon	% Nitrogen	0.5 M CH_3 COOH (mg/100 g)	
					K	Al
1.	Arran	6.1	6.6	1.7	120.6	170.5
2.	Barley Field A	5.7	5.0	1.3	110.5	180.2
3.	Barley Field B	6.0	3.8	0.8	93.6	190.6
4.	Byre	6.0	7.3	2.0	108.9	182.7
5.	Craig	5.9	7.3	1.8	107.2	197.9
6.	Cramel Bank	6.2	8.4	2.0	118.7	170.6
7.	Frost	6.0	8.0	1.3	90.7	182.8
8.	Home Field	5.6	8.0	1.4	95.4	235.7
9.	Haw Thora	5.5	7.5	1.6	76.8	190.9
10.	Holm	6.0	6.4	1.5	98.3	160.4
11.	Mid-Arran	6.0	4.6	1.4	114.6	168.6
12.	Meadow	5.9	7.2	1.5	128.5	166.3
13.	Rose	5.7	5.6	1.2	80.3	179.7
14.	Spinery	6.0	7.7	1.5	94.6	157.9
15.	White Heidi	5.7	7.4	1.3	78.6	186.5
	Average	5.9	6.7	1.5	102.9	182.8
	Minimum	5.5	3.8	0.8	76.8	159.9
	Maximum	6.2	8.4	2.0	120.6	235.7

TABLE 3.14

Mineral Determination for Salen and Loch Eynort Forests (Mull, Skye)

No.	Sample	pH	% Carbon	% N	Total (mg/100 g ± S.D.)					
					Si	Al	Fe	Ca	Mg	Ni
1.	Salen 1 A_1 (0-3)	4.1	25.7	2.9	15680 ± 1286	4562 ± 442	4280 ± 320	295.6 ± 12.5	270.2 ± 16.5	8.2 ± 1.6
2.	Salen 1 A_1^1 (7-9)	4.4	17.6	1.7	18895 ± 1212	8125 ± 354	6437 ± 174	352.5 ± 10.4	256.8 ± 14.4	10.2 ± 2.5
3.	Salen 6 A_{12}^1 (7-10)	4.6	14.4	1.5	18260 ± 1320	7530 ± 480	6675 ± 245	265.8 ± 15.2	259.7 ± 11.6	9.5 ± 1.6
4.	Salen 6 A_1^{12} (4-6)	4.3	16.5	1.6	19886 ± 989	6124 ± 265	4887 ± 126	286.5 ± 12.4	220.5 ± 10.1	10.2 ± 2.2
5.	Salen 6 C_x^1 (14-21)	4.9	4.2	0.2	21200 ± 1210	8826 ± 144	5025 ± 235	354.8 ± 10.4	336.5 ± 15.2	10.3 ± 2.5
6.	Mull, Out Bye A_2	4.1	30.8	2.9	12880 ± 1206	5312 ± 442	4920 ± 260	415.6 ± 12.5	290.5 ± 10.4	8.5 ± 1.8
7.	Mull, Out Bye A_4	4.8	16.8	1.5	16220 ± 1280	7562 ± 738	4610 ± 240	298.6 ± 10.5	260.8 ± 12.2	11.2 ± 2.4
8.	Mull B_2	4.8	14.5	1.3	18210 ± 1250	8980 ± 480	5300 ± 155	350.8 ± 12.2	310.7 ± 10.2	9.6 ± 2.6
9.	Mull B_5	4.9	12.4	1.1	18208 ± 1268	8897 ± 283	4875 ± 215	363.8 ± 13.2	285.4 ± 14.2	9.5 ± 2.2
10.	Mull B_{10}	5.1	10.0	0.9	18100 ± 1120	10810 ± 265	4812 ± 142	382.6 ± 12.5	246.8 ± 6.6	10.7 ± 2.7
11.	Mull C_{23}	5.5	4.8	0.5	19887 ± 1115	9268 ± 362	4820 ± 160	344.8 ± 16.7	310.6 ± 10.5	10.8 ± 2.6
12.	Mull C_{24}	5.7	4.0	0.4	20805 ± 1215	9010 ± 250	4730 ± 110	375.6 ± 15.2	289.6 ± 11.5	9.7 ± 1.7
13.	Loch Eynort 1 A_1	4.3	23.2	2.6	13880 ± 1210	6806 ± 314	5750 ± 250	328.2 ± 12.4	272.5 ± 12.5	10.8 ± 2.6
14.	Loch Eynort 2 A_1 (2 - 3)	4.4	27.5	2.8	12210 ± 1180	5022 ± 220	4980 ± 210	310.5 ± 12.4	283.6 ± 9.8	9.9 ± 1.4
15.	Loch Eynort B_2 (6 - 8)	4.6	19.2	2.0	18908 ± 1118	9405 ± 396	5625 ± 175	336.3 ± 10.2	288.5 ± 12.5	10.3 ± 2.2
16.	Loch Eynort 2 A	4.3	25.2	2.4	10288 ± 1180	5080 ± 240	4350 ± 200	340.2 ± 14.2	318.6 ± 12.2	8.4 ± 1.8
17.	Loch Eynort 2 B_2 (5 - 9)	4.6	18.6	1.5	18285 ± 165	9815 ± 375	5250 ± 150	310.8 ± 15.5	282.8 ± 8.8	9.5 ± 1.5
18.	Loch Eynort C_{12-17}	5.2	14.5	1.2	19880 ± 170	9188 ± 262	5500 ± 180	306.2 ± 10.2	256.7 ± 10.5	10.0 ± 1.8
19.	Loch Eynort C_{15}	5.5	12.9	1.2	19895 ± 155	8202 ± 350	5130 ± 190	280.6 ± 10.6	210.4 ± 10.4	9.6 ± 1.7
20.	Loch Eynort C_{20}	5.8	10.1	0.8	19655 ± 115	7525 ± 250	4670 ± 166	265.7 ± 15.2	202.6 ± 8.2	8.8 ± 1.8
	Average	4.8	16.4	1.5	18332 ± 1995	7939 ± 353	5150 ± 260	326.8 ± 13.7	288.4 ± 6.6	9.8 ± 2.0
	Minimum	4.1	4.0	0.5	10288 ± 1180	4562 ± 442	4280 ± 320	265.7 ± 15.2	202.6 ± 8.2	8.2 ± 1.6
	Maximum	5.8	30.8	2.9	21200 ± 1210	10810 ± 265	6675 ± 245	415.6 ± 12.5	336.5 ± 15.2	11.2 ± 2.4

TABLE 3.15

Silica-Sesquioxide Ratios : Salen and Loch Eynort Forests

No.	Sample	Percentages			Ratios			
		SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3	SiO_2/Fe_2O_3	$SiO_2/Al_2O_3+Fe_2O_3$	Al_2O_3/Fe_2O_3
1.	Salen 1 A_1 (0 - 3)	33.5	24.9	13.0	1.3	2.6	0.9	1.9
2.	Salen 1 A_1 (7 - 9)	40.5	30.6	16.8	1.3	2.4	0.9	1.7
3.	Salen 6 A_{12} (7 - 10)	39.2	28.3	18.0	1.4	2.2	0.8	1.5
4.	Salen 6 A_1 (4 - 6)	42.6	23.0	13.5	1.9	3.2	1.1	1.7
5.	Salen 6 C_x (14 - 21)	45.6	37.4	14.0	1.2	3.3	0.9	2.6
6.	Mull, Out Bye A_2	27.6	20.0	13.2	1.4	2.1	0.8	1.5
7.	Mull, Out Bye A_4	34.7	28.7	1.26	1.2	2.8	0.7	2.2
8.	Mull, Out Bye B_2	34.5	32.5	14.1	1.1	2.5	0.8	2.2
9.	Mull, Out Bye B_5	39.0	38.1	14.0	1.0	2.8	0.8	2.7
10.	Mull, Out Bye B_{10}	38.8	39.5	13.8	1.0	2.8	0.7	2.8
11.	Mull, Out Bye C_{23}	42.6	40.8	14.0	1.0	3.1	0.6	2.9
12.	Mull, Out Bye C_{24}	44.6	40.8	12.2	1.1	3.7	0.9	2.9
13.	Loch Eynort A_1	29.8	25.7	15.0	1.2	2.0	0.8	1.8
14.	Loch Eynort 2 A (2 - 3)	26.1	18.8	14.2	1.4	1.8	0.8	1.3
15.	Loch Eynort B_2 (6 - 8)	40.5	35.5	16.0	1.1	2.6	0.9	2.2
16.	Loch Eynort 2A	22.1	19.3	12.0	1.1	1.9	0.8	1.6
17.	Loch Eynort 2 B_2 (5 - 9)	39.2	34.8	14.2	1.1	2.6	0.7	2.1
18.	Loch Eynort C (12 - 17)	42.6	37.0	14.0	1.2	2.7	0.8	2.3
19.	Loch Eynort C_{15}	42.6	31.5	13.4	1.4	2.9	0.9	2.4
20.	Loch Eynort 2 C_{20}	42.3	28.3	12.5	1.5	3.3	0.9	2.1

TABLE 3.16

Mineral Determination for Pitmedden Forest

No.	Sample	Total (mg/100 g ± S.D.)						
		Si	Al	Fe	Ca	Mg	Mn	Ni
1.	Pit. 1A	18805 ± 1215	2010 ± 230	5825 ± 175	396.7 ± 12.5	288.6 ± 12.2	118.7 ± 10.6	9.8 ± 1.2
2.	Pit. 1B	22854 ± 1250	2362 ± 168	6750 ± 135	428.6 ± 10.3	298.9 ± 10.1	136.8 ± 10.2	11.5 ± 1.3
3.	Pit. 2A	18680 ± 1210	2252 ± 182	5150 ± 140	378.5 ± 14.5	271.2 ± 11.2	106.8 ± 14.2	10.2 ± 1.1
4.	Pit. 2B	23158 ± 1182	2565 ± 175	6250 ± 115	425.3 ± 15.2	295.6 ± 10.4	140.2 ± 8.4	12.5 ± 1.4
5.	Pit. 3A	19525 ± 1250	2095 ± 135	5370 ± 140	379.6 ± 12.5	285.5 ± 15.2	116.4 ± 12.2	10.6 ± 1.5
6.	Pit. 3B	23120 ± 1180	2268 ± 122	5640 ± 160	428.6 ± 12.4	310.6 ± 10.2	132.3 ± 8.3	11.8 ± 1.4
7.	Pit. $3B_3$	24228 ± 1152	2286 ± 120	5287 ± 84	452.5 ± 10.2	290.5 ± 10.4	140.8 ± 12.4	10.3 ± 1.1
8.	Pit. $4A^3$	19505 ± 1155	1955 ± 75	5150 ± 110	392.4 ± 12.4	328.6 ± 12.4	118.2 ± 10.4	8.9 ± 1.1
9.	Pit. $4B_2$	23180 ± 1120	2195 ± 115	6075 ± 125	426.2 ± 14.1	296.3 ± 10.1	141.6 ± 21.2	10.6 ± 2.1
10.	Pit. $4B^2_3$	24350 ± 1150	2280 ± 110	5870 ± 130	450.6 ± 15.5	340.2 ± 10.6	148.7 ± 18.2	11.8 ± 1.2
11.	Pit. $5A^3$	18820 ± 1080	1965 ± 125	4410 ± 110	360.8 ± 16.4	290.8 ± 12.6	130.8 ± 8.8	9.6 ± 1.1
12.	Pit. 5B	22850 ± 1120	2210 ± 120	5120 ± 125	402.8 ± 8.6	320.7 ± 10.5	143.4 ± 7.2	12.3 ± 1.2
13.	Pit. 5Bg	23100 ± 1150	2100 ± 110	4815 ± 145	406.2 ± 14.0	300.2 ± 10.6	118.6 ± 8.5	8.6 ± 0.8
14.	Pit. 6A	17285 ± 1166	2175 ± 195	4670 ± 110	382.7 ± 18.2	275.5 ± 15.2	132.6 ± 10.4	9.2 ± 1.1
15.	Pit. 6B	21855 ± 1125	2450 ± 250	4895 ± 165	396.8 ± 12.4	290.6 ± 10.4	145.3 ± 15.2	10.8 ± 1.2
16.	Pit. $7A_1$	18950 ± 1200	2080 ± 170	4515 ± 125	382.6 ± 18.2	286.8 ± 14.6	130.7 ± 10.5	8.8 ± 1.2
17.	Pit. $7B^1$	22280 ± 1150	2410 ± 120	5710 ± 110	418.2 ± 12.1	320.2 ± 10.2	141.6 ± 9.5	11.4 ± 1.2
18.	Pit. $8A_1$	18660 ± 1140	2120 ± 140	4620 ± 140	355.6 ± 15.4	290.8 ± 12.5	124.8 ± 16.2	9.6 ± 1.4
19.	Pit. $9A^1$	18510 ± 1020	2128 ± 146	4410 ± 130	348.6 ± 10.2	275.6 ± 8.4	133.6 ± 7.5	9.8 ± 1.2
20.	Pit. $9B^1$	23890 ± 1120	2385 ± 135	5915 ± 125	408.6 ± 12.4	310.5 ± 10.5	150.5 ± 12.2	11.2 ± 1.2
	Average	21180 ± 1140	2224 ± 152	5316 ± 138	399.8 ± 11.6	325.7 ± 11.4	138.4 ± 12.5	10.6 ± 1.2
	Minimum	17285 ± 1166	1955 ± 75	4410 ± 110	348.6 ± 10.2	271.2 ± 11.2	106.8 ± 14.2	8.6 ± 0.8
	Maximum	24228 ± 1152	2565 ± 175	6750 ± 135	452.5 ± 10.2	340.2 ± 10.6	150.2 ± 12.2	12.5 ± 1.4

TABLE 3.17

Silica-Sesquioxides Ratios for Pitmedden

No.	Sample	Percentages			Ratios			
		SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3	SiO_2/Fe_2O_3	SiO_2/R_2O_3	Al_2O_3/Fe_2O_3
1.	Pitmedden 1A	40.3	7.9	15.2	5.1	2.7	1.8	0.5
2.	Pitmedden 1B	49.0	9.4	17.8	5.2	2.8	1.9	0.6
3.	Pitmedden 2A	40.0	8.7	15.0	4.6	2.8	1.8	0.6
4.	Pitmedden 2B	49.7	9.8	17.0	5.0	2.9	1.9	0.6
5.	Pitmedden 3A	41.7	7.9	14.7	5.3	2.7	1.9	0.5
6.	Pitmedden 3B	49.5	8.7	16.0	5.7	3.2	2.0	0.7
7.	Pitmedden $3B_3$	51.6	8.3	14.6	6.2	3.3	2.3	0.6
8.	Pitmedden 4A	41.7	7.6	14.4	5.5	2.9	2.0	0.5
9.	Pitmedden $4B_2$	49.6	8.3	15.7	6.0	3.0	2.1	0.5
10.	Pitmedden $4B_3$	52.0	8.7	15.8	5.9	3.1	2.0	0.5
11.	Pitmedden 5A	40.3	7.6	12.3	5.3	3.3	2.4	0.6
12.	Pitmedden 5B	49.0	8.3	12.7	5.9	3.5	1.9	0.6
13.	Pitmedden 5Bg	49.5	7.9	14.0	6.3	4.0	2.2	0.6
14.	Pitmedden 6A	37.1	8.3	12.4	4.5	2.7	1.9	0.6
15.	Pitmedden 6B	46.7	10.2	15.4	4.6	3.8	1.9	0.7
16.	Pitmedden $7A_1$	40.7	7.8	12.6	5.1	3.8	2.1	0.8
17.	Pitmedden 7B	47.8	9.1	15.2	5.2	2.9	2.0	0.6
18.	Pitmedden $8A_1$	40.0	7.9	13.1	5.0	3.1	2.0	0.6
19.	Pitmedden $9A_1$	39.6	8.3	12.6	7.8	3.3	1.9	0.6
20.	Pitmedden $9B_1$	51.2	9.1	16.0	5.6	3.0	2.1	0.8

TABLE 3.18

Mineral Determination for Fiunary Forest

No.	Sample Experimental Plots	% Carbon	(mg/100 g ± S.D.)						
			Si	Al	Fe	Ca	Mg	Mn	Ni
1.	1 BML A	15.2	18860 ± 1120	8675 ± 225	3975 ± 175	898.6 ± 14.6	290.3 ± 10.2	136.2 ± 9.1	9.5 ± 0.9
2.	1 BML B	9.6	20780 ± 1022	9955 ± 175	4088 ± 152	786.5 ± 14.2	310.8 ± 8.6	148.6 ± 8.5	11.2 ± 1.1
3.	3 BML A	18.4	17988 ± 1122	8786 ± 214	3788 ± 122	826.1 ± 16.2	283.6 ± 12.2	131.8 ± 10.5	10.1 ± 1.0
4.	3 BML B	11.7	20210 ± 820	9267 ± 233	3978 ± 132	732.5 ± 12.5	318.5 ± 10.5	143.6 ± 11.4	11.8 ± 1.5
5.	4 BML A	15.8	18775 ± 1125	8799 ± 210	3780 ± 180	891.4 ± 11.3	275.4 ± 15.2	126.8 ± 10.5	9.3 ± 1.1
6.	4 BML B	9.5	19896 ± 1204	9885 ± 125	3898 ± 202	775.6 ± 8.6	298.5 ± 12.5	140.7 ± 9.5	10.8 ± 1.2
7.	5 BF A	16.3	16878 ± 1032	8780 ± 220	3786 ± 214	310.7 ± 10.6	286.5 ± 14.5	135.8 ± 10.4	9.8 ± 1.1
8.	5 BF B	10.1	19785 ± 715	9776 ± 175	4096 ± 154	360.4 ± 10.4	305.8 ± 12.4	142.6 ± 18.5	11.3 ± 1.4
9.	14 BF A	15.5	18266 ± 844	8810 ± 210	3995 ± 155	280.5 ± 12.2	288.7 ± 12.6	130.9 ± 10.4	10.1 ± 0.9
10.	14 BF B	11.2	19686 ± 1120	10125 ± 350	4210 ± 140	322.6 ± 10.2	310.6 ± 10.5	141.8 ± 9.4	11.8 ± 1.4
11.	17 BF A	14.8	18855 ± 745	8950 ± 150	3895 ± 135	285.6 ± 10.5	277.8 ± 13.8	126.7 ± 8.5	9.2 ± 0.8
12.	17 BF B	9.7	20210 ± 1190	10180 ± 220	4180 ± 120	296.4 ± 8.8	306.9 ± 10.9	144.2 ± 10.6	10.9 ± 1.5
13.	2 BFP A	16.3	17650 ± 1150	7885 ± 125	3820 ± 140	286.5 ± 10.7	262.7 ± 12.6	138.6 ± 12.4	11.3 ± 1.3
14.	2 BFP B	11.3	19866 ± 1034	9698 ± 202	4088 ± 120	318.6 ± 16.4	290.5 ± 15.5	146.5 ± 8.5	10.6 ± 1.2
15.	11 BFP A	14.5	18210 ± 1120	8210 ± 140	3868 ± 144	296.7 ± 14.2	280.7 ± 10.7	139.6 ± 10.4	10.1 ± 1.4
16.	11 BFP B	10.2	20850 ± 1220	10212 ± 242	4410 ± 120	340.6 ± 10.5	302.8 ± 10.4	145.7 ± 10.3	11.8 ± 1.2
17.	19 BFP A	16.8	18100 ± 1100	8186 ± 164	3798 ± 132	282.3 ± 12.1	262.7 ± 10.5	132.8 ± 8.8	9.6 ± 1.4
18.	19 BFP B	10.9	20110 ± 1080	10082 ± 182	4280 ± 140	354.6 ± 14.5	310.6 ± 10.4	147.6 ± 13.5	11.8 ± 1.6
19.	9 BMP A	17.0	17100 ± 1100	9268 ± 220	3686 ± 124	265.6 ± 15.4	282.5 ± 12.5	135.8 ± 10.4	10.4 ± 1.2
20.	9 BMP B	12.2	19210 ± 1120	9878 ± 182	3885 ± 155	318.7 ± 14.5	305.7 ± 15.5	146.7 ± 12.2	11.7 ± 1.4
21.	13 BMP A	17.1	17280 ± 1120	8782 ± 266	3787 ± 183	289.6 ± 10.4	230.2 ± 11.2	142.8 ± 8.8	10.2 ± 1.1
22.	13 BMP B	11.8	19680 ± 1080	9960 ± 310	3910 ± 170	372.6 ± 14.2	283.6 ± 17.4	150.2 ± 8.2	11.9 ± 1.2
23.	20 BMP A	16.2	18100 ± 1100	8820 ± 260	3720 ± 180	296.8 ± 16.4	252.7 ± 12.4	136.6 ± 10.2	10.2 ± 1.1
24.	20 BMP B	9.6	19980 ± 1020	9950 ± 320	3950 ± 210	369.8 ± 12.6	310.8 ± 10.5	143.8 ± 8.8	12.9 ± 1.5

continued . . .

TABLE 3.18

continued

No.	Sample Experimental Plots	% Carbon	(mg/100 g ± S.D.)						
			Si	Al	Fe	Ca	Mg	Mn	Ni
25.	7 BM A	17.4	18095 ± 790	9080 ± 290	3868 ± 172	276.4 ± 14.2	244.5 ± 8.5	140.9 ± 8.5	10.1 ± 1.0
26.	7 BM B	11.5	19788 ± 1222	10872 ± 480	3918 ± 182	295.8 ± 8.7	283.8 ± 6.6	146.8 ± 7.2	11.8 ± 1.2
27.	10 BM A	18.5	17855 ± 1025	9282 ± 322	3886 ± 214	288.7 ± 12.5	258.2 ± 10.2	132.7 ± 7.4	9.8 ± 1.2
28.	10 BM B	12.2	19288 ± 1210	10168 ± 254	4089 ± 121	370.8 ± 10.6	288.6 ± 12.4	141.7 ± 9.5	11.3 ± 1.1
29.	21 BM A	17.5	18860 ± 2410	8860 ± 240	3810 ± 190	306.1 ± 14.1	265.8 ± 10.6	150.6 ± 8.5	9.2 ± 0.8
30.	21 BM B	10.1	19850 ± 950	9728 ± 252	4168 ± 172	320.3 ± 10.3	290.9 ± 9.6	154.8 ± 6.6	10.8 ± 1.2
31.	15 SR BM	16.9	18228 ± 1132	8695 ± 205	4080 ± 180	266.4 ± 14.2	230.8 ± 10.8	141.7 ± 11.6	11.7 ± 1.5
32.	15 SR BM	12.2	19280 ± 1120	9682 ± 232	4266 ± 134	302.8 ± 12.5	268.7 ± 12.6	152.5 ± 8.5	12.9 ± 1.6
33.	1 BM AC_{302}	17.1	17100 ± 1100	9720 ± 220	4186 ± 114	286.5 ± 10.5	230.8 ± 8.8	136.2 ± 10.2	10.1 ± 0.9
34.	2 BML AC_{302}	16.3	19200 ± 1010	9096 ± 194	4281 ± 121	855.8 ± 15.2	280.2 ± 12.1	141.8 ± 9.6	10.6 ± 1.2
35.	3 BMP AC_{302}	15.3	17860 ± 1040	8860 ± 240	3989 ± 123	310.7 ± 10.6	265.6 ± 10.2	136.2 ± 8.2	9.6 ± 0.8
36.	Fiunary and Savary Glen A	17.8	16980 ± 1120	9120 ± 220	3867 ± 133	265.8 ± 15.2	189.8 ± 11.8	132.8 ± 7.6	9.8 ± 1.1
37.	Fiunary and Savary Glen B	13.2	19281 ± 1021	11655 ± 550	4182 ± 112	279.8 ± 11.2	228.4 ± 12.4	146.3 ± 12.0	10.9 ± 1.3
	Average		18822 ± 1150	9409 ± 260	3969 ± 154	398.6 ± 12.8	278.5 ± 10.5	138.4 ± 10.2	10.7 ± 1.2
	Minimum		16980 ± 1120	8675 ± 225	3686 ± 124	265.8 ± 15.2	189.8 ± 11.8	126.7 ± 10.5	9.2 ± 0.8
	Maximum		20850 ± 1220	11655 ± 550	4410 ± 120	898.6 ± 14.6	318.5 ± 10.5	154.8 ± 6.6	12.9 ± 1.6

TABLE 3.19

Silica-Sesquioxides Ratios : Fiunary Forest, Experimental Plots

No.	Sample			Percentages			Ratios			
				SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3	SiO_2/Fe_2O_3	SiO_2/R_2O_3	Al_2O_3/Fe_2O_3
1.	1	BML	A	40.5	32.8	10.6	1.3	3.9	1.2	3.1
2.	1	BML	B	44.6	37.4	11.4	1.2	4.0	1.2	3.2
3.	3	BML	A	38.5	33.2	10.2	1.2	3.8	1.1	3.2
4.	3	BML	B	43.3	35.1	11.2	1.3	3.9	1.2	3.4
5.	4	BML	A	40.2	33.2	10.6	1.3	3.8	0.9	3.2
6.	4	BML	B	42.6	37.4	11.3	1.1	3.8	0.9	3.4
7.	5	BF	A	36.2	35.1	10.4	1.0	3.5	0.8	3.4
8.	5	BF	B	42.4	37.0	11.2	1.1	3.8	0.9	3.3
9.	14	BF	A	39.2	33.2	11.8	1.2	3.3	0.9	3.3
10.	14	BF	B	42.2	38.1	12.4	1.1	3.4	0.8	3.4
11.	17	BF	A	39.9	33.6	11.2	1.2	3.6	0.9	3.0
12.	17	BF	B	43.4	38.5	12.1	1.1	3.6	0.9	3.2
13.	2	BFP	A	37.9	29.8	10.9	1.3	3.5	0.9	2.7
14.	2	BFP	B	42.6	36.6	11.8	1.2	3.6	1.1	3.1
15.	11	BFP	A	39.0	30.9	11.3	1.3	3.5	0.9	2.7
16.	11	BFP	B	44.6	38.5	12.7	1.2	3.5	0.9	3.0
17.	19	BFP	A	38.8	30.9	10.9	1.3	3.6	0.9	2.9
18.	19	BFP	B	43.1	37.8	12.1	1.1	3.6	0.9	3.1
19.	9	BMP	A	36.6	35.1	10.1	1.1	3.6	0.8	3.5
20.	9	BMP	B	41.1	37.4	11.3	1.1	3.6	0.9	3.3
21.	13	BMP	A	37.1	33.2	10.9	1.1	3.4	0.8	3.1
22.	13	BMP	B	42.0	37.6	11.3	1.1	3.7	0.9	3.3
23.	20	BMP	A	38.8	33.2	10.4	1.2	3.7	0.9	3.2
24.	20	BMP	B	42.7	37.6	11.4	1.1	3.7	1.1	3.3
25.	7	BM	A	38.7	34.3	11.2	1.1	3.5	0.9	3.1

continued ...

TABLE 3.19

continued

No.	Sample	Percentages			Ratios			
		SiO_2	Al_2O_3	Fe_2O_3	SiO_2/Al_2O_3	SiO_2/Fe_2O_3	SiO_2/R_2O_3	Al_2O_3/Fe_2O_3
26.	7 BM B	42.4	41.1	11.3	1.0	3.8	0.8	3.6
27.	10 BM A	38.3	35.1	10.7	1.1	3.6	0.9	3.3
28.	10 BM B	41.3	38.5	11.3	1.1	3.7	0.8	3.4
29.	21 BM A	38.5	33.6	10.6	1.2	3.6	0.9	3.2
30.	21 BM B	42.5	36.6	11.4	1.2	3.7	0.9	3.3
31.	15 SR BM A	39.0	32.9	11.9	1.2	3.3	0.9	2.8
32.	15 SR BM B	41.3	36.6	12.4	1.1	3.3	1.1	3.0
33.	1 BM A C302	36.6	36.6	12.2	1.0	3.0	0.6	3.0
34.	2 BML A C302	41.1	34.4	12.5	1.2	3.3	0.9	2.8
35.	3 BMP A C302	38.3	33.6	11.5	1.1	3.3	0.9	2.9
36.	Fiunary, Savary Glen A	36.4	32.8	11.3	1.1	3.2	0.8	2.9
37.	Fiunary, Savary Glen B	41.2	44.1	12.1	0.9	3.4	0.7	3.6

TABLE 3.20

Mineral Determination for Fiunary and Savary Glen Forests

No.	Sample	Total (mg/100 g ± S.D.)						
		Si	Al	Fe	Ca	Mg	Mn	Ni
1.	Fiunary 2A	7860 ± 760	6656 ± 266	2410 ± 210	266.8 ± 12.2	216.9 ± 11.8	108.5 ± 12.2	7.2 ± 1.2
2.	Fiunary 2B	20180 ± 1210	11025 ± 277	4180 ± 190	410.8 ± 16.2	282.6 ± 12.4	152.8 ± 4.2	11.8 ± 1.4
3.	Fiunary, Savary Glen 5 A_1	17280 ± 1120	10850 ± 246	3985 ± 215	306.5 ± 12.5	261.8 ± 10.7	115.2 ± 15.2	10.2 ± 1.1
4.	Fiunary, Savary Glen 5 A_1 (granite)	18560 ± 1240	11658 ± 1066	4028 ± 172	330.6 ± 15.2	275.2 ± 15.6	180.8 ± 12.4	10.1 ± 1.1
5.	Fiunary, Savary Glen B	20270 ± 1150	12625 ± 965	4985 ± 155	395.0 ± 14.8	286.8 ± 14.2	166.7 ± 14.2	12.5 ± 1.2
6.	Fiunary, Savary Glen C	20395 ± 1180	10185 ± 285	4868 ± 162	406.7 ± 14.3	278.2 ± 12.2	161.1 ± 11.6	11.0 ± 1.0
7.	Fiunary, Savary Glen A 2	10665 ± 1235	9458 ± 226	3185 ± 184	268.8 ± 12.4	260.2 ± 18.4	180.6 ± 10.6	8.4 ± 1.0
8.	Fiunary, Savary Glen 5 B_2	19867 ± 1033	12850 ± 250	5218 ± 172	418.7 ± 22.3	288.6 ± 12.6	192.8 ± 12.4	12.3 ± 1.2
9.	Savary Glen A_1	17855 ± 1120	9688 ± 212	4062 ± 138	308.3 ± 16.2	229.7 ± 17.7	218.8 ± 12.8	10.8 ± 1.4
10.	Savary Glen B_2	19920 ± 1080	10855 ± 655	4722 ± 178	410.6 ± 12.6	289.7 ± 11.8	224.6 ± 16.1	12.2 ± 2.0
11.	Savary Glen B_3	20850 ± 1150	12628 ± 272	4525 ± 215	386.4 ± 14.4	272.8 ± 12.4	250.0 ± 10.0	12.1 ± 1.1
12.	Savary Glen C	20168 ± 1120	12280 ± 220	4620 ± 180	415.8 ± 10.8	280.8 ± 12.8	215.8 ± 10.5	11.6 ± 1.4
	Average	17835 ± 1120	10814 ± 425	4232 ± 182	388.8 ± 13.6	280.6 ± 12.8	178.2 ± 12.1	9.9 ± 1.1
	Minimum	7860 ± 760	6656 ± 266	2410 ± 210	266.8 ± 12.2	216.9 ± 11.8	108.5 ± 12.2	7.2 ± 1.2
	Maximum	20850 ± 1150	12628 ± 272	5218 ± 172	418.7 ± 22.3	288.6 ± 12.6	250.0 ± 10.0	12.5 ± 1.2

TABLE 3.21

Silica-Sesquioxide Radios : Fiunary and Savary Glen Forests

No.	Sample	Percentages			Ratios			
		SiO_2	Al_2O_3	Fe_2O_3	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{SiO_2}{R_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
1.	Fiunary 2A	16.9	25.3	6.9	0.7	2.4	0.5	3.7
2.	Fiunary $2B_2$	43.3	41.5	12.1	1.0	3.6	0.8	3.4
3.	Fiunary, Savary Glen 5A	37.1	41.2	11.6	0.9	3.2	0.7	3.6
4.	Fiunary, Savary Glen $5A_1$ (granite)	39.9	44.2	11.8	0.9	3.4	0.7	3.8
5.	Fiunary, Savary Glen B	43.5	47.6	14.5	0.9	3.0	0.7	3.3
6.	Fiunary, Savary Glen C	43.7	38.5	14.2	1.1	3.1	0.8	2.7
7.	Fiunary, Savary Glen A 2	22.9	35.9	9.2	0.7	2.5	0.5	3.9
8.	Fiunary, Savary Glen $5B_2$	42.6	48.7	15.0	0.9	2.8	0.7	3.2
9.	Savary Glen A_1	38.4	36.6	11.8	1.0	3.3	0.8	3.1
10.	Savary Glen B_2	42.6	41.2	13.6	1.0	3.1	0.8	3.0
11.	Savary Glen B_3	43.8	46.5	13.3	0.9	3.3	0.7	3.5
12.	Savary Glen C	44.8	43.8	13.0	1.0	3.5	0.8	3.4

TABLE 3.22

Spruce needles (mineral constituents) from Pitmedden, Fiunary and Savary Glen Forests (experimental Plots), 4 - 5 year old, on Basalt Brown.

No.	Sample	mg g^{-1} ± S. D., oven-dry									
		Si	Al	P	Ca	K	Mg	Na	Fe	Mn	Ni
1.	Pitmedden 1	12.7 ± 0.6	0.09 ± 0.03	4.9 ± 0.4	4.6 ± 0.5	2.1 ± 0.4	0.84 ± 0.16	0.53 ± 0.03	0.15 ± 0.01	0.14 ± 0.02	0.004
2.	Pitmedden 2	12.2 ± 0.8	0.08 ± 0.02	5.0 ± 0.8	4.8 ± 0.6	2.2 ± 0.5	0.93 ± 0.12	0.56 ± 0.03	0.14 ± 0.03	0.14 ± 0.02	0.004
3.	Pitmedden 3	11.8 ± 0.7	0.10 ± 0.02	4.5 ± 0.5	4.7 ± 0.3	2.4 ± 0.6	0.86 ± 0.14	0.49 ± 0.02	0.14 ± 0.02	0.13 ± 0.03	Nil
4.	Pitmedden 4	13.2 ± 0.8	0.08 ± 0.03	5.3 ± 0.6	4.8 ± 0.4	2.2 ± 0.7	0.94 ± 0.12	0.51 ± 0.04	0.13 ± 0.02	0.09 ± 0.02	Nil
5.	Pitmedden 7 Compartment 105	12.9 ± 1.1	0.10 ± 0.03	5.0 ± 0.6	4.7 ± 0.4	2.3 ± 0.5	0.85 ± 0.10	0.59 ± 0.03	0.12 ± 0.03	0.10 ± 0.02	0.003
6.	1 BML	14.1 ± 1.1	0.25 ± 0.04	4.8 ± 0.8	5.0 ± 0.3	1.8 ± 0.3	0.68 ± 0.12	0.65 ± 0.05	0.12 ± 0.03	0.09 ± 0.03	0.005
7.	3 BML	14.2 ± 1.2	0.32 ± 0.03	4.9 ± 0.6	4.9 ± 0.4	1.9 ± 0.4	0.65 ± 0.15	0.69 ± 0.08	0.11 ± 0.02	0.10 ± 0.03	Nil
8.	4 BML	14.6 ± 1.3	0.31 ± 0.03	5.0 ± 0.7	4.9 ± 0.3	2.1 ± 0.5	0.67 ± 0.11	0.72 ± 0.12	0.12 ± 0.06	0.08 ± 0.02	0.004
9.	5 BF	14.3 ± 0.9	0.19 ± 0.02	5.6 ± 0.5	3.9 ± 0.2	1.9 ± 0.3	0.66 ± 0.11	0.55 ± 0.12	0.11 ± 0.04	0.06 ± 0.02	Nil
10.	14 BF	14.5 ± 1.2	0.22 ± 0.03	5.2 ± 0.7	3.9 ± 0.4	2.2 ± 0.3	0.71 ± 0.12	0.53 ± 0.10	0.12 ± 0.05	0.07 ± 0.02	Nil
11.	17 BF	15.6 ± 1.4	0.21 ± 0.04	5.4 ± 0.6	3.7 ± 0.3	1.8 ± 0.2	0.67 ± 0.13	0.59 ± 0.08	0.11 ± 0.04	0.08 ± 0.03	0.004
12.	2 BFP	13.9 ± 1.5	0.21 ± 0.05	5.1 ± 0.7	3.9 ± 0.3	2.3 ± 0.3	0.65 ± 0.15	0.56 ± 0.06	0.11 ± 0.05	0.08 ± 0.04	0.003
13.	11 BFP	14.4 ± 1.2	0.18 ± 0.06	5.5 ± 0.5	4.0 ± 0.3	1.9 ± 0.3	0.68 ± 0.18	0.55 ± 0.10	0.12 ± 0.04	0.09 ± 0.03	0.003
14.	19 BFP	14.1 ± 1.1	0.20 ± 0.07	5.3 ± 0.6	3.8 ± 0.2	1.8 ± 0.2	0.63 ± 0.15	0.52 ± 0.10	0.12 ± 0.03	0.12 ± 0.03	0.007
15.	9 BMP	13.2 ± 0.9	0.32 ± 0.08	4.6 ± 0.7	3.2 ± 0.5	1.6 ± 0.3	0.70 ± 0.12	0.47 ± 0.12	0.13 ± 0.04	0.17 ± 0.03	0.006
16.	13 BMP	13.3 ± 1.0	0.37 ± 0.07	4.5 ± 0.6	3.0 ± 0.2	1.8 ± 0.2	0.65 ± 0.15	0.52 ± 0.10	0.14 ± 0.04	0.20 ± 0.05	Nil
17.	20 BMP	13.6 ± 1.2	0.39 ± 0.06	4.3 ± 0.5	2.8 ± 0.3	1.7 ± 0.2	0.62 ± 0.10	0.48 ± 0.10	0.13 ± 0.06	0.19 ± 0.04	0.005
18.	7 BM	12.2 ± 0.8	0.70 ± 0.05	2.5 ± 0.5	2.7 ± 0.3	1.4 ± 0.2	0.63 ± 0.06	0.48 ± 0.07	0.14 ± 0.05	0.20 ± 0.06	0.007
19.	10 BM	13.4 ± 1.0	0.69 ± 0.06	3.1 ± 0.7	3.3 ± 0.2	1.5 ± 0.3	0.62 ± 0.05	0.54 ± 0.06	0.13 ± 0.04	0.19 ± 0.06	0.008
20.	21 BM	12.6 ± 1.2	0.72 ± 0.05	2.8 ± 0.6	3.0 ± 0.2	1.6 ± 0.3	0.60 ± 0.05	0.52 ± 0.05	0.21 ± 0.21	0.21 ± 0.07	0.006
21.	12 SR BM	12.0 ± 1.0	0.73 ± 0.06	2.4 ± 0.5	2.6 ± 0.1	1.4 ± 0.2	0.62 ± 0.04	0.46 ± 0.06	0.14 ± 0.04	0.22 ± 0.06	0.005
22.	15 SR BM	11.8 ± 1.2	0.70 ± 0.05	2.2 ± 0.4	2.5 ± 0.2	1.6 ± 0.2	0.58 ± 0.05	0.48 ± 0.06	0.15 ± 0.04	0.20 ± 0.05	0.005

continued ...

TABLE 3.22

continued

No.	Sample	mg g^{-1} ± S.D., oven-dry									
		Si	Al	P	Ca	K	Mg	Na	Fe	Mn	Ni
	Compartment 302										
23.	1 BM	12.8 ± 0.8	0.72 ± 0.06	2.8 ± 0.4	2.9 ± 0.1	1.2 ± 0.2	0.62 ± 0.06	0.51 ± 0.05	0.13 ± 0.04	0.20 ± 0.05	0.005
24.	2 BML	14.0 ± 1.2	0.35 ± 0.05	4.0 ± 0.5	4.2 ± 0.6	1.8 ± 0.3	0.66 ± 0.05	0.58 ± 0.04	0.12 ± 0.04	0.13 ± 0.03	0.004
25.	3 BMP	13.9 ± 1.1	0.41 ± 0.05	4.2 ± 0.4	3.2 ± 0.2	1.4 ± 0.2	0.64 ± 0.06	0.53 ± 0.05	0.12 ± 0.04	0.18 ± 0.03	Nil
26.	4 BOP	14.3 ± 1.1	0.27 ± 0.04	4.6 ± 0.4	3.3 ± 0.3	1.5 ± 0.2	0.66 ± 0.05	0.50 ± 0.05	0.11 ± 0.03	0.16 ± 0.04	0.005
	Compartment 375										
27.	Fiunary 1 (55)	15.5 ± 1.3	0.57 ± 0.07	3.2 ± 0.6	2.5 ± 0.1	1.6 ± 0.3	0.58 ± 0.04	0.56 ± 0.06	0.09 ± 0.02	0.20 ± 0.04	0.004
28.	Fiunary 2 (55)	14.8 ± 1.1	0.52 ± 0.08	3.4 ± 0.5	2.6 ± 0.2	1.8 ± 0.2	0.62 ± 0.03	0.54 ± 0.05	0.11 ± 0.02	0.18 ± 0.06	Nil
29.	Savary Glen 1	12.4 ± 1.2	0.78 ± 0.08	1.7 ± 0.5	2.6 ± 0.08	1.1 ± 0.2	0.62 ± 0.03	0.56 ± 0.04	0.14 ± 0.06	0.22 ± 0.04	0.009
30.	Savary Glen 2	10.7 ± 1.0	0.86 ± 0.05	1.6 ± 0.4	2.7 ± 0.1	0.9 ± 0.1	0.58 ± 0.07	0.51 ± 0.04	0.15 ± 0.04	0.24 ± 0.04	0.010

TABLE 3.23

Percentage of Chemical Composition of Spruce Needles (over-dry) from Pitmedden, Fiunary and Savary Glen Forests

No.	Sample	oven-dry %								
		N	P	Si	K	Ca	Mg	Na	Fe	Al
1.	Pitmedden 1	1.32	0.45	1.27	0.21	0.46	0.08	0.05	0.015	0.009
2.	Pitmedden 2	1.29	0.50	1.22	0.22	0.48	0.09	0.06	0.014	0.008
3.	Pitmedden 3	1.42	0.45	1.18	0.24	0.48	0.09	0.05	0.015	0.010
4.	Pitmedden 4	1.45	0.53	1.32	0.21	0.49	0.09	0.05	0.014	0.008
5.	Pitmedden 7	1.56	0.50	1.28	0.23	0.47	0.08	0.06	0.013	0.010
	Compartment 105									
6.	1 BML	1.40	0.48	1.40	0.18	0.50	0.07	0.07	0.012	0.025
7.	3 BML	1.50	0.49	1.42	0.19	0.49	0.06	0.07	0.011	0.032
8.	4 BML	1.38	0.50	1.44	0.21	0.49	0.07	0.07	0.012	0.031
9.	5 BF	1.46	0.56	1.42	0.19	0.39	0.07	0.06	0.011	0.019
10.	14 BF	1.50	0.52	1.44	0.22	0.39	0.07	0.05	0.011	0.022
11.	17 BF	1.53	0.54	1.56	0.18	0.37	0.07	0.06	0.013	0.021
12.	2 BFP	1.62	0.51	1.39	0.25	0.39	0.07	0.06	0.011	0.021
13.	11 BFP	1.65	0.55	1.44	0.18	0.39	0.07	0.06	0.012	0.018
14.	19 BFP	1.60	0.53	1.41	0.18	0.38	0.06	0.05	0.012	0.020
15.	9 BMP	1.35	0.46	1.28	0.15	0.31	0.07	0.05	0.012	0.032
16.	13 BMP	1.46	0.45	1.30	0.19	0.30	0.06	0.05	0.013	0.037
17.	20 BMP	1.40	0.43	1.33	0.16	0.32	0.06	0.05	0.013	0.039
18.	7 BM	1.30	0.25	1.22	0.14	0.27	0.06	0.05	0.014	0.070
19.	10 BM	1.23	0.31	1.26	0.15	0.33	0.06	0.05	0.013	0.069
20.	21 BM	1.16	0.28	1.35	0.16	0.30	0.06	0.05	0.015	0.072
21.	12 SR BM	1.00	0.24	1.20	0.14	0.26	0.06	0.05	0.014	0.073
22.	15 SR BM	0.90	0.22	1.18	0.16	0.25	0.06	0.05	0.015	0.070

continued ...

TABLE 3.23

continued

No.	Sample	oven-dry %								
		N	P	Si	K	Ca	Mg	Na	Fe	Al
	Compartment 302									
23.	1 BM	1.10	0.28	1.28	0.12	0.29	0.06	0.05	0.013	0.072
24.	2 BML	1.28	0.40	1.40	0.18	0.42	0.07	0.06	0.012	0.035
25.	3 BMP	1.32	0.42	1.39	0.14	0.32	0.06	0.05	0.012	0.041
26.	4 BOP	1.50	0.46	1.43	0.15	0.33	0.07	0.05	0.011	0.027
	Compartment 375									
27.	Fiunary 1 (55)	1.40	0.32	1.55	0.16	0.25	0.06	0.06	0.008	0.057
28.	Fiunary 2 (55)	1.33	0.34	1.48	0.18	0.26	0.06	0.05	0.010	0.052
29.	Savary Glen 1	0.80	0.17	1.24	0.11	0.26	0.06	0.06	0.014	0.078
30.	Savary Glen 2	0.75	0.16	1.07	0.09	0.27	0.06	0.05	0.015	0.086

TABLE 3.24

Simple correlation coefficients (r) for soil test values and percentage of nutrient elements in needles.

No.	Soil Tests	Needles
1.	K-Exchange, meg/100 gm	0.630*
	Acetic-soluble K	0.710*
2.	Ca-Exchange, meg/100 gm	0.610*
	Acetic-soluble Ca	0.582*
3.	Mg-Exchange, meg/100 gm	0.828**
	Acetic-soluble Mg	0.798**
4.	Nitrogen	0.588**
5.	Acetic soluble P	0.700*

* Significant r at 1% level

** Significant r at 5% level

TABLE 3.25

Aluminium Analysis : Comparison between Atomic absorption and oxine-chloroform methods (Accuracy and Precision)

No.	Sample		Atomic Absorption Method mg/100 g ± S. D.	Overall S. D.	Oxine-Chloroform Method mg/100 g ± S. D.	Overall S. D.
1.	Pitmedden	1A	112.4 ± 10.2		114.5 ± 14.6	
2.	Pitmedden	1B	37.2 ± 3.1		35.6 ± 4.1	
3.	Pitmedden	2A	152.2 ± 12.2		155.4 ± 13.3	
4.	Pitmedden	2B	32.8 ± 3.8		33.6 ± 3.3	
5.	Pitmedden	3A	115.4 ± 4.4		116.8 ± 6.6	
6.	Pitmedden	3B	123.3 ± 13.3		120.7 ± 15.2	
7.	Pitmedden	4A	182.5 ± 10.4		179.5 ± 11.6	
8.	Pitmedden	$4B_2$	145.6 ± 8.4		148.8 ± 7.6	
9.	Pitmedden	5A	152.4 ± 8.2	8.2	154.6 ± 9.4	9.5
10.	Fiunary	2A (top road)	1210.8 ± 120.4		1230.7 ± 140.6	
11.	Fiunary	2B	1456.2 ± 144.2		1462.4 ± 148.2	
12.	Fiunary	2C	1285.8 ± 135.4		1282.6 ± 132.4	
13.	Fiunary	B_2 (micashist)	1495.2 ± 115.2		1508.5 ± 120.5	
14.	Fiunary, Savary Glen	$5A_1$	1550.2 ± 244.1		1562.2 ± 252.4	
15.	Fiunary, Savary Glen	B	1648.4 ± 252.2		1642.6 ± 260.5	
16.	Savary Glen	A	1588.3 ± 222.1		1610.8 ± 180.2	
17.	Savary Glen	B_2	1678.2 ± 128.4	170.2	1694.2 ± 110.2	167.7
	All Extracts			89.2		88.6

3.6 SUMMARY OF ANALYTICAL FINDINGS

Routine analytical determinations, which include loss on ignition, pH, exchangeable cations, percentage carbon, nitrogen and acetic soluble phosphorus, potassium, calcium, magnesium, sodium, aluminium and nickel were carried out on each sample.

Furthermore, samples from different areas, dilute calcium chloride and oxalate and dithionite extractants were used for extracting aluminium, iron, silicon and manganese for comparing the amounts of these elements extracted by different extractants.

Soil and plant samples have been analysed for total silica by using hydrofluoric acid and a second mineral acid. The decomposition was achieved in a specially designed vessel made of teflon. This acid digestion vessel, provides a rapid method for dissolving a sample, prevents contamination, assures complete recovery by elements volatization losses (see Chapter V). Nitric and sulphuric acid mixtures were used to destroy the organic matter, increase the rate of dissolution and raise the temperature of the solution.

3.6.1 LOSS ON IGNITION

The loss on ignition values for the organo-mineral soils. There is a big variation in the loss on ignition. In general, there is a marked decrease with depth. In Pitmedden Forest, the loss on ignition varies from 3.5 - 9.8% while in Fiunary Forest and Savary Glen, the loss on ignition varies from 9.5 - 65.4%.

3.6.2 CARBON AND NITROGEN

The per cent carbon and nitrogen decrease down the profile in all soil samples and in all forests tested.

(i) Pitmedden Forest

The per cent total carbon varies from 0.5 - 4.8 and the per cent nitrogen varies from 0.3 - 1.5 (see Table 3.11).

(ii) Fiunary, Savary Glen Forest

The per cent total carbon varies from 3.8 - 32.1 and the per cent nitrogen varies from 0.5 - 3.3 (see Table 3.12).

(iii) Fiunary Forest, Experimental Plots

The per cent total carbon varies from 9.6 - 18.5.

(iv) Salen Forest, Mull

The per cent total carbon varies from 4.0 - 30.8, and the per cent nitrogen varies from 0.2 - 3.2 (see Table 3.14).

(v) Loch Eynort, Skye

The per cent total carbon varies from 10.2 - 27.5, and the per cent nitrogen varies from 0.8 - 3.0 (see Table 3.14).

Meanwhile, the per cent of nitrogen in spruce needles varies from 1.3 - 1.6 in Pitmedden Forest and from 1.1 - 1.7 in Fiunary Forest (Experimental Plots, see Table 3.23).

3.6.3 pH VALUE AND EXCHANGEABLE CATIONS (;EC)

3.6.3.1 In the Basalt brown forest soils with imperfect drainage, the pH values increase with depth (down the profile):-

(i) The pH values in Pitmedden forest vary from 5.6 - 6.4.

(ii) The pH values in Fiunary and Savary Glen Forest vary from 3.8 - 5.2.

(iii) The pH values in Fiunary Forest, experimental plots, vary from 4.3 - 6.0.

(iv) The pH values vary from 4.1 - 5.7 in Salen Forest, while in Loch Eynort, they vary from 4.3 - 5.8 (see Table 3.14).

3.6.3.2 Exchangeable Cations

(i) Exchangeable Calcium

The values for exchangeable calcium vary with major soil group, parent material and drainage class.

In the case of Basalt brown forest soils with imperfect drainage, there is an increase in value with depth. The values recorded for Pitmedden Forest (non-calcareous gley) tend to be high and show an increase down the profile. The values vary from [illegible] m eq/100 g to [illegible] m eq/100 g (see Table 3.11). On the other hand, the values recorded for Fiunary and Savary Glen Forest (acidic soil) tend to be low or moderate and show an increase down the profile, the values vary from [illegible] m eq/100 g (see Table 3.12).

(ii) Exchangeable Magnesium

The values for exchangeable magnesium when moderate to low are generally 1/10 to 1/5 of the exchangeable calcium (Mitchell and Jarvis, 1956). The brown forest soils with free drainage contain moderate amounts of exchangeable magnesium (0.[illegible] - [illegible] m eq/100 g).

In the brown forest soils classed as imperfectly drained, the concentration of exchangeable magnesium increases with depth. The values for Pitmedden Forest tend to be moderate, varying from [illegible] m eq/100 g (see Table 3.11) and the values for Fiunary and Savary Glen Forest also tend to be moderate, varying from 1.0 - 3.0 m eq/100 g .

(iii) Exchangeable Potassium

The values for exchangeable potassium in the freely drained brown forest soils decrease with depth.

The brown forest soils with imperfect drainage show a decrease with depth whilst the values for Pitmedden Forest tend to be moderate or high, varying from 0.3 - 0.9 m eq/100 g and the values for Fiunary and Savary Glen Forest tending to be moderate 0.15 - 0.5 m eq/100 g .

(iv) Exchangeable Sodium

The values for this cation in the brown forest soils with imperfect drainage show an increase with depth. The values recorded for Pitmedden Forest vary from 0.6 - 1.0 m eq/100 gm and the values for Fiunary, Savary Glen Forest vary from 0.27 - 0.87 m eq/100 g .

(v) Exchangeable Aluminium

The values for this cation increase with depth in the brown forest soils with imperfect drainage, but there are no significant trends in Pitmedden Forest, the values varying from 0.45 - 3.58 m eq/100 g (see Table 3.11). The values for Fiunary and Savary Glen vary from 3.3 - 16.8 m eq/100 g (see Table 3.12).

(vi) Exchangeable Manganese

The values for this cation are very low in the Basalt brown forest soils. In several cases, this cation is only detected in the upper horizons.

The values for Pitmedden Forest vary from 0.0 - 0.1 m eq/100 g. , and the values for Fiunary and Savary Glen Forest vary from 0.06 - 0.52 m eq/100 g. .

3.6.4 ACETIC OR READILY SOLUBLE PLANT NUTRIENTS

3.6.4.1 Acetic-soluble Phosphorus

The amount of readily soluble phosphorus present nearly always decreases in the B horizon compared with the A horizon of imperfectly drained brown forest soils, see Chapter IV (Tables 4.01 and 4.02).

3.6.4.2 Acetic-soluble Potassium

The values of soluble potassium in Pitmedden Forest and Fiunary and Savary Glen Forest soils show a decrease with depth. The values for Pitmedden Forest shown in Table 3.01, vary from 36.2 - 106.4 mg/100 g , with an average 69.8 mg/100 g . The values in Fiunary and Savary Glen Forest shown in Table 3.02 vary from 33.2 - 72.6 mg/100 g , with an average of 51.2 mg/100 g .

3.6.4.3 Acetic-soluble Calcium

The values for soluble calcium in the brown forest soils with imperfect drainage normally show an increase in value with depth. The values recorded for Pitmedden Forest shown in Table 3.01 vary from

158.2 - 360.8, with an average of 210.4 mg/100 g .

The values recorded for Fiunary and Savary Glen Forest shown in Table 3.02, vary from 80.2 - 165.9 mg/100 g , with an average of 140.8 mg/100 g .

3.6.4.4 Acetic-soluble Magnesium

The values for this metal in the brown forest soils with imperfect drainage decrease with depth and show a minimum in the B (g) horizon. The values recorded for Pitmedden Forest shown in Table 3.01 vary from 42.4 - 84.3 mg/100 g with an average of 59.8 mg/100 g .

The values recorded for Fiunary and Savary Glen Forest shown in Table 3.02 vary from 29.4 - 64.2 mg/100 g , with an average of 46.4 mg/100 g .

3.6.4.5 Acetic-soluble Sodium

The values for soluble sodium decrease with depth. The values for Pitmedden Forest shown in Table 3.01, vary from 33.2 - 84.5 mg/100 g , with an average of 60.1 mg/100 g . The values for Fiunary Forest shown in Table 3.02 vary from 19.5 - 68.2 mg/100 g , with an average of 42.6 mg/100 g of soil.

3.6.4.6 Acetic-soluble Aluminium

Aluminium is determined by oxine-chloroform and atomic absorption methods for all soil samples, (Table 3.25).

The values for soluble aluminium in the brown forest soils classed as imperfectly drained increase with depth, but in Basalt brown forest soils there is a maximum in the B horizon.

The values for Pitmedden Forest (Table 3.01) vary from 32.8 - 182.5 mg/100 g., with an average of 106.2 mg/100 g. The values for Fiunary and Savary Glen Forest (Table 3.02) vary from 638.6 - 1678.2 mg/100 g., with an average of 1150.2, which is about ten times greater than the value in Pitmedden Forest.

3.6.4.7 Acetic-soluble Nickel

The values for soluble nickel in brown forest soils are very low and reach a maximum in the B horizon. Several samples only contain this trace metal in the upper horizons.

The values for Pitmedden Forest vary from 0.2 - 1.5 mg/100 g. with an average of 0.8 mg/100 g.

The values for Fiunary and Savary Glen Forest (Table 3.02) vary from 0.5 - 2.1 mg/100 g, with an average of 0.9 mg/100 g..

3.6.5 USE OF DILUTE CALCIUM CHLORIDE FOR THE EXTRACTION OF ALUMINIUM, SILICON and IRON

3.6.5.1 Extractable Aluminium

The values for soluble aluminium in the brown forest soils with imperfect drainage increase with depth. The values for Pitmedden Forest (Table 3.03) vary from 3.7 - 14.2 mg/100 g, with an average of 9.4 mg/100 g.

The values for Fiunary Forest (Table 3.04) vary from 13.5 - 40.6 mg/100 g., with an average of 22.8 mg/100 g.

3. 6. 5. 2 Extractable Iron

The values for extractable iron in the brown forest soils increase with depth. The values recorded for Pitmedden Forest vary from 0. 40 - 0. 93 mg/100 g , with an average of 0. 65 mg/100 g (Table 3. 03).

The values for Fiunary and Savary Glen Forest vary from 0. 52 - 4. 54 mg/100 g , with an average of 2. 43 mg/100 g .

3. 6. 5. 3 Extractable Silicon

Although silicon is abundant in most soils, its solubility relationships are not fully understood. McKeague and Cline (1963 a, b) studied the forms and concentration of dissolved silicon in water extracts of soils. The values of soluble silicon in Pitmedden Forest (Table 3. 03), vary from 5. 3 - 18. 2 mg/100 g , with an average of 11. 2 mg/100 g , using 0. 01 M $CaCl_2$ solution and 4. 2 - 18. 2 mg/100 g , with an average of 12. 4 mg/100 g using 0. 01 M $MgSO_4$ solution as extractant.

The values of soluble silicon in Fiunary Forest (Table 3. 04) varies from 5. 2 - 18. 6 mg/100 g , with an average 12. 4 mg/100 g . Meanwhile, results shown in Table 3. 04 as well, vary from 4. 6 - 17. 2 mg/100 g , with an average 11. 8 mg/100 g by using 0. 01 M $MgSO_4$ solution.

Noteworthy, the results given above after three days of shaking.

3. 6. 6 DITHIONITE AND OXALATE-EXTRACTABLE ALUMINIUM AND IRON AND SILICON, MAGNESIUM, MANGANESE, NICKEL

3. 6. 6. 1 Aluminium

The values of Aluminium in the brown forest soils with imperfect drainage increase with depth. The values recorded for Pitmedden Forest (Table 3. 05), vary from 550 - 989 mg/100 g with an average of 755 mg/100 g .

The values recorded for Fiunary and Savary Glen Forest (Table 3. 06) vary from 1269 - 3595 mg/100 g , with an average of 3253 mg/100 g .

The values of Aluminium in Fiunary Forest, experimental plots, (Table 3. 07), vary from 1780 - 3610 mg/100 g , with an average of 2521 mg/100 g .

In Salen and Loch Eynort Forests, the values (Table 3. 08), vary from 1997 - 3692 mg/100 g , with an average of 2918 mg/100 g .

On the other hand, the Dithionite-extractable aluminium values in Pitmedden Forest vary from 356 - 810 mg/100 g , with an average of 625 mg/100 g (Table 3. 09).

The values in Fiunary Forest, experimental plots, (Table 3. 10) vary from 1680 - 2975 mg/100 g , with an average of 2110 mg/100 g .

3. 6. 6. 2 Iron

The values for iron in the brown forest soils increase with depth. The values recorded for:

(i) Pitmedden Forest (Table 3. 05), vary from 1212 - 1850 mg/100 g , with an average of 1395 mg/100 g .

(ii) Fiunary and Savary Glen (Table 3. 06) vary from 1890 -

4175 mg/100 g with an average of 3780 mg/100 g .

(iii) Fiunary Forest, experimental plots, (Table 3.07) vary from 2786 - 4186 mg/100 g , with an average of 3578 mg/100 g .

(iv) Salen and Loch Eynort Forests, the values (Table 3.08) vary from 1836 - 4085 mg/100 g , with an average of 3165 mg/100 g .

On the other hand, the results of Dithionite extractable iron for:-

(i) Pitmedden Forest (Table 3.09) vary from 1890 - 2895 mg/100 g , with an average of 2390 mg/100 g .

(ii) Fiunary Forest, experimental plots, (Table 3.10) vary from 3280 - 3989 mg/100 g , with an average of 3492 mg/100 g .

3.6.6.3 Manganese

The values of Manganese in brown forest soils with imperfect drainage decrease with depth. The values recorded for:-

(i) Pitmedden Forest (Table 3.05), vary from 24.6 - 60.6 mg/100 g , with an average of 41.2 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.06) vary from 40.5 - 75.3 mg/100 g , with an average of 56.1 mg/100 g .

(iii) Fiunary Forest, experimental plots, (Table 3.07), vary from 48.5 - 75.8 mg/100 g with an average of 60.2 mg/100 g .

(iv) Salen and Loch Eynort Forests (Table 3.08) vary from 31.4 - 80.9 mg/100 g , with an average of 54.8 mg/100 g .

Dithionite extractable Manganese for Pitmedden Forest vary from 28.7 - 62.7 mg/100 g , with an average of 44.5 mg/100 g .

Fiunary Forest, experimental plots, (Table 3.10) vary from 55.6 - 108.6 mg/100 g , with an average of 68.2 mg/100 g .

3.6.6.4 Magnesium

The values for agnesium in brown forest soils with imperfect drainage decrease with depth. The values recorded for:

(i) Pitmedden Forest (Table 3.05) vary from 50.6 - 98.6 mg/100 g , with an average of 78.8 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.06) vary from 45.6 - 80.2 mg/100 g , with an average of 69.8.

(iii) Fiunary Forest, experimental plots (Table 3.07) vary from 60.8 - 108.2 mg/100 g , with an average of 74.7 mg/100 g .

3.6.6.5 Nickel

The amount of nickel extracted varied with soils and extractants. It has been observed that of all the extractants, Grigg's reagent (acid ammonium oxalate buffer to pH) proved to be most efficient for the extraction of nickel from soils. Acetic acid was second. The values recorded in brown forest soils increases in B horizon as follows:-

(i) Pitmedden Forest (Table 3.05) vary from 0.8 - 2.9 mg/100 g , with an average of 2.0 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.06) vary from 0.7 - 3.3 mg/100 g , with an average of 2.2 mg/100 g .

(iii) Fiunary Forest, experimental plots (Table 3.07) vary from 1.3 - 3.0 mg/100 g , with an average of 2.2 mg/100 g .

(iv) Salen, Loch Eynort Forests (Table 3.08) vary from 0.7 - 3.0 mg/100 g , with an average of 1.8 mg/100 g .

3.6.6.6 Silicon

Much of the Silicon in acid ammonium oxalate, and especially in dithionite extracts of the brown forest soils extracted by shaking for 24 hr., most likely comes from the silicate clay minerals and from quartz rather than from the release of occluded silicon by the dissolution of iron oxide compounds as has been suggested (McKeague and Cline, 1963 a; Hoyt and Nyborg, 1971 a). A second source may be due to differences between the quartz sand and kaolinite samples and these same materials as they occur in the soil. Solubility of silicon would be affected by differences in particle size (McKeague and Cline, 1963 a), and probably by differences in the degree of crystallinity and the amount of amorphous silicate material present (Gamble and Daniels, 1972).

The values recorded in the brown forest soils increase with depth. The values recorded for:

(i) Pitmedden Forest (Table 3.05) vary from 58.2 - 176.2 mg/100 g , with an average of 122.8 mg/100 g . The

results (Table 3.09) for Dithionite extracts, vary from 80.3 - 182.9 mg/100 g , with an average of 124.8 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.06) vary from 36.6 - 118.2 mg/100 g , with an average of 96.8 mg/100 g .

(iii) Fiunary Forest, experimental plots (Table 3.07) vary from 80.7 - 128.6 mg/100 g , with an average of 102.4 mg/100 g .

(iv) Salen and Loch Eynort Forests (Table 3.08) vary from 26.3 - 128.6 mg/100 g , with an average of 82.5 mg/100 g .

3.6.7 TOTAL METALS

3.6.7.1 Silicon

Silicon is determined by atomic absorption and the colorimetric, molybdenum blue method (see Chapter V).

The values of silicon in brown forest soils with imperfect drainage increase with depth. The values recorded for:

(i) Pitmedden Forest (Table 3.16), vary from 17285 - 24228 mg/100 g , with an average of 21180 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.20) vary from 7860 - 20850 mg/100 g , with an average of 17835 mg/100 g .

(iii) Fiunary Forest, experimental plots, (Table 2.18) vary

from 16980 - 20850 mg/100 g , with an average of 18822 mg/100 g .

(iv) Salen and Loch Eynort Forests (Table 3.14) vary from 12880 - 21200 mg/100 g , with an average of 18332 mg/100 g.

3.6.7.2 Aluminium

The values of Aluminium in brown forest soils with imperfect drainage increase with depth, especially in B horizon. The values recorded for:

(i) Pitmedden Forest (Table 3.16) vary from 1955 - 2565 mg/100 g , with an average of 2224 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.20) vary from 6656 - 12628 mg/100 g , with an average of 16814 mg/100 g .

(iii) Fiunary Forest, experimental plots (Table 3.18) vary from 8675 - 11655 mg/100 g. , with an average of 9409 mg/100 g .

(iv) Salen and Loch Eynort Forests (Table 3.14) vary from 4562 - 10810 mg/100 g , with an average of 7938 mg/100 g .

3.6.7.3 Iron

The values of iron in brown forest soils with imperfect drainage increase with depth and reach a maximum in the B horizon. The values recorded for:

(i) Pitmedden Forest (Table 3.16) vary from 4410 - 6750 mg/100 g , with an average of 5316 mg/100 g .

(ii) Fiunary and Savary Glen Forest (Table 3.20) vary from 2410 - 5218 mg/100 g , with an average of 4232 mg/100 g .

(iii) Fiunary Forest, experimental plots (Table 3.18) vary from 3686 - 4410 mg/100 g , with an average of 3969 mg/100 g

(iv) Salen and Loch Eynort Forests (Table 3.14) vary from 4280 - 6675 mg/100 g , with an average of 5150 mg/100 g .

3.6.7.4 Total Ca, Mg, Mn and Ni.

The values of these metals in brown forest soils generally increase with depth. The results are shown in Tables 3.14 - 3.20 and are as follows:-

(i) Pitmedden Forest

Ca : vary from 348.5 - 452.5 mg/100 g , with an average of 339.8.

Mg : vary from 271.2 - 340.2 mg/100 g , with an average of 325.7.

Mn : vary from 106.8 - 150.2 mg/100 g , with an average of 138.4.

Ni : vary from 8.6 - 12.5 mg/100 g , with an average of 10.6

(ii) Fiunary and Savary Glen Forest

Ca : vary from 266.9 - 418.7 mg/100 g , with an average of 388.8.

Mg : vary from 216.9 - 288.6 mg/100 g , with an average of 280.6.

Mn : vary from 108.5 - 250.0 mg/100 g , with an average of 178.2.

Ni : vary from 7.2 - 12.5 mg/100 g , with an average of 9.9.

(iii) Fiunary Forest, experimental plots

Ca : vary from 265 - 898.5 mg/100 g , with an average of 398.6.

Mg : vary from 189.8 - 318.5 mg/100 g , with an average of 278.5.

Mn : vary from 126.7 - 154.8 mg/100 g , with an average of 138.4.

Ni : vary from 9.2 - 12.9 mg/100 g , with an average of 10.7.

(iv) Salen Forest and Loch Eynort Forest

Ca : vary from 265.7 - 415.6 mg/100 g , with an average of 326.8.

Mg : vary from 202.6 - 336.5 mg/100 g , with an average of 288.4

Mn : vary from 110.8 - 145.6 mg/100 g , with an average of 128.8.

Ni : vary from 8.2 - 11.2 mg/100 g , with an average of 9.8.

3.6.8 SILICA-SESQUIOXIDE RATIOS AND PERCENTAGES

The percentages of silica, aluminium oxide and iron oxide and the following molecular ratios, SiO_2/Al_2O_3, SiO_2/Fe_2O_3, SiO_2/R_2O_3, Al_3O_3/Fe_2O_3 are given in Tables 3.15 - 3.21. Silica-sesquioxides ratios indicate the relative leaching and differential movement of iron and

aluminium oxides compared with silica and thus enable a comparison to be made between soils of various major soil groups.

The percentage of silica in brown forest soils with imperfect drainage, generally increase slightly down the profile (Tables 3.15 - 3.21). There is, however, a marked increase in the silica content within the Basalt brown forest soils profile. Maximum concentrations of iron oxide in B_2 horizon are noted in some of the profiles, but variations in the silica-sesquioxides ratios are small (Tables 3.17 - 3.19) and translocation of iron oxide from the surface is therefore slight.

Maximum concentrations of aluminium oxide appear in the B horizon of these profiles and variations in the silica-sesquioxides ratios are small (Tables 3.15 - 3.21).

3.6.9 RESPONSE OF SITKA SPRUCE TO NUTRIENTS ON BASALT BROWN EARTHS

3.6.9.1 Concentration of Mineral Elements in Spruce Needles

The concentration of each element in a given type of plant tissue varies greatly with the time of sampling and type of environment (Beeson, 1941; Wells, 1965). The characteristic content was found to vary according to the activity of the respective element in the soil, and according to age of the tissue, cultural conditions and climate.

The concentration range of mineral elements of sitka spruce are expressed as (mg/g) of the over-dried sample or as percentage (Tables 3.22 and 3.23).

* The Si contents of needles vary from 10.7 - 15.6 mg/g . The variations in the Si content are very small.

* The Al contents of needles, vary from 0.08 - 0.86 mg g^{-1}. The variations in the Al contents are very large (Table 3.22). The critical Al level appears to be 0.07% or more, especially with these samples from the unfertilized plots in Fiunary Forest, compartments 105 and 302, and samples from Savary Glen where extremely high levels of Al were found.

* The P contents of needles, vary from 1.6 - 5.6 mg g^{-1}, with an average 4.2 mg g^{-1} in the experimental plots. The P contents of needles from the unfertilized plots (especially SR BM) or Savary Glen, were very low. The critical P level appears to be 0.2% or more.

* The Nitrogen contents of needles, vary from 1.0 - 1.66%. Without including Savary Glen samples, the variation in the N contents is small.

* The K contents of needles, vary from 0.9 - 2.5 mg g^{-1}. The variations in the K contents are not very large.

* The Ca contents of needles, vary from 2.4 - 5.0 mg g^{-1}. The variations in the Ca contents are small.

* The Mg contents of needles, vary from 0.56 - 0.94 mg g^{-1}. The variations in the Mg contents are very small.

* The Fe contents of needles, vary from 0.09 - 0.15 mg g^{-1}. The variations in the Fe content are very small.

3. 6. 9. 2 Nutrient Relationships Between Soils and Needles of Sitka Spruce

Highly significant correlations were found between nutrient levels in the soil and in the needles of 4 - 5 year old sitka spruce from Fiunary Forest, experimental plots, and samples from Pitmedden Forest.

(i) Nitrogen

A significant correlation was found between mineralized N in mg g^{-1} and percentage N in the needles. The r = 0. 588, is significant at 5% level.

(ii) Phosphorus

A highly significant (1% level) correlation was shown (Table 4. 10). The correlation between the amount of P extracted from the soil by 0. 5 M acetic acid, the available P test and the uptake P by sitka spruce was r = 0. 700.

(iii) Potassium

There was a highly significant correlation between K content of each horizon using two soil tests (Table 2. 24). The correlation coefficients were 0. 630 and 0. 710.

(iv) Calcium

Correlations between soil test values for Ca and per cent Ca in needles were highly significant (5% level) (Table 3. 24). The per cent Ca in the needles increased with age of needles.

(v) Magnesium

Correlations between soil test values for Mg and per cent Mg in needles (Table 3. 24) were significant at 5% level.

3. 6. 9. 3 Growth Response

The average heights of the trees in the experimental plots on Fiunary Forest in 1980 are recorded in Table 2. 03, Chapter II. As the experimental plots were established over a period of six years, heights in that table show the response to fertilizers after application. Statistically significant increases in growth were obtained in five of the seven treatments. The P treatments were well ahead, especially BOP, (Fig. 2. 03) - the pasture site. In the forest site, BF is well ahead followed by the two treatments, BFP and BMP (Table 2. 03 and Figs. 2. 01, 2. 05). The lime plots fell behind - as it was expected - after two years (Table 2. 03).

3. 7 CONCLUSIONS

Sitka spruce were shown to grow on soil with a range of physical and chemical properties.

Comparison of several soil extraction methods in order to find a measure of soil aluminium revealed high levelsof aluminium in West Argyll forests in particular. High aluminium concentration was shown to have an adverse effect on yield. The study showed that surface application of lime and phosphate have a beneficial effect on yield of sitka spruce even when the soils have a high capacity to fix phosphate.

Foliage analysis was shown to have promise for evaluating nutrient status of trees, particularly when standards for deficiency and response curves are known.

Significant yield increases were noted from the first year

with trees supplied with lime and phosphate, and inoculated with mycorrhiza compared with control.

The concentration of nutrients particularly phosphate in the foliage were markedly increased on the fertilized plots.

Foliar analytical data was useful in predicting deficiency or toxicity levels of such nutrients as phosphorus, nitrogen and aluminium.

Highly significant correlation was found between nutrients levels in the soil and in the needles.

CHAPTER IV

PHOSPHORUS STATUS OF BASALT-BROWN EARTHS

4.1 MAINTENANCE OF PHOSPHORUS STATUS

4.1.1 THE NATURE OF SOIL PHOSPHORUS

The phosphorus content of most mineral soil falls between 0.02 and 0.5 per cent phosphorus, and a general average of 0.05 per cent (0.12 per cent P_2O_5) frequently is representative of soils (compared to an average of 0.12 per cent phosphorus in the earth's crust (Bear, 1964). About half the soil phosphorus occurs in combination with organic matter of surface soils and the remainder occurs in mineral or inorganic combination (Black, 1968). Soil phosphorus can be considered as non-available, potentially available and immediately available. Immediately available phosphorus is the inorganic form occurring in the soil solution and which is almost exclusively orthophosphate (Russell, 1973).

Plants are unable to absorb phosphorus directly from solid compounds or from organic phosphorus compounds, even though the latter may be in soil solution (Russell, 1973).

4.1.2 TYPES OF PHOSPHATE IN SOILS

It can be appreciated that phosphate is held in soils by a number of different mechanisms, each of which affects the concentration of phosphate in the soil solution in a different way.

Soil phosphates can be put into three groups:-

1. Phosphates present in the soil solution. This is very little and negligible compared with the other forms.
2. Phosphates present in the soil organic matter.
3. Inorganic phosphates including both definite phosphate compounds and surface films of phosphate held on inorganic particles.

4.1.3 ORGANIC PHOSPHATES

There is still considerable doubt on the phosphate compounds present in organic matter, but it is almost certain none of them are directly available to the plant. The importance of the organic phosphates is two-fold. On soils low in phosphate, put down to grass, for example, the rate of build up of humus may be limited by the lack of phosphate, for the C/P ratio in humus is usually between 100 and 200, and inorganic or available phosphate can be converted into unavailable forms by the process. Again, in soils low in inorganic phosphate, the phosphate supply to the crop can be very dependent on the relationship between the periods when the soil humus is decomposing and releasing phosphate and those when the crop is making demands on the soil phosphates. More work has been done on the factors controlling the liberation of phosphate by the decomposition of organic matter than its lock-up due to humus accumulation (Russell, 1973). One of the important factors which controls the rate of mineralisation of this phosphate is the number of times the soil becomes really dry between rewettings and another factor is temperature. The warmer the soil the more rapid the rate of decomposition (Eid and Black, 1954).

This source of phosphate is naturally more important than the lower level of available inorganic phosphate. The soil solution also contains some organic phosphates and the amount of phosphate present in this form may be several times greater than the soluble inorganic phosphate (Pierre and Parker, 1927). There is some doubt, however, about its value as a source of phosphate for plants (Russell, 1973).

4.1.4 INORGANIC PHOSPHORUS

Inorganic soil phosphorus chemistry has been reviewed in numerous publications (Lyon et al., 1956; Thompson, 1959; Black, 1968; Pierre et al., 1953). Fractionation has been one of the approaches to a study of inorganic phosphorus. In the soil, phosphorus can be classified into four main groups:

(i) Calcium phosphate

Calcium phosphates exist in several forms, the most important of which are:-

1. $Ca(H_2PO_4)_2\ H_2O$, monocalcium phosphate, which is water soluble, and the dominant phosphate of super phosphate fertilizer.
2. $Ca\ H\ PO_4\ 2\ H_2O$ dicalcium phosphate, both hydrated and dehydrated. The dehydrate is metastable and goes over to the dehydrated form relatively easily and both are only slightly soluble in water.
3. $Ca_8\ H_2\ (PO_4)_6\ 5\ H_2O$, octacalcium phosphate.
4. $Ca_3(PO_4)_2$ tricalcium phosphate, which is certainly formed in high temperature slags.

5. $Ca_{10}(PO_4)_6(OH)_2$ hydroxyapatite, which is the phosphatic constituent of bones and teeth. An important part of the chemistry of calcium phosphates in soils is that of apatite and particularly hydroxy-apatite.

(ii) Iron and Aluminium Phosphates

In well drained acid soils, one of the principal aluminium phosphates belongs to the isomorphous variscite - barrandite-strengite group (Russell, 1973). Variscite having the formula $Al\ PO_4\ 2\ H_2O$, strengite having the formula $Fe\ PO_4\ 2\ H_2O$, and barrandite being a mixture of the two in almost any proportions $(Al, Fe)(OH)_2\ H_2\ PO_4$ or $(Al, Fe)\ PO_4\ 2\ H_2O$ (Wright and Peech, 1961). When K or NH_4 is high, as in fertilizer bands, these ions are incorporated as in taranakite - $K_3\ Al_5\ H_6\ (PO_4)_8\ 18\ H_2O$ or its ammonium analogue (Wada, 1959) or other (K, NH_4) salt such as $(K, NH_4)\ (Al, Fe)_3\ H_8\ (PO_4)_6\ 6\ H_2O$ (Lindsay and Stephenson, 1959).

Wavellite - $Al_6\ (F, OH)_6\ (PO_4)_4\ 9\ H_2O$ has been identified by (Dyal, 1953) in soil.

It is likely that iron and aluminium phosphates occur in many soils in the form of films, a few molecules thick at most (Russell, 1973). These films are probably held on the surface of hydrated ferric and aluminium oxide films, or on ferric and aluminium ions forming part of the surface layer of clay crystals.

(iii) Phosphate dissolved in the Soil Solution

The immediate source of phosphate for crops growing in soil is

probably that of the inorganic phosphate ions in the soil solution. This concentration varies widely for different soils. It can be below 10^{-8} M in some very poor tropical soils, of the order of 10^{-6} M in temperate soils known to be deficient in phosphate, 10^{-5} M in many soils of moderate phosphate status and over 10^{-4} M in some soils known to be well supplied. (10^{-5} M corresponds to 0.3 ppm of phosphorus in the soil solution).

Fried and co-workers (1957) have shown that in a normal soil moderately well supplied with phosphate, soil phosphate can go into solution at a very much faster rate than roots can take it up. The concentration needed for good growth probably also depends on the degree of dissociation of the phosphate anion. Most, if not all, crops take up $H_2PO_4^-$ more readily than the HPO_4^{2-} ions and above pH 7 the relative concentration of the divalent ion is greater than that of the monovalent ion, taking the second dissociation constant of H_3PO_4 as $pK_2 = 7.2$ (Russell, 1973). The minimum phosphate concentration needed for reasonable growth depends in part on the microbiological environment of the root. Many rhizosphere organisms, for example, will compete with the root for phosphate, when the phosphate concentration is low, reducing considerably the amount of phosphate available to the plant (Barber and Loughman, 1967). On the other hand, if the phosphate level is low, mycorrhizal roots are likely to form which are more efficient phosphate scavengers than uninfected roots. Also, under some conditions, the rhizosphere micro-organisms will contain species that will solubilise phosphate from compounds of very low solubility and so increase the phosphate supply to the plant.

4.2 STUDIES ON THE AVAILABILITY OF PHOSPHORUS IN THE SOILS

4.2.1 INTRODUCTION

Phosphorus determinations for soils have received and are still receiving extensive attention from soil chemists because of the importance of phosphorus in soil fertility.

The chemistry of phosphorus in solution as well as in soil is rather complex, and methods of analytical determination have required exacting attention to every controllable detail. Many different extracting solutions have been recommended.

Methods of analysis for the level of available phosphate in soils are in most demand for annual crops, many of which need a good supply early on in their growth period, so they can only draw on phosphate that is readily accessible and desorbable. The principle underlying the methods in common use for temperate soils involves determining the amount of phosphate in a soil sample.

The principle of the method is to shake a sample of soil with a solution designed to dissolve the fractions of phosphorus that are available to plant roots.

The extract is then analysed for soluble phosphorus and the results correlated with actual uptake of phosphorus from the soil by the plant.

The extractants used include:-

(i) 0.5 M sodium bicarbonate (pH 8.5) (Olsen et al., 1954).

Probably this method is the most generally useful for soils that are not too acid. Recently, it has been recommended by ADAS as a routine method for determining available phosphate in soils in England and Wales.

(ii) 0.03 N NH_4F and 0.025 N H Cl (Bray and Kurtz, 1945). This method has been used widely as an index of available phosphorus in soils.

(iii) 0.5 M acetic acid (Williams and Stewart, 1941). This extractant is commonly used by the Advisory Service in Scotland.

(iv) 0.5 M ammonium acetate (pH 4.8). This extractant is a modification of Morgan's method (1937).

(v) Finally, among the most promising methods that tend to stimulate the conditions affecting the uptake of ions by plant are those involving the use of anion-exchange resins to extract phosphorus from soils (Amer et al., 1955; Cooke and Hislop, 1963).

This Chapter enumerates several procedures in detail, including total phosphorus in soils, and spruce needles, organic phosphorus and fractionation of soil phosphorus. In some instances, suggestions for alternative procedures or modification to existing procedures are made.

The different procedures for estimating available phosphorus have been compared and their relative efficiency judged by the degree of:

(i) Correlation of extractable soil phosphorus with plant uptake of phosphorus.

(ii) Correlation of extractable phosphorus with forms of phosphorus in soils.

As an objective of extension, personnel involved in soil work is to reduce the time and cost of routine soil tests carried out to estimate plant available phosphorus. This aspect was also borne in mind in the study.

4.2.2 METHODS FOR PHOSPHORUS DETERMINATION

Once in solution, phosphorus can be estimated volumetrically, complexometrically, gravimetrically and colorimetrically.

(i) Volumetric methods

The classic methods of determining soluble orthophosphate are described by Vogel (1962).

(ii) Gravimetric method

The gravimetric determination of phosphate involves precipitation as phosphomolybdate which is then weighed. The method was applied to soil analysis by Lorenz (1901) and more recently has been described by Strzemienski (1955). The procedure is both lengthy and tedious and is considered unsuitable for routine work.

(iii) Colorimetric methods

The most commonly employed methods of determining phosphorus in solution are those dependent upon the formation of coloured complexes.

Nowadays in soil laboratories, the element is determined in this manner exclusively, and with modern techniques, the method is by far the simplest and quickest and is capable of a high degree of accuracy.

There are two main colorimetric procedures, each of which has advantages over the other in certain circumstances. The first depends upon the combination of phosphorus with the molybdate ion and the second upon its reaction with vanadomolybdate. The most extensively used method is the first and was introduced by Osmund (1881). Phosphorus reacts with molybdate to form a heteropolymolybdic complex with phosphorus as the central co-ordinating atom.

$$H_3PO_4 + 12\ H_2Mo\ O_4 \longrightarrow H_3P\ (Mo_3\ O_{10})\ x + 12\ H_2O$$

Phosphorus, however, is not unique in this manner of combination, and other ions, for example, Si^{4+} (described in ChapterV) can react with molybdate in the same way. In practice, suitable precautions have to be taken against this. The complex is yellow-coloured but on partial reduction some of the Mo^{6+} is converted to Mo^{3+} and/or Mo^{5+} and the complex assumes a characteristic blue colour.

Many different reducing agents have been advocated to form molybdenum blue. Snell and Snell (1949) list over thirty variations and the selection of the appropriate reagent depends upon the required sensitivity and freedom from interference.

Jackson (1958) lists four methods of reduction, each most suitable under specific conditions:-

(a) Reduction by chlorostannous acid in sulphuric acid.

(b) Reduction by chlorostannous acid in hydrochloric acid.

(c) Reduction by molybdenum in sulphuric acid.

(d) Reduction by 1, 2, 4-amino-naphtholsulphuric acid in sulphuric or perchloric acid.

Murphy and Riley (1962) proposed an ascorbic acid procedure for phosphate determination in water. The ascorbic acid procedure has been recommended for phosphate determinations in soil extracts (Colwell, 1963; Watanable and Olsen, 1965; Durge and Paliwal, 1967; John, 1970). Alexander and Robertson (1970) for total phosphorus in soils. Of the many alternative reducing agents available, ascorbic acid has become favoured due to the fact that the blue colour of the reduced complex is stable for a long time, enabling reduced solutions to be kept overnight if necessary before measurement.

4.2.3 MATERIALS AND METHODS EXTRACTION

4.2.3.1 Materials

About 120 soil samples for this study were collected at different times from different forest sites (Fiunary and Savary Glen in North West Argyll; Salen Forest on Mull Island; Loch Eynort, Skye; Pitmedden Forest in the East Coast of Scotland, Hallborns soils (as described in Chapter II). The soil samples were selected to represent a range of levels of available phosphorus and to have as much a variation as possible within the soil samples.

Soil samples were air-dried, sieved and passed through a 2 mm sieve. The pH (1 : 2.5 soil-water suspension) ranges from 3.9

to 6.4.

The organic matter content of the soils varies from 0.6% to 33.2% carbon (see Chapter III, given in Table 3.12).

4.2.3.2 Chemical Analysis

All laboratory analyses were performed in duplicate or triplicate samples of soil. Extractable phosphorus was determined using five procedures. In all cases, phosphorus in the filtered soil extract was measured colorimetrically by the method of Murphy and Riley (1962) as modified by John (1970), using ascorbic acid as reductant.

4.2.3.2.1 Olsen's Method (1954)

4.2.3.2.1.1 Reagents

1. Sodium bicarbonate (Na H CO_3) solution, 0.5 M. The pH of this solution was adjusted to 8.5 with M Na OH. A fresh solution was prepared before use if it had been standing over one month in a glass container. Store the solution in a polyethylene container for periods longer than one month, but must check the pH of the solution.

2. Ammonium molybdate ($(NH_4)_6$ Mo_7O_{24} $4H_2O$) solution. 15 gm of ammonium molybdate was dissolved in 300 ml of warm deionized water. The mixture was filtered if necessary and allowed to cool. 342 ml of concentrated H Cl was then added gradually with mixing, and the contents diluted to one litre with deionized water.

3. Carbon black: used carbon black BPL 30 x 140 or other suitable carbon source (Olsen used carbon black G).

4. Stannous chloride ($Sn\ Cl_2\ 2\ H_2O$), concentrated solution.

10 gm of $Sn\ Cl_2\ 2\ H_2O$ was dissolved in 25 ml concentrated H Cl. A fresh solution was prepared every one month or less. The solution was stored in a refrigerator.

5. Stannous chloride, dilute solution. 0.5 ml of the concentrated $Sn\ Cl_2$ solution was added to 66 ml of deionized water. The diluted solution was prepared for each set of determinations.

6. Standard phosphorus solution: 0.4393 g of potassium dihydrogen phosphate ($KH_2\ PO_4$) was dissolved in deionized water and the solution diluted to one litre with deionized water. The solution contained 100 µg of phosphorus per ml.

7. Dilute phosphorus solution: 20 ml of the standard phosphorus solution was diluted to one litre with deionized water. This solution contained 2 µg of phosphorus.

4.2.3.2.1.2 Procedure

5 g of soil, one teaspoonful of carbon black BPL (30 x 140) after rewashing with $Na\ H\ CO_3$, or other suitable carbon black, and 100 ml of the extracting solution were added to 4 oz extraction bottles. The bottles were shaken for 30 min. The suspension was filtered through Whatman No. 42 filter paper. More carbon black was added if necessary to obtain a clear filtrate, and the bottles were shaken immediately before pouring the suspension into the funnel.

A 5 ml aliquot of the extract was placed in a 25 ml volumetric flask and 5 ml of the ammonium molybdate solution was slowly added

into the flask. After rapid evolution of CO_2 had ceased, the flask was gently shaken to mix the contents after which the neck of the flask was washed down with deionized water to avoid direct contact of the Sn Cl_2 solution with the concentrated ammonium molybdate solution. The contents were diluted to ~ 22 ml with deionized water. 1.0 ml of dilute Sn Cl_2 solution was added to the flasks, the solution diluted to volume and the contents mixed immediately. The absorbance of the solution was measured, 10 min. after addition of the Sn Cl_2 solution at 660 mn. A standard curve was prepared as follows:-

Aliquots of dilute phosphorus solution containing from 2 to 25 ppm of phosphorus were pipetted into 25 ml volumetric flasks and 5 ml of the Na H CO_3 extracting solution added to each flask. The colour was developed as stated above. The absorbance was plotted against phosphorus concentration and the results expressed as P in ppm of soil. The relation between the phosphorus soluble in the extract and the expected yield response to applied fertilizer phosphorus is as follows:-

$<$ 5 ppm, a response, between 5 and 10 ppm, a probable response and $>$ 10 ppm, a response unlikely.

i.e. µg of phosphorus/5 ml of the unknown X4 equals ppm of phosphorus for the procedure described here.

4.2.3.2.1.3 Comments

The same procedure described above was repeated using ascorbic acid as the reducing agent (described 4.2.3.2.3.1) instead of Sn Cl_2 H Cl.

4.2.3.2.2 Fluoride Extractable Phosphorus of Soils

The F^- ion has the special property of complexing Al^{+++} and Fe^{3+} ions in acid solution, with consequent release of phosphorus held in the soil by these trivalent ions. The reaction in acid solution may be represented as follows:-

$$3N\,H_4\,F + 3HF + Al\,PO_4 \longrightarrow H_3\,PO_4 + (NH_4)_3\,Al\,F_6$$

$$3N\,H_4\,F + 3HF + Fe\,PO_4 \longrightarrow H_3\,PO_4 + (NH_4)_3\,Fe\,F_6$$

The formula - $Al\,PO_4$ represents various hydrated and hydroxyl phosphates of aluminium, including any adsorbed or precipitated surface layers on oxides and alumino-silicates. The formula $Fe\,PO_4$ similarly represents various hydrated and hydroxyl phosphates of iron, including adsorbed or precipitated surface layers on iron oxides. The reaction with $Fe\,PO_4$ (Equation b) does not go to completion for concretionary or iron-oxide coated iron phosphate (Jackson, 1958), so phosphorus from $Al\,PO_4$ can be fractionated by neutral 0.5 N - NH_4F extraction. The $(NH_4)_3\,Al\,F_6$ may precipitate in the presence of a large excess of fluoride.

4.2.3.2.2.1 Reagents

1. Ammonium fluoride (NH_4F),N: 37 g of NH_4F was dissolved in deionized water and the solution diluted to 1 litre and stored in a polyethylene bottle.

2. Hydrochloric acid, 0.5 N: 20.2 ml of concentrated H Cl was diluted to a volume of 500 ml with deionized water.

3. Extracting solution: 15 ml of 1.0 N NH_4F and 25 ml of 0.5 N H Cl were added to 460 ml of deionized water, to give

solutions of 0.03 N with respect to NH_4F and 0.025 N for H Cl.

4. Stannous chloride ($Sn\ Cl_2\ 2\ H_2O$), stock solution: 10 g of $Sn\ Cl_2$ was dissolved in 25 ml of concentrated H Cl and the solution kept in a refrigerator in a polyethylene bottle. A fresh solution was prepared every six weeks.

5. Ammonium molybdate: 15 g of ammonium molybdate was dissolved in 350 ml deionized water. 350 ml of 10 N H Cl was added to the flask slowly with stirring. The contents cooled and water added to obtain a volume of 1 litre. The solution was stored in a black glass-stoppered bottle. A fresh solution was prepared every one month.

6. Stannous chloride (dilute solution): 1 ml of $Sn\ Cl_2$ stock solution was mixed with 333 ml of deionized water. A fresh solution was prepared every 2 hr as needed.

4.2.3.2.2.2 Procedure

1 g of soil was weighed into an extraction bottle or tube and 7 ml of the extracting solution added. The container was shaken for 1 min. and the contents filtered through Whatman No. 42 paper. If the filtrate was not clear, the solution was poured back through the filter.

To 2 ml of the filtrate, 5 ml of deionized water and 2 ml of ammonium molybdate solution were added, and the contents well mixed. 1 ml of the $Sn\ Cl_2$ dilute solution was added and the solution mixed again. After 5 or 8 min. and before 15 min., the colour was measured at 660 mn. A standard curve was prepared including the 2 ml of extracting solution in the range of 0.2 to 10 ppm of phosphorus per ml.

The optical density of the standard was plotted against the concentration of phosphorus ppm. The concentration of extractable phosphorus was calculated as follows:-

ppm of phosphorus in soil = ppm of phosphorus in solution x $\frac{10}{2}$ x $\frac{7}{1}$

= ppm of phosphorus in solution x 35

Comments: variation in the ratios of soil to extracting solution and in the shaking times have been recommended by othersand also tried here.

The soil test values are interpreted in general as follows:-

<3 ppm, very low; 3 - 7 ppm, low; 7 - 20 ppm, medium and >20 ppm, high.

4.2.3.2.3 0.5 M acetic acid - Williams and Stewart's Method (1941)

4.2.3.2.3.1 Reagents

1. 0.5 M acetic acid: 28.3 ml of analar acetic acid was diluted to 1 litre with deionized water.

2. Sulphuric acid (3 N): 83.4 ml of analar $H_2 SO_4$ was added to a volumetric flask containing about 500 ml deionized water. The flask was cooled and the solution diluted to 1 litre with deionized water.

3. Ammonium molybdate solution: 5 g of $((NH_4)_6 MO_7 O_{24} 4 H_2O)$ was dissolved in water and diluted to 250 ml with deionized water.

4. Ascorbic acid solution: 4.4 g of reagent was dissolved in deionized water and diluted to 250 ml as this solution deteriorates slowly on standing, and it was best prepared fresh as required.

5. Reducing solution: A mixture of 125 ml of 3 N sulphuric acid, 38 ml of ammonium molybdate solution and 60 ml of ascorbic acid

solution were added to 250 ml with deionized water. The reagent solution was faint green in colour and should be prepared immediately before use.

6. Standard phosphorus solution: 0.4393 g. of KH_2PO_4 were weighed accurately and dissolved in deionized water. The solution was diluted to 1 litre with deionized water. The solution contained 100 ppm phosphorus per ml.

7. Dilute phosphorus solution: 20 ml of the standard phosphorus solution was diluted to 1 litre with deionized water. The solution contained 2 ppm of phosphorus per ml.

4.2.3.2.3.2 Procedure

10 g. of soil sample weighed into 4 oz. screw cap extraction bottles, and 100 ml 0.5 M acetic acid added. The bottles were shaken overnight. The extracts were filtered through Whatman No. 42 paper. A 5 ml aliquot of the extract was placed in a 25 ml volumetric flask. 15 ml of the reducing solution added and the flask gently shaken to mix, and the contents diluted to the mark. The solutions were allowed to stand overnight and the optical densities measured at 660 mn against the reagent blank. A standard curve was prepared as follows:-

Aliquots of dilute phosphorus solution containing from 0.5 to 10 ppm phosphorus were pipetted into 25 ml volumetric flasks, 5 ml of acetic acid extracting solution and 15 ml of the reducing solution added and the flask shaken well to mix the contents. The optical density was plotted against the concentration of phosphorus. The soil test values were

interpreted in general as follows:-

Low $<$2.2 mg/100 g ; High $>$4.5 mg/100 g .

4.2.3.2.4 0.5 M Ammonium acetate: a modification of Morgan's Method

4.2.3.2.4.1 Reagents

1. Ammonium acetate (0.5 M, pH 4.8)

38.54 g of ammonium acetate was dissolved in deionized water, the solution diluted to 1 litre with deionized water, the pH of the solution was adjusted to 4.8 with acetic acid. Other reagents used were described in 4.2.3.2.3.1.

4.2.3.2.4.2 Procedure

10 g of soil samples were weighed into 4 0Z screw cap extraction bottles, and 100 ml 0.5 M CH_3 COO NH_4 at pH 4.8 added, the bottles were shaken for 16 hr. then filtered through Whatman No. 42 paper. A 5 ml aliquot of the extract was placed in a 25 ml volumetric flask, 15 ml of the reducing solution added and the contents made up to the mark.

The solutions were allowed to stand overnight and the optical densities were measured at 660 nm against the reagent blank. A standard curve was prepared as for the previous procedure.

4.2.3.2.5 Anion-Exchange Resin Method (AER)

A fundamentally new approach to the problem of estimating soil phosphorus availability was made possible by the introduction of anion-exchange resins. An anion-exchange resin partially charged with

bicarbonate can be used in a simple procedure to estimate phosphate release from soil.

It is recommended that resin in the bicarbonate form should be used for both routine as well as more advanced analysis of the ability of soils to supply phosphate to plants.

A final procedure for the analysis is described here, see ChapterV, for a comparison and investigation for a suitable form of a resin.

4.2.3.2.5.1 Preparation and treatment of the resin

The resin was sieved by passing through an 85 mesh sieve. The coarse fraction which would not pass through the sieve was used. The resin was converted to the Cl^- form by eluting with M Na Cl solution and removing the excess chloride by washing with water. After cautious air-drying to facilitate handling of the resin, the beads, which had a diameter larger than 0.40 mm.

Transformation of the resins from the chloride form to other anionic forms (bicarbonate, hydroxyl) was carried out by column elution. Solution of 0.5 M Na H CO_3 or 0.5 m Na OH were added, until chloride could no longer be detected in the eluate. The excess ions were then removed with water and the resins were again air-dried.

4.2.3.2.5.2 Experimental Procedure

The resin used was Dowex 1 x 8 with a bead diameter of 0.4 to 0.8 mm. 4 gm sample of air-dried soil (passed through a 2 mm sieve) and 4 gm of resin were transferred to a 4 oz screw top shaking bottle. A

constant amount of water (100 ml) was used in all experiments and the contents shaken in a rotary shaker for 24 hours. After shaking, the suspension was transferred to a sieve (100 mesh sieve) to separate the resin from the soil. The pH of the soil suspension was then measured.

The resin beads were placed in a leaching tube and the phosphate removed by leaching with 1 M Na Cl solution.

Aliquots of 100 ml were collected in volumetric flasks and analysed (ascorbic acid method) until no more phosphate was detected. The amounts of phosphorus collected from the resin were added together to give the available phosphorus released from the soil.

4.2.3.2.6 Determination of total phosphorus in soils

Phosphorus occurs in soil in both inorganic and organic forms, the relative proportions of which vary with organic matter content. Usually the organic forms predominate. The element tends to accumulate in the finer fractions of soil and thus increases as the clay content increases.

The determination of total phosphorus in soils involves conversion of organic phosphorus to inorganic phosphorus and subsequent determination of orthophosphate in the extract. Selected procedures for analysis of total phosphorus in soils are described by Jackson (1958) and Mattingley and Talibudeen (1967). Three basic methods have been employed to bring the total phosphorus in a soil into solution - (i) digestion with strong acids, (2) Fusion with alkali ($Na_2 CO_3$) and (3) ignition followed by acid extraction. The acids recommended for digestion are perochloric or hydrofluoric acid.

Perochloric acid is preferred as silica is removed by filteration and methods exist for the determination of the resultant soluble phosphate in which perochloric acid does not interfere. Perochloric acid digestion procedures are more amenable to routine estimation of total phosphorus in a large number of soil samples. In this work, the digestions were carried out in conical flasks on a sand-bath at a temperature of 180 - 200°C instead of Kjeldahl apparatus as described by Jackson (1958). The objective of this study was to develop a simple procedure for extracting phosphorus from soils by $HClO_4$ digestion and determination of extracted orthophosphate with the ascorbic acid method of Murphy and Riley (1962) as modified by John (1970).

4.2.3.2.6.1 Procedure

All steps were carried out in a fume cupboard. A 2 g. of soil (100 mesh) was weighed and transferred to a 500 ml conical flask. 30 ml of aristar conc. HNO_3 was added. If the sample was high in organic matter, 20 ml of HNO_3 was used for ordinary soil. 30 ml of aristar perochloric $HClO_4$ acid was then added. The preliminary oxidation and digestion was carried out at 120°C on a sand-bath, designed to remove $HClO_4$ fumes. A funnel had to be used when refluxing the $HClO_4$ during the digestion step in the flask. With a slight increase of temperature up to 200°C, the $HClO_4$ digestion of the sample was carried out until the solution appeared colourless. Usually this required 4 - 5 hr. On completion of the digestion, dense white fumes of $HClO_4$ appeared and the silica became white. When the digestion was completed, the flask was removed, and after cooling, 2 -50 ml aliquots of deionized water were added and the solution transferred through a filter into a 250 ml

volumetric flask. The residue was washed with water and the volume adjusted to the mark. Reagent blanks were run in duplicate. All steps were carried out in parallel with the sample. Phosphorus was determined colorimetrically

Soil test: $<$ 44 mg/100 g. , low; $>$132 mg/100 g. , high.

4.2.3.2.7 Determination of total phosphorus in plant tissue (spruce needles

The phosphate in plants exists in both inorganic and organic forms. The inorganic fraction is largely concentrated in the vascular sap as orthophosphate ions (Russell, 1973).

The inorganic phosphate in the plants is usually some hundred times greater in concentration than that of the solution in which the plants are grown (Lawton, 1961). Hence, plants have the ability to extract and concentrate phosphate from the soil.

The organic phosphorus compounds in nature constitute an extremely diverse chemical group. Among the many types of phosphorus containing substances outlined by Arron (1953) are phytin, phospholipids, nucleoproteins and nucleic acids. Phosphorylated sugars, adenine nucleotides, pyridine nucleotides, flavin nucleotides and other phosphates that act as prosthetic groups of enzymes.

The proportion of plant phosphorus in organic and inorganic forms varies considerably depending on the part of the plant tested, the relative age of the plant tissue and to some extent, the nature of the extractant.

4.2.3.2.7.1 Procedure

Preparation of plant sample: wet oxidation.

Dry tissue sample at 70°C, individual spruce needles. The samples were ground to pass a 80 mesh screen. 1 g of dried powdered plant tissue was weighed out, transferred into a 500 ml conical flask and 5 ml of aristar HNO_3 added. The flask was swirled to moisten the entire mass of tissue, and then placed on a steam plate for 30 min. A funnel was placed at the top of the flask to exhaust the oxides of nitrogen and to condense untreated acid fumes. The suspension was boiled until nearly dry. The pre-digestion with nitric acid required approximately 45 min. The digestion flask and contents were cooled slightly, then an appropriate amount of the ternary mixture of acids (HNO_3 - H_2SO_4 $HClO_4$), ratio 10 : 1 : 4 added, consisting of 5 ml for each g of tissue used. Digestion was carried out at 180 - 200°C until dense white fumes of H_2SO_4 and $HClO_4$ were evolved. The digestion was continued at this temperature until the acid had largely volatilized. When the digestion was complete, the flask was removed. Once it cooled sufficiently, 50 ml of deionized water was added and the solution transferred through a filter to a 100 ml volumetric flask. The conical flask was washed with water and made to volume. An aliquot was taken for analysis by the phosphomolybdate method using ascorbic acid as reducing agent (see article 4.2.3.2.3.1). Reagent blanks were included in the analysis and were run in parallel with the samples.

4.2.3.2.8 Fractionation of soil phosphorus

Inorganic phosphates present in the soil can be classifed into

four main groups: calcium phosphate, aluminium phosphate, iron phosphate, and the reductant-soluble phosphate extractable after removal of the first three forms.

Neutral ammonium fluoride in a single extraction dissolves aluminium phosphate completely, iron phosphate slightly and apatite negligibly. When the phosphate extraction ratio corresponds to that of 1 gm soil to 50 ml extractant sodium hydroxide completely dissolves iron phosphate and aluminium phosphate but apatite not at all. Sulphuric acid dissolves apatite and aluminium phosphate and iron phosphate completely (Chang and Jackson, 1957).

The fluoride and alkali extractions, therefore, must precede the acid extraction to obtain complete separation of these three chemical forms of phosphate. The reductant soluble iron phosphate is dissolved by a reduction-chelation treatment with sodium dithionite-citrate after fluoride, alkali and acid extractions.

4.2.3.2.8.1 Fractionation of soil phosphorus was accomplished by the Chang and Jackson (1957) fraction method, with the variation that the organic matter present in the iron phosphate extract was flocculated and filtered instead of centrifuging.

Organic and inorganic phosphorus were estimated by the method of Mehta et al. (1954).

4.3 RESULTS AND DISCUSSION

The different procedures for estimating available phosphorus (Tables 4.01 - 4.05) have been compared and their relative efficiencies

judged by the degree of correlation obtained with phosphorus uptake by the plant (spruce needles) (Table 4.10).

The popularity of this approach is due to the fact that comparison of soil test values with analysis of plants grown on the soil offers, a simple and rapid method of evaluating the soil tests under a wide variety of conditions.

The 0.5 N Na H CO_3 method (Olsen et al., 1954) employs a solution of pH 8.5, designed to control the ionic acitivity of Ca, through the solubility product of Ca CO_3, during the extraction of calcareous soils. As the carbonate activity in the soil is raised by this solution, the calcium activity is decreased. Thus some phosphate from the surface of the calcium phosphate is extracted through the solubility product of calcium phosphate. As Ca activity decreases, phosphate activity increases. The importance of buffering carbonate during extraction is illustrated by the two trends produced by carbonic acid in calcare ous soils:

(a) a trend towards increased solubility of calcium phosphate as expected with an acid, and

(b) a trend towards decreased solubility of calcium phosphate owing to the increased calcium activity as Ca CO_3 is dissolved by the carbonic acid.

The reagent also extracts some phosphate from the surface of aluminium and iron phosphates, which are more abundant in acid and neutral soils (Tables 4.01 and 4.05). By depressing the aluminium and iron activities, the aluminium (Cole and Jackson, 1951) by aluminate complex

formation and iron (Chang and Jackson, 1957) by precipitation as the oxide, the phosphate activity is increased by the solubility product principle (Kittrick and Jackson, 1955). It is important to maintain the Ca activity low enough in all soils (alkaline, neutral, or acid) to prevent reprecipitation of the liberated phosphate as calcium phosphate.

Some serious technical problems arise in using 0.5 M sodium bicarbonate to extract available soil phosphate:

1. The most important factor is the appreciable quantities of organic matter which are dissolved, causing the extracts to vary in colour from pale yellow with mineral soils to dark brown with soils high in organic matter (see Chapter, III, Tables 3.12 and 3.14). Peats were very dark coloured indeed.

2. Olsen et al (1954) used activated charcoal to decolourize their soil extracts, but introduced new difficulties. None of the activated charcoal available in the United Kingdom was suitable because of the high soluble phosphate content.

3. Difficulties were experienced in obtaining clear filtrates of soil extracts especially from clay soils.

4. Stannous chloride was not entirely satisfactory for reducing the molybdophosphate complex because organic matter in soil extracts cause instability of the blue colour Watanable and Olsen(1962, 1965) used ascorbic acid as reducing agent to overcome these objections. The present study has confirmed that. The reproducibility and stability of the ascorbic acid method was shown to be superior to that of the stannous chloride process (Table 4.08). Olsen's method appears to be the only

reliable method for measuring soluble phosphorus in calcareous soils (Olsen et al., 1954; Matar and Samman, 1975). Much would be gained and nothing lost by introducing it to analyse all soils containing more than a few per cent of $CaCO_3$.

Olsen's method has also given good indications of phosphorus availability on neutral soils. The present study has confirmed this (Table 4.05). The method of Bray and Kurtz (1945) has been widely used as an index of available phosphorus in soils. The combination of HCl and NH_4F is designed to remove easily acid-soluble forms of phosphorus, largely calcium phosphates and a portion of the aluminium and iron phosphates (Olsen and Dean, 1965). The NH_4F dissolves aluminium and iron phosphates by its complex ion formation with these matal ions in acid solution. In general, this method has been recommended as being the most successful on acid soils. Some modifications used more extracting solution per unit weight of soil, and others increase the shaking time up to 5 min. Some serious problems arise:-

1. Many of the extracts were highly coloured especially these soils with organic matter (see Chapter III, Tables 3.12, 3.14).

2. Difficulties were experienced in obtaining clear filtrates of the soil extracts. Generally, the results obtained were more reproducible with anion-exchange resin method than with the acid-fluoride method (Tables 4.01 - 4.05 and 4.08).

The Advisory Service in Scotland generally recommends the 0.5 M CH_3COOH method (Williams and Stewart, 1941) for estimating available phosphorus in soils.

The present study revealed (Tables 4.01 - 4.05) that this extractant removes very small amounts of phosphorus, but the correlation is significant with uptake of phosphorus by spruce (Table 4.10). 0.5 M ammonium acetate extract adjusted to pH 4.8, a modification of the procedure of Morgan (1937) was recommended for estimating available phosphorus. The present study revealed that this extractant removes very very small amounts of phosphorus (Tables 4.01 -4.05), but the correlation is significant with uptake of phosphorus by spruce (Table 4.10). Very promising results were obtained with the anion-exchange resin method. The amounts of phosphorus extracted by AER as compared with the methods of Olsen et al (1954), Bray and Kurtz (1945), 0.5 M CH_3 COOH, 0.5 M CH_3 COO NH_4 (Tables 4.01 - 4.05). The results listed in Tables 4.01 - 4.05 gave the highest degree of correlation with the crop response (Table 4.10).

The possibility of measuring phosphorus release by the use of anion-exchange resin has been reported in previous studies (Amer et al., 1955; Gunary and Sutton, 1967; Bache and Rogers, 1970). So detection of the native (Scotland) forms of soil phosphorus which are the main sources of phosphorus sorbed by resin would be of great importance in identifying phosphorus potentially available to plants.

Sibbesen (1978) recommended that resins in the bicarbonate form should be used for both routine as well as more advanced analyses of the ability of soils to supply phosphate to plants. The present study has confirmed this. The bicarbonate form of the resin has an advantage over the chloride form, because the former is only slightly

dependent on the amount of soil and resin type used. Furthermore, the release of bicarbonate ions from the resin to the soil suspension resembles the natural, chemical conditions that are prevailing in the rhizosphere of actively growing plant roots.

The amount of phosphorus extracted by H CO_3 resin was much greater than by Cl resin from an acid soil. This has been confirmed recently by Bache and Ireland (1980), due to lower anion and higher desorbing anion concentration.

4.3.1 CORRELATIONS BETWEEN SOIL TEST DATA AND PHOSPHORUS FORMS

Comparisons were made between the soil test values and phosphorus forms by means of linear regression analysis. The simple linear correlation coefficients between soil phosphorus fractions and phosphorus extracted by soil test methods are shown in Table 4.10. Most of the extractants correlated highly with Al-P, except resin-P. Similar correlations were made between the sum of Al-P and Fe-P and soil test values. It appears that most of the methods used extracted some proportions of Al-P and Fe-P and to some extent other forms of phosphorus as revealed by the correlation coefficients (Table 4.10). Although the amount of phosphorus extracted by the different methods varied, many of the results were well correlated. It is probable that the same form or forms of phosphorus were being extracted by two tests which were closely correlated. However, this does not imply in all cases that the same or a proportional amount of phosphorus was being removed from each inorganic source by any two methods.

It has been reported (Chang and Juo, 1962) that correlations between soil tests and phosphorus forms depend on which form of phosphorus is dominant in soil, for example, the highly significant and positive correlation between phosphorus extracted by three of the soil test methods and Al-P and sum of Al-P and Fe-P.

4.3.2 CORRELATIONS OF PHOSPHORUS UPTAKE WITH SOIL TESTS

One of many purposes of the experimental plots in the Fiunary Forest (See Chapter II) was to measure seedling phosphorus uptake and use these to evaluate the various soil tests (Table 4.03).

Phosphorus extracted by Na H CO_3, NH_4 F, CH_3 COOH, NH_4 OAC resin and Al-P and sum of Al-P and Fe-P, total phosphorus in soil and total phosphorus in mycorrahiza were correlated with phosphorus uptake in spruce (Table 4.10).

Olsen phosphorus did not correlate significantly with phosphorus uptake (Table 4.10), many workers have reported poor correlation between Olsen phosphorus and phosphorus uptake (Olsen et al., 1954; Mattar and Samman, 1975). Bray phosphorus did correlate significantly with phosphorus uptake (Fig. 4.03). Many workers have reported a good correlation between Bray phosphorus and phosphorus uptake (Kacar and Shokravi, 1967; Enwezor, 1977). Further analysis of the pine data showed the 0.5 M NH_4 OAC (pH 4.8) and 0.5 M CH_3 OAC extractable P were significantly correlated with phosphorus uptake. The correlation coefficients were 0.707, 0.700 respectively. This is consistent with earlier work in which Wilde et al. (1965) and Alban (1972) found that NH_4 OAC, resin

0.002 N H_2 SO_4 extractable were significantly related to site index of red pine, which removes small amounts of phosphorus are more relevant for predicting fertilizer response of forest species (Alban, 1972; Humphreys and Pritchett, 1972). The resin extractable phosphorus correlated highly with uptake of the test plant and in all cases was superior to any other single measurement for predicting phosphorus uptake (Fig. 4.01).

Many workers have reported better correlation between the resin extractable phosphorus with uptake by plants than other methods using single extractants (Gunary and Sutton, 1967; Bache and Rogers, 1970; Metwally et al., 1975; Kodeba and Boyle, 1978).

This is presumably because it emulates the desorbing effect of plant roots better than the usual chemical extractants (Bache and Ireland, 1980). Advantages of the resin method are that it is not significantly influenced by soil characteristics such as texture and it does simulate the mode of phosphorus uptake by plants. Furthermore, soil total phosphorus gave the best correlation with resin extractable phosphorus (Fig. 4.02). This value was significant at the 1% level.

The correlation coefficients (r) of soil total phosphorus and soil extractable phosphorus were 0.457 with Olsen phosphorus 0.626 with Bray phosphorus 0.569 with 0.5 M CH_3 OAC and 0.554 with 0.5 NH_4 OAC (pH 4.8).

4.3.3 PHOSPHORUS UPTAKE IN RELATION TO OTHER SOIL PROPERTIES

Soil properties other than the forms of phosphorus influence the

Fig.4.01 The Correlation Of Resin Extractable P. With Plant Uptake Of P.

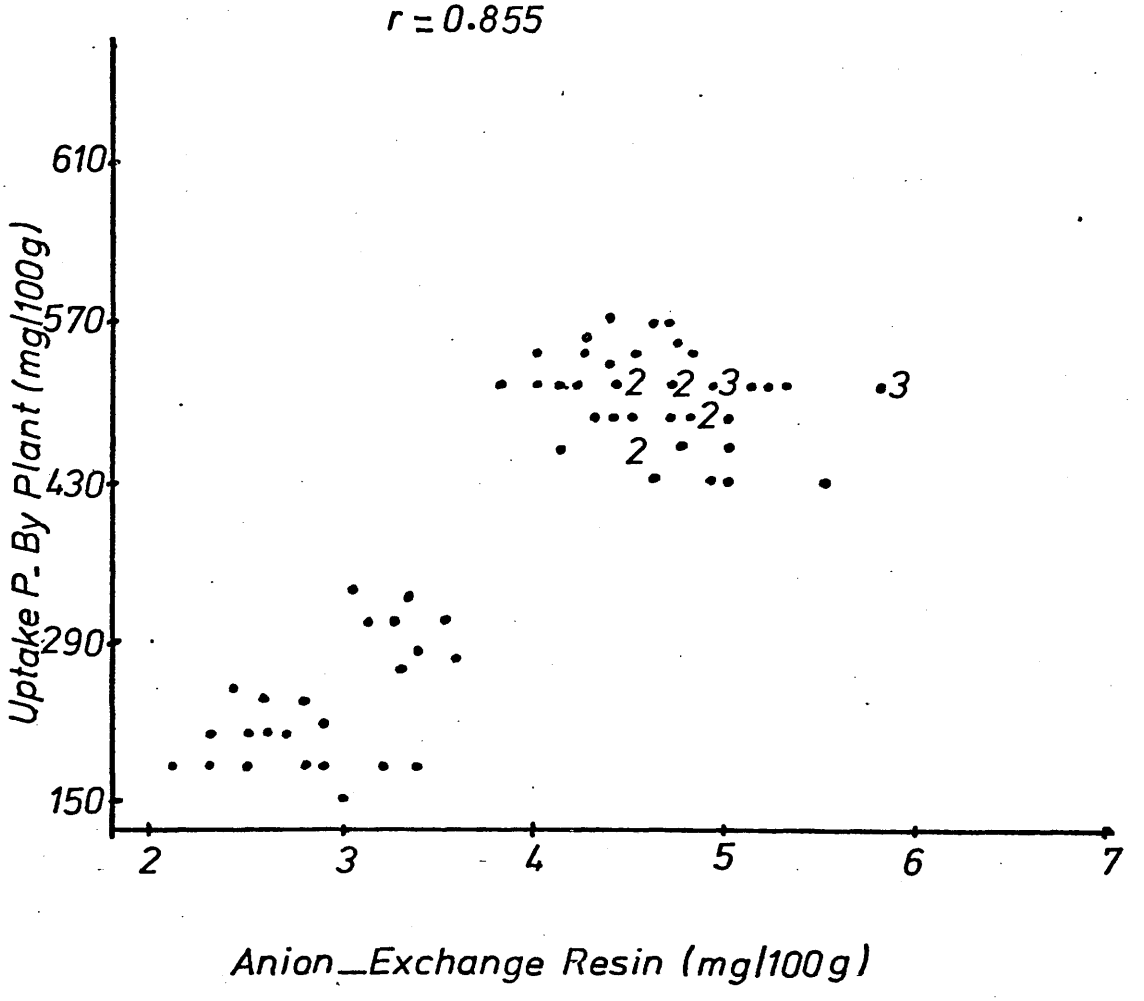


Fig.4.02. The Correlation Of Resin Extractable P. With Total P In Soil.

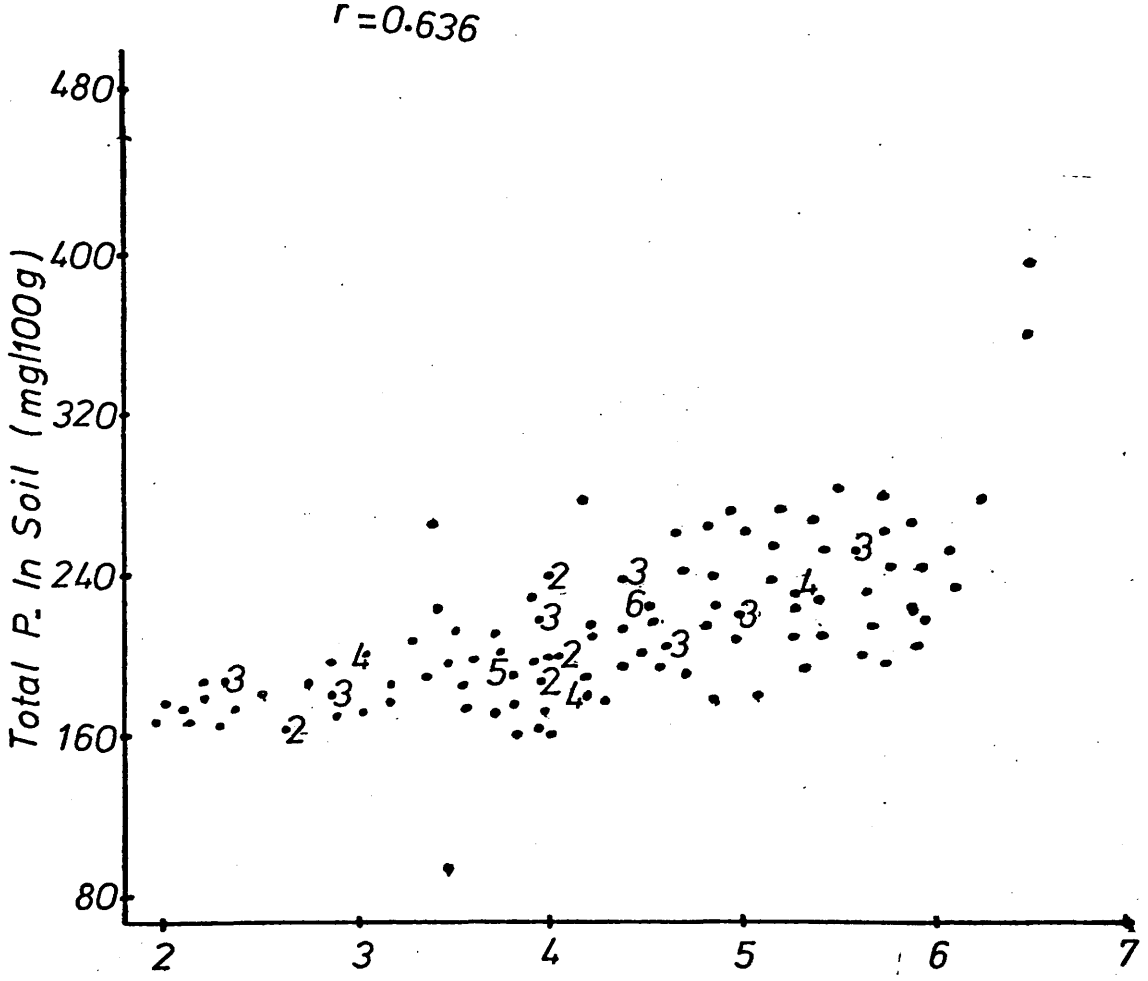


Fig.4.03 The Correlation Of Bray + Kurtz 's Method With Plant Uptake Of Phosphorus.

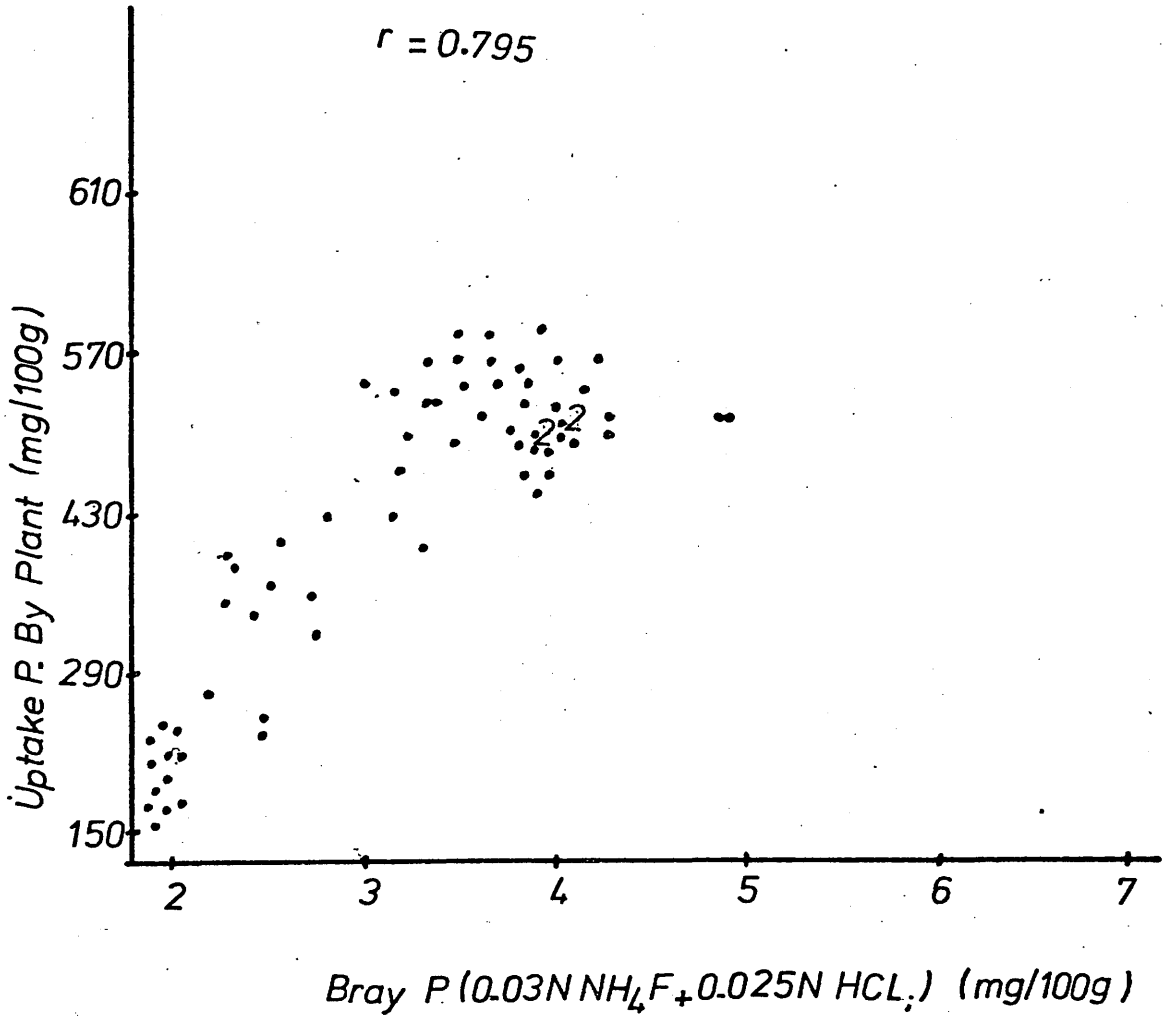
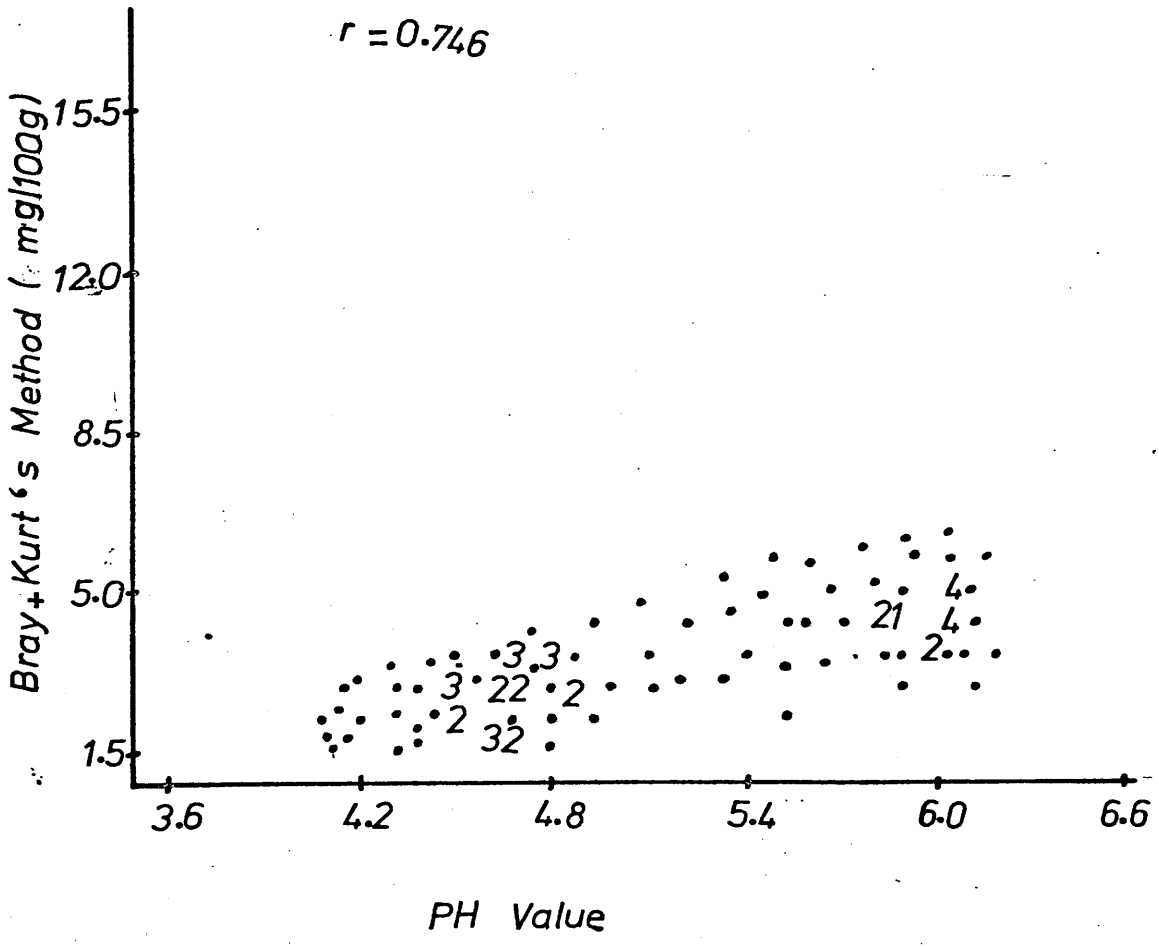


Fig.4.04 The Correlation Of Bray+Kurt's Method With PH Value.



amount of phosphorus absorbed from soil by a plant. In order to examine some of these and determine the merit of their inclusion in soil tests for routine evaluation of phosphorus availability, pH, organic matter, (Table 4.10) showed the simple correlation for the relationship between the soil variables, pH, organic matter available phosphorus. There is a positive and significant correlation between pH and uptake phosphorus by plant (r = 525).

The effect of pH on phosphorus uptake could result from the dependence on pH of the distribution of different inorganic phosphorus fractions in the soil and their relative solubility in the extractants. There is a very poor correlation between organic matter and phosphorus uptake. The organic forms of phosphorus are of importance in fertility. They are an indirect source of the soluble forms of phosphates, as well as nitrates when soil organic matter is decomposed.

Basalt brown earths contain large amounts of total phosphorus (Table 4.07). In the intermediate category are basic igneous granite and mica-schists. Total phosphorus in Pitmedden and Fiunary Forests (experimental plots) is very high (Tables 4.01, 4.03), with an average of 194.3 and 216.7 mg/100 g respectively (Table 4.07). Total phosphorus in Fiunary, Savary Glen in Morven, West Argyll, Salen Forest in Mull and Loch Eynort Forest in Skye (see Chapter II) is high (Tables 4.01 - 4.04). Total phosphorus in Hallbarns soil (Table 4.05) is very high.

4.3.4 ORGANIC PHOSPHORUS

The content of organic phosphorus in Pitmedden Forest varies from 321 - 1807 ppm, with an average of 1166, which comprises between 37.7% and 70% of the total phosphorus present, with an average of 58% (Table 4.07). The content of organic phosphorus in Fiunary Forest varies from 819 - 1550 ppm, with an average of 1318 ppm. This comprises between 53% and 65%, with an average of 62% (Table 4.07). There is a positive correlation (r = 0.519) between pH value and organic matter.

The more acid soils tend to accumulate more organic phosphorus. Thompson (1959), McDonnell and Walsh (1956). Williams and Saunders (1956), related soil phosphorus to texture. They concluded that this clay fraction contains most of the organic and inorganic phosphorus. This has been confirmed in this study. Black and Goring (1952) have suggested that the organic phosphorus accumulation in the acid soils of their study was due to the fact that the resistance to mineralization is greater in acid than in alkaline soil. This has been confirmed in this study.

4.3.5 INORGANIC PHOSPHORUS FORMS

Inorganic soil phosphorus has been reviewed in numerous publications, including Lyon et al. (1959), Thompson, (1959), Black, 1968 and Pierre et al. (1953).

The discussion which is largely based on these fractionations has been one of the approaches to a study of inorganic phosphorus. The Chang and Jackson fractionation results (Table 4.06) in six

fractions viz:

1. Water soluble phosphorus
2. Aluminium phosphate
3. Iron phosphate
4. Iron coated
5. Calcium phosphate
6. Occluded phosphate

The water soluble phosphorus probably includes soil solution phosphorus and saloid 'bound phosphorus', as cited by Black (1968) who noted that the orthophosphate in the soil solution averaged 0.03 ppm, hence the "water-soluble phosphorus" is mainly saloid bound and possibly consists of the more soluble phosphates such as sodium, potassium, magnesium and ammonium phosphates. In the present study, the average is 7 ppm and varies from 3 ppm to 12 ppm in Pitmedden Forest, with an average of 5 ppm at a variation from 2 ppm to 7.2 ppm in Fiunary Forest.

The aluminium phosphate average is 32 ppm and varies from 22 ppm to 52 ppm in Pitmedden. The aluminium phosphate average is 85 ppm and varies from 61 ppm to 94 ppm in Fiunary Forest (Table 4.06). It has been well known for many years that aluminium phosphate is closely associated with low pH and numerous workers have discussed aluminium phosphate in relation to free and soluble aluminium.

The iron phosphate varies from 107 ppm to 190 ppm, with an average of 158 ppm in Pitmedden Forest, and varies from 70 ppm to 102 ppm with an average of 84 ppm in Fiunary Forest (Table 4.06).

There was generally an increase in this fraction with lower pH, as has been observed by earlier workers. This relationship was closer than that for aluminium phosphate. There were also close relationships between the aluminium and iron, free aluminium, iron oxides and aluminium and iron phosphates.

The calcium phosphate varied from 286 ppm to 420 ppm, with an average 358 ppm, and from 192 ppm to 360 ppm, with an average 243 ppm, in Pitmedden and Fiunary Forests respectively (Table 4.06). The relationship of this fraction to pH and calcium content was also quite evident. The reductant soluble iron phosphate varies from 63 ppm to 98 ppm, with an average 77 ppm in Pitmedden Forest, and varies from 136 ppm to 226 ppm, with an average 188 ppm in Fiunary Forest. It was postulated that this is phosphate which has become coated with oxide.

The occluded phosphate is considered to be the least available and represents phosphorus physically bound within particles of soil materials. In Pitmedden Forest it represents less than 5.5% of the total inorganic phosphorus, with an average of 45.6 ppm. In Fiunary Forest it represents 32.5% of total inorganic phosphorus, with an average of 268 ppm.

It is noteworthy that this fraction in Scottish soils is different generally from that found in several American soils studied recently. Because of its nature (other physical and chemical properties), this fraction is probably one of the least available forms to plants. However, the thickness of the iron oxide film and the high soluble aluminium

content may be important considerations in its availability.

4.4 CONCLUSION

The most successful of the extractants for predicting phosphorus uptake was found to be anion exchange (AER). The correlation coefficient was 0.855, significant at 0.1%.

Phosphorus uptake by spruce correlated significantly with 0.03 N NH_4 F + 0.025 N H Cl Bray phosphorus - r = 0.795; 0.5 M NH_4 OAC phosphorus - r = 0.707, 0.5 M CH_3 OAC phosphorus - r = 0.700, 0.5 M Na H CO_3 phosphorus - r = 0.482.

The Anion exchange resin method in the bicarbonate form is very suitable for routine examination of soils under the conditions met in practice.

For acid soils, the phosphorus extracted by H CO_3 - resin was much greater than that by Cl-resin.

The advantages of the resin method are that it is not significantly influenced by soil characteristics such as texture and other soil properties. The results support the general observation that extractants which remove small amounts of phosphorus, for example, ammonium fluoride, acetic acid are more useful in evaluating short-term phosphorus availability in forest soils.

TABLE 4.01

Amounts of phosphorus in the soils as determined by different methods (mg/100 g)

No.	Soil (Pitmedden Forest)	Olsen's 0.5 M $NaHCO_3$ (pH 8.5)	Bray and Kurtz 0.03N NH_4F + 0.025 N HCl.	Williams and Stewart 0.5 M CH_3COOH	Modification of Morgan's 0.5 M CH_3COONH_4 (pH 4.8)	Anion-Exchange Resin	Total Phosphorus in soil	Total Phosphorus in Mycorrhiza	Total Phosphorus in spruce needles
1.	Pit. 1A	4.25	3.93	2.25	2.65	4.95	224.0	425	490
2.	Pit. 1B	4.35	3.85	2.00	2.25	4.85	180.6		
3.	Pit. 2A	4.60	4.20	2.45	2.70	5.10	196.8	430	500
4.	Pit. 2B	4.20	4.00	2.16	2.30	4.50	166.8		
5.	Pit. 3A	4.50	4.20	2.00	2.40	4.90	197.6	436	500
6.	Pit. 3B	4.10	3.95	2.00	2.18	4.45	180.0		
7.	Pit. 4A	5.20	5.00	2.60	2.80	5.90	226.9	445	510
8.	Pit. 4B	5.40	4.95	2.95	3.10	5.94	210.6		
9.	Pit. $4B_3$	4.86	4.60	2.20	2.30	5.10	185.0		
10.	Pit. $4A_1$	4.80	4.75	2.20	2.50	5.95	220.0		
11.	Pit. 5A	4.45	4.20	2.10	2.30	5.00	224.0	430	
12.	Pit. 5B	4.10	3.95	2.00	2.00	4.50	178.8		
13.	Pit. 5Bg	4.00	3.90	1.80	1.90	4.30	165.5		
14.	Pit. 5Cg	3.10	2.95	1.82	1.85	3.60	85.0		
15.	Pit. 6A	4.40	4.10	1.90	1.98	4.73	170.8		
16.	Pit. 6B	3.40	3.20	1.80	1.70	3.85	160.0		
17.	Pit. $7A_1$	5.20	4.90	2.95	3.00	5.30	230.6		510
18.	Pit. $7B^1$	4.90	4.20	2.60	2.80	4.90	178.2		
19.	Pit. $7A_2$	4.80	4.90	2.80	2.95	5.50	225.6		
20.	Pit. $8A_1^2$	5.00	4.70	2.40	2.50	5.10	240.8		
21.	Pit. $9A_1$	5.60	5.10	3.00	2.95	5.90	256.3		520
22.	Pit 9B	5.50	5.00	2.80	2.90	5.60	250.8		
23.	Pit. $11A_1$	5.70	5.20	3.00	3.60	6.60	396.8		

TABLE 4.02

Amounts of phosphorus in the soils as determined by different methods (mg/100 g)

No.	Soil Fiunary and Savary Glen Forests	Olsen's 0.5 M Na H CO_3 (pH 8.5)	Bray and Kurtz 0.03 N NH_4 F + 0.025 N H Cl.	Williams and Stewart 0.5 M CH_3 COOH	Modification of Morgan's 0.5 M CH_3 COO N H_4 (pH 4.8)	Anion-Exchange Resin	Total Phosphorus in soil
1.	Fiunary 2A	0.9	1.7	1.5	1.6	2.3	148.0
2.	Fiunary 2B	1.1	1.9	1.4	1.6	2.5	158.8
3.	Fiunary B_2 (micaschist)	1.2	2.2	1.5	1.5	2.7	140.0
4.	Fiunary 2C	1.0	1.8	1.3	1.5	2.2	130.4
5.	Fiunary $2A_{ie}$	0.0	1.2	1.0	1.3	2.5	135.0
6.	Fiunary $1A_1$	1.0	2.4	1.2	1.6	2.7	230.0
7.	Fiunary, Savary Glen $5A_1$	0.9	2.1	1.3	1.5	2.5	236.0
8.	Fiunary 5, Savary Glen A	0.8	2.3	1.5	1.7	2.7	186.0
9.	Fiunary, Savary Glen B	0.7	2.0	1.2	1.4	2.4	170.0
10.	Fiunary, Savary Glen C	0.6	1.7	1.0	1.2	2.2	158.9
11.	Fiunary, Savary Glen An2	0.0	1.3	1.0	1.1	2.3	140.8
12.	Fiunary, Savary Glen $5B_2$	0.8	1.9	1.1	1.2	2.7	180.8
13.	Savary Glen A_1	0.6	1.95	1.0	1.2	2.8	160.5
14.	Savary Glen B_2	0.8	1.9	1.1	1.2	2.6	145.0
15.	Savary Glen B_3	0.8	1.8	1.0	1.1	2.5	132.8
16.	Savary Glen C	0.6	1.7	0.8	1.0	1.9	125.0

TABLE 4.03

Amounts of phosphorus in the soils as determined by different methods (mg/100 g)

No.	Soil Fiunary Forest Experimental Plots	Olsen's 0.5 M Na H CO_3 (pH 8.5)	Bray and Kurtz 0.03N NH_4 F + 0.025 N H Cl.	Williams and Stewart 0.5 M CH_3 COOH	Modification of Morgan's 0.5 M CH_3 COO N H_4 (pH 4.8)	Anion-Exchange Resin	Total Phosphorus in soil	Total Phosphorus in Mycorrhiza	Total Phosphorus in spruce needles
1.	1 BML A	2.00	4.20	1.30	1.40	5.20	227.4	425	520
2.	1 BML B	2.10	3.95	1.62	1.66	5.00	220.5		
3.	3 BML A	1.86	4.10	1.20	1.26	4.50	238.7	390	485
4.	3 BML B	1.80	3.88	1.37	1.40	5.00	219.8		
5.	4 BML A	2.00	4.00	1.25	1.35	5.00	233.0	400	510
6.	4 BML B	1.80	3.90	1.60	1.67	4.60	228.0		
7.	5 BF A	1.78	3.75	1.24	1.30	4.70	215.1	500	560
8.	5 BF B	1.65	3.18	1.70	1.73	4.60	203.0		
9.	14 BF A	1.85	3.00	1.50	1.60	4.10	220.8	520	550
10.	14 BF B	1.60	2.90	1.62	1.65	4.00	213.2		
11.	17 BF A	1.90	3.30	1.45	1.52	4.40	230.0	510	540
12.	17 BF B	1.75	3.00	1.60	1.63	4.00	218.0		
13.	2 BFP A	2.20	4.00	1.62	1.66	5.00	238.9	530	520
14.	2 BFP B	2.00	3.70	1.80	1.86	4.30	213.2		
15.	11 BFP A	2.10	3.97	1.70	1.77	4.80	228.0	500	500
16.	11 BFP B	1.90	3.60	1.96	1.92	4.20	206.3		
17.	19 BFP A	1.90	3.93	1.78	1.82	4.85	226.8	505	510
18.	19 BFP B	1.72	3.75	1.90	1.95	4.40	210.5		
19.	9 BMP A	1.98	4.00	1.80	1.85	5.00	213.7	365	460
20.	9 BMP B	1.80	3.85	1.95	1.95	4.40	203.0		
21.	13 BMP A	2.10	3.95	1.45	1.50	4.50	226.9	330	440
22.	13 BMP B	2.18	3.90	1.60	1.55	5.30	206.8		
23.	20 BMP A	2.00	2.88	1.46	1.50	4.90	232.5	350	430
24.	20 BMP B	1.94	2.25	1.50	1.60	4.60	212.0		

continued ...

TABLE 4.03

continued

No.	Soil Fiunary Forest Experimental Plots	Olsen's 0.5 M Na H CO_3 (pH 8.5)	Bray and Kurtz 0.03N NH_4 F + 0.025 N H Cl.	Williams and Stewart 0.5 M CH_3 COOH	Modification of Morgan's 0.5 M CH_3 COO N H_4 (pH 4.8)	Anion-Exchange Resin	Total Phosphorus in soil	Total Phosphorus in Mycorrhiza	Total Phosphorus in spruce needles
25.	7 BM A	1.20	1.65	0.00	0.00	2.90	190.2	260	198
26.	7 BM B	1.40	1.95	1.00	1.20	2.10	168.7		
27.	10 BM A	1.20	1.85	0.85	1.10	2.70	188.0	240	210
28.	10 BM B	1.22	1.90	1.00	1.50	2.50	160.6		
29.	21 BM A	1.10	1.70	0.80	1.10	2.60	190.7	230	190
30.	21 BM B	1.22	1.98	0.70	1.00	2.30	172.0		
31.	15 SR BM A	1.00	1.80	0.80	1.30	2.25	185.0	185	176
32.	15 SR BM B	1.00	1.90	0.70	1.20	2.10	168.4		
33.	18 SR BM A	1.10	1.70	0.00	1.00	2.20	192.9	170	160
34.	18 SR BM B	1.10	1.85	0.8	1.30	2.10	175.0		
35.	Compartment 302								
36.	1 BM A	1.20	1.85	0.92	0.96	2.80	190.0	250	185
37.	1 BM B	1.00	1.80	0.80	1.20	2.30	165.2		
38.	2 BML A	1.37	2.50	1.20	1.60	4.20	195.8	390	494
39.	2 BML B	1.20	2.40	1.40	1.60	3.80	178.7		
40.	3 BMP A	1.22	2.35	1.37	1.90	4.50	206.8	375	450
41.	3 BMP B	1.50	2.30	1.50	1.58	4.10	180.0		

TABLE 4.04

Amounts of phosphorus in the soils as determined by different methods (mg/100 g.)

No.	Soil Salen, Aut-Dabloch Forests	Olsen's 0.5 M Na HCO_3 (pH 8.5)	Bray and Kurtz 0.03 N NH_4 F + 0.025 N H Cl.	Williams and Stewart 0.5 M CH_3 COOH	Modification of Morgan's 0.5 M CH_3 COO N H_4 (pH 4.8)	Anion-Exchange Resin	Total Phosphorus in Soil
1.	Salen 1 A_1 (0 - 3)	0.9	2.6	1.3	1.5	3.1	188.5
2.	Salen 1 A_1 (7 - 9)	1.2	3.3	1.5	1.7	4.0	198.2
3.	Salen 1 A_{12} (7 - 10)	1.2	3.5	1.56	1.8	4.1	282.5
4.	Salen 6 A_1 (4 - 6	1.1	3.2	1.6	1.75	3.9	235.8
5.	Salen 6 C_{14} - 21	2.3	3.1	1.5	1.8	3.8	178.2
6.	Out Byeland Mull A_2	0.9	2.3	1.7	2.0	3.2	258.8
7.	Mull A_4	1.0	3.3	1.8	3.0	4.0	230.0
8.	Mull B_5	1.3	3.10	1.5	2.2	4.0	182.5
9.	Mull B_{10}	1.4	3.3	1.6	2.1	3.95	176.5
10.	Mull C_{23}	1.5	3.3	1.8	1.95	3.80	165.2
11.	Mull C_{24}	1.7	3.8	1.7	1.9	4.0	160.0
12.	Aut Dabhoch 1A_1	1.3	2.7	1.5	1.6	3.7	210.2
13.	Aut Dabhoch 2A	1.4	3.0	1.4	1.5	3.93	225.0
14.	Aut Dabhoch 1B_2 (3 - 5)	1.5	3.4	1.5	1.6	4.0	194.2
15.	Aut Dabhoch B_2 (6 - 8)	1.55	3.5	1.6	1.6	4.1	198.6
16.	Aut Dabhoch 2B_2 (5 - 9)	1.5	3.5	1.5	1.7	3.85	186.0
17.	Aut Dabhcch C_{12-17}	1.6	3.2	1.6	1.8	3.80	182.9
18.	Aut Dabhoch 2C_{15}	1.9	3.1	1.6	1.8	3.88	175.0
19.	Aut Dabhoch 2C_{20}	2.1	3.2	1.7	1.7	3.70	166.2
20.	Aut Dabhoch B_3	2.0	3.4	1.5	1.7	3.90	195.0

TABLE 4.05

Amounts of phosphorus in the soils as determined by different methods (mg/100 g.)

No.	Soil Hallborns Soil	Olsen's 0.5 M Na HCO_3 (pH 8.5)	Bray and Kurtz 0.03 N NH_4F + 0.025 N H Cl.	Williams and Stewart 0.5 M CH_3COOH	Modification of Morgan's 0.5 M CH_3COONH_4 (pH 4.8)	Anion-Exchange Resin	Total Phosphorus in Soil
1.	Arran	10.0	9.2	5.8	5.95	9.9	270.0
2.	Byre	9.6	9.2	8.8	9.0	9.8	295.9
3.	Craig	14.0	12.5	10.0	11.8	14.1	280.9
4.	Cramel Bank	8.95	8.0	6.6	7.1	8.8	265.7
5.	Barley Field A	13.5	12.0	9.5	10.4	14.0	340.0
6.	Barley Field B	12.0	11.2	8.6	9.8	13.0	238.8
7.	Frost	9.5	8.3	8.1	8.6	10.8	274.5
8.	Holim	14.6	13.2	12.0	12.8	14.0	295.5
9.	Home Field	12.5	10.8	9.4	10.3	13.0	277.0
10.	How Thora	8.9	7.9	7.7	8.0	9.1	250.2
11.	Meadow	10.4	9.6	9.2	9.5	10.6	280.2
12.	Mid-Arran	11.0	9.7	9.5	9.6	10.8	270.0
13.	Spinery	8.84	7.85	6.8	6.95	8.75	260.3
14.	Rose	9.5	8.6	8.2	8.2	9.9	244.2
15.	White Hiedi	8.8	7.5	7.3	7.2	9.1	230.8
16.	Barley Field	7.8	6.8	6.6	6.7	7.6	250.0

TABLE 4.06

Soil Phosphorus Fractionation

No.	Soil Pitmedden Forest	Inorganic Phosphorus Fractions (mg/100 g:)							
		Water Soluble	Al	Fe	Ca	Reductant Soluble Fe-Phosphate	Occluded Al-Fe	Active	Total
1.	Pit. 1A	0.8	4.1	10.7	42.0	6.8	4.0	56.8	68.6
2.	Pit. 1B	0.9	3.7	16.4	37.2	6.4	4.6	57.3	69.2
3.	Pit. 2A	0.9	3.4	13.2	39.6	7.0	4.2	56.2	68.7
4.	Pit. 2B	1.1	3.1	18.1	39.0	6.6	4.5	60.2	72.8
5.	Pit. 3A	0.9	3.8	12.3	37.2	7.6	4.1	53.3	65.9
6.	Pit. 3B	1.0	2.7	17.8	34.7	7.8	5.0	55.2	69.8
7.	Pit. 4A	1.1	3.7	14.2	38.2	6.3	4.2	56.1	67.7
8.	Pit. 4B	0.9	2.5	19.2	35.7	7.6	5.1	57.2	71.6
9.	Pit. $4B_3$	0.8	2.2	19.5	37.8	8.9	4.2	59.2	74.4
10.	Pit. 5A	0.5	4.0	13.0	34.0	7.2	4.3	53.0	65.0
11.	Pit. 5B	0.3	3.1	18.2	28.6	9.3	5.0	49.9	64.5
12.	Pit. 5Bg	1.0	2.7	17.6	31.0	8.6	3.6	50.9	64.1
13.	Pit. 5Cg	0.8	2.0	16.0	30.1	8.1	2.2	38.1	49.4
14.	Pit. 6A	1.2	5.2	17.2	35.2	7.6	5.6	57.6	72.0
15.	Pit. 6B	1.1	5.0	19.8	30.9	9.8	6.9	55.7	73.5
16.	Pit. $7A_1$	0.9	3.5	15.3	35.2	7.5	4.2	54.0	66.6
17.	Pit. $7A_2$	0.7	3.3	14.2	38.9	7.8	4.6	56.4	67.6
18.	Pit. 7B	1.0	2.7	18.2	41.2	8.3	5.3	62.1	76.7
19.	Pit. $8A_1$	0.7	2.8	14.5	35.1	8.1	5.0	52.4	66.2
20.	Pit. $9A_1$	1.3	3.2	15.6	37.2	8.0	4.5	56.0	69.8
	Overall	0.7	3.2	15.8	35.8	7.7	4.56	55.0	68.1
	Minimum	0.3	2.2	10.7	28.6	6.3	2.2	38.1	49.4
	Maximum	1.2	5.2	19.0	42.0	9.8	6.9	60.2	76.7

continued . . .

TABLE 4.06

continued

No.	Soil Fiunary Forest Expt. Plots	Inorganic Phosphorus Fractions (mg/100 g)							
		Water Soluble	Al	Fe	Ca	Reductant Soluble Fe-Phosphate	Occluded Al-Fe	Active	Total
21.	1 BML A	0.6	6.2	7.8	33.2	14.6	14.2	47.6	76.0
22.	1 BML B	0.5	7.8	8.2	30.0	16.3	16.8	46.0	79.6
23.	3 BML A	0.6	6.9	8.5	34.2	13.6	15.3	49.6	79.1
24.	3 BML B	0.6	8.3	9.6	30.0	15.8	17.6	47.9	81.9
25.	4 BML A	0.7	6.1	8.9	36.0	15.3	13.2	51.0	80.6
26.	4 BML B	0.5	7.3	10.2	28.7	16.1	17.8	46.2	80.6
27.	5 BF A	0.5	8.3	7.0	24.3	17.5	18.2	39.6	75.8
28.	5 BF B	0.4	8.9	8.7	20.9	20.0	20.0	38.5	78.9
29.	14 BF A	0.4	8.2	6.8	23.3	18.3	17.8	38.3	74.8
30.	14 BF B	0.3	8.8	8.5	18.2	20.6	19.7	35.5	76.1
31.	2 BFP A	0.65	8.5	7.2	20.6	19.1	28.8	36.3	84.8
32.	2 BFP B	0.5	9.0	8.3	19.2	20.8	20.9	36.5	78.4
33.	11 BFP A	0.6	8.0	7.6	21.8	19.6	29.8	37.4	87.4
34.	11 BFP B	0.45	8.8	8.9	19.6	21.0	26.8	37.3	85.5
35.	19 BFP A	0.7	7.8	8.0	23.8	20.0	26.9	39.6	87.2
36.	9 BMP A	0.72	8.6	8.9	25.0	21.3	28.9	42.5	94.5
37.	9 BMP B	0.6	9.0	9.6	20.0	22.6	28.8	38.6	90.6
38.	13 BMP A	0.65	8.5	8.3	24.3	19.5	26.2	41.0	87.3
39.	13 BMP B	0.55	9.4	8.5	19.6	21.3	25.0	37.5	84.3
40.	7 BM A	0.2	6.6	10.2	20.1	21.3	22.9	36.9	84.4
41.	7 BM B	0.3	7.2	9.0	17.8	22.6	26.9	35.0	84.7
	Overall	0.5	8.5	8.4	24.3	18.8	26.8	40.8	78.2
	Minimum	0.2	6.1	7.0	18.2	13.6	13.2	35.0	74.8
	Maximum	0.72	9.4	10.2	36.0	22.6	29.8	51.0	90.6

TABLE 4.07

Inorganic, organic and total phosphorus in soils (mg/100 g)

No.	Soil Pitmedden Forest	Inorganic phosphorus	Organic phosphorus	Total phosphorus	% inorganic phosphorus	% organic phosphorus
1.	Pit. 1A	73.3	150.7	224.0	32.7	67.3
2.	Pit. 1B	74.0	106.6	180.6	41.0	59.0
3.	Pit. 2A	73.8	123.0	196.8	37.5	62.5
4.	Pit. 2B	77.3	89.5	166.8	46.4	53.6
5.	Pit. 3A	70.7	126.9	197.6	45.8	64.2
6.	Pit. 3B	76.0	103.7	180.0	42.5	57.5
7.	Pit. 4A	73.5	153.4	226.9	32.4	67.6
8.	Pit. 4B	77.5	133.4	210.5	36.7	63.3
9.	Pit. $4B_3$	79.5	105.5	185.0	43.0	57.0
10.	Pit. 5A	69.8	154.2	224.0	31.2	68.8
11.	Pit. 5B	68.8	110.0	178.8	38.5	61.5
12.	Pit. 5Bg	68.4	97.0	165.5	41.4	58.6
13.	Pit. 5Cg	52.9	32.1	85.0	62.3	37.7
14.	Pit. 6A	76.7	83.3	160.0	48.0	52.0
15.	Pit. 6B	77.4	93.4	170.8	45.3	54.7
16.	Pit. $7A_1$	71.9	158.7	230.6	31.2	68.8
17.	Pit. $7A_2$	72.8	152.8	225.6	32.3	67.7
18.	Pit. 7B	80.2	98.0	178.2	45.0	55.0
19.	Pit. $8A_1$	71.0	169.8	240.8	29.5	70.5
20.	Pit. $9A_1$	75.6	180.7	256.3	29.3	70.3
	Overall	73.0	116.6	194.3	42.0	58.0
	Minimum	52.9	32.1	85.0	29.3	37.7
	Maximum	80.2	180.7	256.3	62.3	70.5

continued ...

TABLE 4.07

continued

No.	Soil Fiunary Forest Expt. plots	Inorganic phosphorus	Organic phosphorus	Total phosphorus	% inorganic phosphorus	% organic phosphorus
21.	I BML A	81.0	146.4	227.4	35.6	64.4
22.	1 BML B	84.5	136.0	220.5	38.9	61.1
23.	3 BML A	84.0	154.7	238.7	35.2	64.8
24.	3 BML B	86.0	133.8	219.8	39.2	60.8
25.	4 BML A	85.2	148.5	233.7	36.5	63.5
26.	4 BML B	84.6	143.0	228.0	37.3	62.7
27.	5 BF A	80.5	134.6	215.1	37.5	62.5
28.	5 BF B	83.4	119.6	203.0	41.1	58.9
29.	14 BF A	79.5	141.3	220.8	36.1	63.9
30.	14 BF B	80.2	133.0	213.2	37.6	62.4
31.	2 BFP A	89.8	149.1	238.9	37.6	62.4
32.	2 BFP B	82.9	130.3	213.2	38.9	61.1
33.	11 BFP A	92.2	135.8	228.0	40.4	59.6
34.	11 BFP B	90.8	115.5	206.3	44.1	55.9
35.	19 BFP A	92.3	144.5	236.8	39.0	61.0
36.	9 BMP A	99.5	114.2	213.7	46.6	53.4
37.	9 BMP B	95.1	108.0	203.0	46.8	53.2
38.	13 BMP A	92.3	134.6	226.9	40.7	59.3
39.	13 BMP B	89.8	117.0	206.8	43.4	56.6
40.	7 BM A	86.4	103.8	190.2	45.4	54.6
41.	7 BM B	86.9	81.9	168.7	51.5	48.5
	Overall	82.4	131.8	216.7	37.9	62.1
	Minimum	79.5	81.9	168.7	35.6	48.5
	Maximum	92.3	154.7	238.9	51.5	64.8

TABLE 4.08

Precision of data for phosphorus determination on five different extracts, from five soil samples by the proposed ascorbic acid method and the Sn - HCl method.

No.	Extractant	Soil Samples	Ascorbic acid method Mean ppm S. D.	Overall S. D.	Sn - HCl Method Mean ppm S. D.	Overall S. D.
1.	Anion-Exchange Resin	Arran	99.0 ± 0.19		96.4 ± 0.38	
		Craig	141.0 ± 0.23		138.0 ± 0.60	
		Byre	98.0 ± 0.37		95.0 ± 0.62	
		Cramel Bank	88.0 ± 0.22		86.2 ± 0.48	
		Spinery	87.5 ± 0.26	0.25	84.8 ± 0.40	0.52
2.	Bray and Kurtz ($0.03\ N\ NH_4F$ + $0.025\ N\ HCl$)	Arran	92.0 ± 0.21		88.0 ± 0.48	
		Craig	125.0 ± 0.26		122.0 ± 0.60	
		Byre	92.0 ± 0.38		88.5 ± 0.52	
		Cramel Bank	80.0 ± 0.28		76.6 ± 0.55	
		Spinery	78.5 ± 0.31	0.288	72.0 ± 0.68	0.566
3.	Olsen ($0.5\ M\ NaHCO_3$) pH 8.5	Arran	100.0 ± 0.26		94.0 ± 0.48	
		Craig	140.0 ± 0.36		127.0 ± 0.64	
		Byre	96.0 ± 0.28		90.0 ± 0.68	
		Cramel Bank	89.5 ± 0.38		82.3 ± 0.55	
		Spinery	88.4 ± 0.21	0.30	83.6 ± 0.66	0.63
4.	$0.5\ M\ CH_3COOH$	Arran	58.0 ± 0.29		62.0 ± 0.44	
		Craig	100.0 ± 0.37		98.6 ± 0.74	
		Byre	88.0 ± 0.66		86.5 ± 0.72	
		Cramel Bank	66.0 ± 0.39		64.2 ± 0.76	
		Spinery	68.0 ± 0.50	0.44	66.0 ± 0.68	0.67
5.	$0.5\ M\ CH_3COONH_4$	Arran	59.5 ± 0.44		61.0 ± 0.64	
		Craig	118.0 ± 0.38		110.0 ± 0.68	
		Byre	90.0 ± 0.36		88.0 ± 0.66	
		Cramel Bank	71.0 ± 0.38		70.0 ± 0.74	
		Spinery	69.5 ± 0.55	0.422	68.0 ± 0.89	0.722
	All Extracts			0.34		0.63

TABLE 4.09

Soil Phosphorus Analytical Methods

No.	Method	Extractant	Time of Shaking (Contact time)	Soil : Extractant Ratio
1.	Available Phosphorus: Olsen	0.5 M Na H CO_3 at pH 8.5	30 min.	1 : 20
2.	Available Phosphorus: Bray 1	0.63 N NH_4F + 0.025 N HCl	1 min.	1 : 7
3.	Available Phosphorus: Williams and Stewart	0.5 M CH_3 COOH	16 hr.	1 : 10
4.	Available Phosphorus: A modification of Morgan's method	0.5 M CH_3 COO NH_4 at 4.8	16 hr.	1 : 10
5.	Available Phosphorus: AER	Bicarbonate-Resin, 1 MNaCl	24 hr.	1 : 25
6.	Water-soluble Phosphorus (Chang and Jackson)	1 N NH_4 Cl	0.5 hr.	1 : 50
7.	Aluminium Phosphorus (Chang and Jackson)	0.5 N NH_4F	1.0 hr.	1 : 50
8.	Iron Phosphorus (Chang and Jackson)	0.1 N Na OH	17.0 hr.	1 : 50
9.	Calcium Phosphorus (Chang and Jackson)	0.5 N H_2 SO_4	1.0 hr.	1 : 50
10.	Reductant Solution Iron Phosphorus (Chang and Jackson)	0.3 M Na citrate	15 min.	1 : 40
11.	Occluded (Chang and Jackson)	0.5 N NH_4 F	1.0 hr.	1 : 50
12.	Organic Phosphorus (Mehta et al.)	H Cl, 0.5 N Na OH	12.0 hr.	1 : 250
13.	Inorganic Phosphorus (Mehta et al.)	H Cl, 0.5 N Na OH	12.0 hr.	1 : 250
14.	Total Phosphorus (Modification of Jackson's method)	H NO_3, H Cl O_4	6.0 hr.	1 : 10 : 15

TABLE 4.10

Simple correlation coefficients relating phosphorus extracted by soil test method and total phosphorus in soil, Mycorrhiza, spruce and other soil properties. (P = phosphorus)

No.		Soil Tests									
		AER	Olsen P	Bray P	CH_3 OAC P	NH_4 OAC P	pH Value	0. M	Total P	P uptake (spruce)	Total P in Mycorrhiza
1.	Olsen P	0.663*									
2.	Bray P	0.901*	0.741*								
3.	CH_3OAC P	0.793*	0.828*	0.819*							
4.	NH_4OAC P	0.789*	0.852*	0.839*							
5.	pH Value	0.639*	0.832**	0.746*	0.650*	0.683**					
6.	0. M	0.285	0.640	0.383	0.503	0.509	0.519				
7.	Total P	0.636**	0.457**	0.626**	0.569**	0.554**	0.418	0.356			
8.	P uptake (spruce)	0.855*	0.482**	0.795*	0.700*	0.707*	0.525**	0.075	0.498**		
9.	Total P in Mycorrhiza	0.090	-0.082	0.123	0.106	0.102	-0.090	-0.130	-0.143	0.567	
10.	Al-P	0.345***	0.530	0.770**	0.636**	0.660**	0.280	0.260	0.55	0.295	0.270
11.	Al + Fe P	0.338	0.540***	0.704**	0.560**	0.580**	0.310	0.282	0.580	0.283	0.263

* significant at 0.1% level

** significant at 1% level

*** significant at 5% level

CHAPTER V

ANALYTICAL PROBLEMS IN THE DETERMINATIONS OF SILICON AND PHOSPHORUS

5.1 SILICON

5.1.1 INTRODUCTION

The objectives of this investigation were to find accurate and preferably routine and rapid methods for the determination of silicon in soil and plant material.

Silicon may be determined by gravimetric, titrimetric and colorimetric procedures. All methods depend upon the conversion of silic ious material to silicic acid ($Si(OH)_4$).

In the gravimetric methods silicic acid is dehydrated to silicon dioxide (SiO_2). Gravimetric procedures are not sufficiently sensitive for the accurate determination of silicon.

For a long time many analyses have been carried out on the determination of silicon in several materials using a range of crucibles for the decomposition of the silicate material.

Sodium and potassium hydroxides are used for the decomposition of silicate minerals (Riley, 1958; Jeffery, 1970). This decomposition occurs at temperatures much less than those required for fusion with sodium carbonate.

Platinum crucibles are subject to considerable attack from molten alkali. Silver and gold crucibles have been suggested, as the attack by molten alkali is much less. However, silver and gold crucibles have somewhat lower melting points (960°C and 1063°C respectively)

compared with platinum (Jeffery, 1970) and the crucibles can, therefore, easily be damaged by over heating.

Earlier analysts recommended that iron or nickel crucibles could be used for these fusions (Bennett et al., 1961; Govett, 1961). Riley (1958) has developed a method for analysis of silicon in which the sample is decomposed by fusion with sodium hydroxide in a silver crucible. The use of a silver crucible in place of a nickel or iron crucible enables the fusion to be carried out more rapidly. Volk and Weintraub (1958) recommended a platinum crucible for the determination of silicon in plant tissue. The ashing step was carried out in a platinum crucible with concentrated $H_2 SO_4$ and then fusion with sodium carbonate.

Several analysts (Langmyhr and Graff, 1959; Bernas, 1968) successfully decomposed a number of silicate materials in rocks and dusts by hydrofluoric acid in a teflon vessel.

Langmyhr and Sveen (1965) recommended hydrofluoric acid as a powerful agent for decomposing silicates.

The present investigation demonstrated that a mixture of hydrofluoric acid and a second mineral acid is a more effective and powerful decomposing agent than hydrofluoric acid alone.

5.1.2 METHODS FOR THE DECOMPOSITION AND DETERMINATION OF SILICON

The different procedures adopted for the decomposition of silicate material in soils and plants have been compared and their relative efficiencies judged. A considerable amount of time has been devoted to this particular subject to ensure that the results are reliable.

The methods are as follows:-

(i) Fusion with alkali hydroxide (Riley, 1958):

The method is based on that of Shapiro and Brannock (1956) which has been considerably modified to increase the accuracy without loss of speed. The sample is decomposed by fusion with sodium hydroxide in a silver crucible in a muffle furnace at 800°C. The residue is dissolved in water, acidified and diluted to volume.

Standard Silica Solution (50 µg/ml):

Pure silica was ignited in a vitreosil crucible over a meker burner for 20 min., cooled in a desiccator and 0.05 gm weighed out accurately into a silver crucible together with 1.5 g Na OH pellets. The covered crucible was heated for 5 min. at 750 - 800°C, cooled and 20 ml deionised water added. It was heated on a steam bath and then poured into a litre beaker containing 20 ml 2.5 N H_2SO_4 and 600 ml deionized water. It was mixed on a magnetic stirrer and diluted to 1 litre, the resulting solution containing 50 µg SiO_2/ml.

Sodium hydroxide blank was similarly prepared. Both solutions were stored in plastic bottles in a refrigerator at 3°C.

Standard Curve:

Standard solutions were prepared in duplicate by pipetting x ml. Standard SiO_2 solution was put into a 50 ml flask, where x = 0 to 10 ml, followed by 10 - x ml fusion blank and making it up to about 30 ml with water. The pH of this solution was 1.7. The reagents were added with the help of a stop-watch. 2 ml ammonium molybdate was added with mixing, giving the yellow colour of silico-12-molybdate. After exactly

10 min., 15 ml of reducing solution (Metol solution) as explained in Section 3.4.3.2 was added with mixing. The solutions were made to 50 ml, shaken and allowed to stand for 3 hr. Optical densities of the blue solutions were read in 1 cm cells, at 810 nm against the reagent blank, and a standard curve was constructed for 0 - 10 μg SiO_2/ml.

Sample Solutions:

A solution of monomeric silicic acid free of organic or other reducing agents. Aliquots of sample were pipetted into a beaker and made to 20 ml with water, and the amount of 2.5 N H_2SO_4 or 5 N Na OH required to bring them to pH 1.6 - 1.7 noted. These amounts were used to prepare the solutions for reagent addition.

(ii) Fusion with Alkali Hydroxide (Jeffery, 1970):

Sodium and potassium hydroxides are efficient fluxes for the decomposition of silicate minerals. This decomposition occurs at temperatures much lower than those required for fusion with sodium carbonate. The ease with which silicate minerals dissolve in molten alkali is deceptive in that the accessory mineral fraction is likely to remain unattacked unless the fusion is prolonged.

Procedure:

A nickel crucible was cleaned with hot dilute hydrochloric acid, rinsed with water and dried on a hot plate. Approximately 2 g of sodium or potassium hydroxide, the amount required for the fusion was weighed out, covered with a lid and heated gently over a small flame for a few min. The desiccator was allowed to cool. The sample (200 mg) was

weighed directly on to the melt and the crucible transferred to a hot plate set at full heat (~ 300°C). The temperature of a hot plate (~ 300°C) at full heat is sufficient just to fuse the melt, when always the reaction with the sample to occur. Once the sample was completely wetted by the alkali, the crucible was transferred to a piece of asbestos board, and the fusion continued over a low flame for the prescribed period (~ 1 hr). The crucible was cooled and then poured into a 100 ml polyethylene beaker. The beaker was placed in a water bath maintained near 100°C. After the melt had dissolved, the crucible was removed with tongs and rinsed several times with water, collecting the rinsings which were cooled and transferred to a polyethylene bottle, calibrated and made up to 100 ml.

(iii) Official Method of Analysis:

Sand and silica (Horwitz et al., 1975)

5 - 10 g of sample was ignited in a flat-bottomed platinum in a furnace, at 500 - 600°C until the residue was white or nearly so. The residue was moistened with 5 ml H Cl, boiled for 2 min., evaporated to dryness and heated on a steam bath for 3 hr. to render SiO_2 soluble. The residue was moistened with 5 ml H Cl, boiled for 2 min., 5 ml water added, then heated on water bath for a few minutes, filtered through a hardened paper and washed thoroughly. To this filtrate, filtrate and washing from the alkali solution was added (SiO_2 determination b).

(a) Sand

The residue from the filter was washed into a platinum dish and boiled for 5 min., with 20 ml saturated $Na_2 CO_3$ solution. A few drops of 10% Na OH solution were added, after settling, the contents were decanted through an ignited and weighed gooch crucible. The residue was boiled in a dish with another 20 ml portion of $Na_2 CO_3$ solution and decanted as before, and the process repeated. The residue was transferred to a gooch crucible and washed finally with hot water until Cl-free. The filter and contents were dried, ignited at 500°C - 550°C and weighed as $Si O_2$.

(b) Alkali-Soluble $Si O_2$

The alkali filtrate and washings from (a) were combined, acidified with H Cl, evaporated to dryness and 5 ml H Cl added. The contents were evaporated and dehydrated by heating for 2 hr. at 110°C - 120°C. The residue was moistened with 5 ml H Cl, boiled for 2 min., 10 ml water added, and heated on a water bath for 15 min. The contents were filtered through ashless filter paper ignited and the gooch crucible weighed, washed with hot water, ignited at 500°C - 550°C and weighed as $Si O_2$.

(iv) Fusion with alkali carbonate: (Volk and Weintraub, 1958)

This method has been described as a micro-method for the determination of silicon in plants. The sample is decomposed in a platinum crucible.

Preparation of plant sample:

The sample is dried at 70°C and ground to pass a 20 mesh screen (BS).

Dissolution of silicon:

50 mg of dry plant tissue was weighed out and transferred to a platinum crucible. With each set of samples a reagent blank was carried through all stages of the operation.

Six drops of concentrated sulphuric acid was added to each crucible and heated on an electric hot plate until the sulphuric acid had ceased to fume. The charred tissue was then carefully ignited with a Fisher burner, increasing the heat gradually until a white ash was obtained. To the ash, approximately 0.5 g of pure anhydrous sodium carbonate was added, and the mixture fused for 20 min. at the maximum temperature of the burner (~900°C). The molten contents were swirled periodically to keep the sides of the crucible free of adhering ash. The crucible was cooled and placed in a 100 ml polyethylene beaker containing 30 ml of deionized water and 3 ml of 3 M hydrofluoric acid. To hasten solution of the melt, the beaker was placed in a water bath maintained near 100°C. After the melt had dissolved, the crucible was removed with tongs and rinsed several times with water, collecting the rinsings in the original beaker. The solution was concentrated to ~30 ml, cooled and transferred to a polyethylene bottle calibrated at 50 ml. If the plant tissue contained much manganese, a blue coloured melt was obtained, and the manganese precipitated when the melt was dissolved. In such instances the contents of the beaker was filtered into the calibrated

flask. No silicon was lost by this procedure. Just prior to the colorimetric determination, the acidic solution was adjusted to approximate neutrality, using 1 M sodium hydroxide and 0.1 M hydrochloric acid with two drops phenophthalein. The solution was diluted to 50 ml.

Colour Development

A 1 - 20 ml aliquot containing 10 - 50 μg of silicon was transferred to a polyethylene or glass flask after steeping in a nitric-sulphuric acid-bath. The contents were diluted to 20 ml, 3 ml of molybdate reagent was added, and the contents of the flask mixed by swirling. After exactly 10 min., 15 ml reducing agent (metol solution) was added rapidly, and the solution was diluted to 50 ml, mixed and allowed to stand 3 hr., to complete the reduction. The absorbance was measured in 1 cm cells at 810 nm.

(v) Decomposition with hydrofluoric acid and second mineral acid in a teflon vessel:

The rapid decomposition of silicates was achieved in a specially designed vessel made of teflon without volatilization losses by hydrofluoric acid at 240°C. The method was explained earlier in Chapter III, Section 3.3.7.

5.1.3 RESULTS AND DISCUSSION

In formulating a method for the determination of silicon it is desirable that conditions be such that the colour is reproducible, rapid with less attention and yields clear solutions.

In the case of Volk and Weintraub's method (1958) for the determination of silica in plant material using a platinum crucible, some of the problems suffered were:-

1. The ashing procedure dehydrates and insolubilizes a portion of the plant silicon. The silicon must be converted to a completely soluble form by fusion with sodium carbonate before the ash is dissolved.

2. A 20 min. fusion as recommended is not sufficient to allow any ash adhering to the sides of the crucible to be brought into the melt. Moreover, the melting point of anhydrous sodium carbonate is 852°C, which requires a lot of heat. Generally low results are obtained (Table 5.01).

This latter observation correlates with that of Govett (1961), who found that for alkali fusions, sodium hydroxide was preferred, because the carbonate fusion gave low and erratic values in all samples. The other methods were more reliable.

In the gravimetric method, where silicic acid is dehydrated to silicon dioxide (SiO_2), very low results are obtained (Table 5.01). Gravimetric procedures are not sufficiently sensitive for the accurate determination of silicon.

The use of a silver crucible (Riley, 1958) in place of a nickel crucible as recommended by Govett (1961) and Jeffery (1970) enables the fusion to be carried out more rapidly and yields much clearer solutions. However, difficulties have been experienced when attempting to clean nickel crucibles, and they have only a short life due to erosion and

becoming porous. The high alkali medium (sodium hydroxide or sodium carbonate) tends to creep out of crucibles when it is heated. A lot of sample is still insoluble or unfused - very low results were obtained (see Table 5. 01).

Finally, the decomposability in hydrofluoric acid and a second mineral acid in a teflon vessel offers certain advantages than employing hydrofluoric acid as the decomposing agent for silicate:-

(a) Decomposition and evaporation can be done in plastic vessels and thus expensive platinum equipment is no longer a pre-requisite for the analysis of soil.

(b) The sample is not contaminated by the vessel used in the decomposition, as in the case of a fusion.

(c) The final solution is very clear, and the result much more reproducible.

(d) Silicon may be determined irrespective of the presence of boron and fluorine.

Other advantages which have been discussed by Langmyhr and Graff (1965):

(e) Methods for the determination of the alkali metals and iron (II) can be incorporated in the scheme.

(f) The decomposing agent can be removed quantitatively be evaporation.

The results shown in Table 5. 01 were more reproducible and more reliable than alternative methods.

The boric acid is present to suppress fluoride interference during analysis. The borate removes interference from excess fluoride by

forming fluoroboric acid (HBF_4) between HF and $H_3 BO_3$ (Sharpe, 1954).

The present investigation indicates that a mixture of hydrofluoric and sulphuric acids is more effective as a decomposing agent than hydrofluoric acid alone as recommended by Langmyhr and Sveen (1965). The teflon vessels should be placed in the freezer (-18°C) for 2 hr. after the digestion and dissolution of silicate material has been completed, due to the volatilization of silicon as silicon tetrafluoride ($Si F_4$), (see Table 5.02). While Langmyhr and Graff (1965) believe that no loss of silicon has taken place.

The high overall reliability achieved in this simplified method for silicate analysis provides satisfactory accuracy and that the silicon brought into solution as fluosilicic acid can be determined spectrophotometrically as the yellow silico-12-molybdate and the reduction of molybdenum blue, or it can be measured directly by atomic absorption spectroscopy. The results are shown in Table 5.03.

5.1.3.1 Critical Factors in the Colorimetric Determination

(i) Conditions for the formation of silicomolybdic acid

The formation of silicomolybdic acid in solution having the formula ($H_4 (Si MO_{12} O_4)$) is governed primarily by the hydrogen ion concentration and by the concentration and nature of both the molybdate and silicic acid present.

Variation in pH is clearly important, but not exclusively so, with regard to the variation in the development of yellow silicomolybdate complexes. This variation is due to the effect of pH upon the state of the

molybdate ions and, as pointed out by Mullin and Riley (1955), the rate of formation of silicomolybdate is dependent upon the degree of polymerization of the molybdate formed.

The degree of polymerization increases rapidly with the acidity of the solution (Lindquist, 1951). The reactions on acidification are considered to be:-

$$(Mo\ O_4)^{-2} \longrightarrow (Mo_7\ O_{24})^{-6} \longrightarrow (Mo_8\ O_{26})^{-4} \longrightarrow \text{larger complexes}$$

The rate of formation of silicomolybdate is therefore likely to be greatly dependent upon the degree of polymerization of the molybdate which is formed.

Ringbom et al. (1959) quoted Lindquist (1951) as saying that $Mo\ O_4^{-2}$ ions are stable at pH values greater than 6.4. Around pH 4.5 paramolybdate ions $(Mo_7\ O_{24})^{-6}$ are formed which are transformed into octomolybdate ions $(Mo_8 O_{26})^{-4}$ at a pH of 1.5 - 2.8. Ringbom et al. (1959) believed that low absorbance α-acid is formed from the paramolybdate ion, and the high absorbance β-acid from the octomolybdate ion.

Strickland (1952 a, b) suggested that concentration must be considered together with acidity. Thus at suitable acidities and solutions more dilute than 0.01 M with respect to $Mo\ O_4^{-2}$ the following takes place:

$$4\ Mo\ O_4^{-2} + 6\ H^+ \rightleftharpoons Mo_4\ O_{13}^{-2} + 3\ H_2O$$

Whilst at higher concentrations:

$$5\ Mo\ O_4^{-2} + 4\ Mo_4\ O_{13}^{-2} \rightleftharpoons 3\ (Mo_7\ O_{24})^{-6}$$

In solutions more concentrated than 0.05 - 0.1 M, and acidified with 1 - 1.5 equiv. acid, $2\ Mo_7O_{24}^{-6} + 4\ Mo_4O_{13}^{-2} \rightleftharpoons 5\ Mo_6O_{20}^{-2}$

Strickland (1952 b) correlated the β-forming species with the meta ion, $Mo_4O_{13}^{-2}$, but failed to identify the *α*-forming species. Therefore, the amount of β-silicomolybdic acid formed and the rate of formation, will depend upon the amount of β-forming species in the molybdate added.

Truesdale and Smith (1975) recommended that the primary factors to be considered are the pH and molybdate concentration of the reaction mixture. Thus the main controlling factor in the formation of silicomolybdic acid appears to be the acidity of the solution. To determine the optimum acidity and pH for the formation of silicomolybdic acid, samples of standard sodium silicate solution containing 50 μg of silicon were treated with various volumes of 1 M hydrochloric acid, diluted to 40 ml, 3 ml of 5% ammonium molybdate solution added, and the solution diluted to 50 ml. The intensity of the yellow colour was measured at 810 nm. The results (Table 5.04) and (Fig. 5.01) indicate that the formation of silicomolybdic acid is completed over the pH range 0.64 - 3.1, and the maximum absorbance (corresponding to the formation of predominantly β-silicomolybdic acid) occurs at pH 1.9 ± 0.10, see Fig. 5.01.

The absorbance is much reduced in solutions more acidic than pH 1.2, presumably owing to polymerization of the silicic acid.

Govett (1961) recorded that the maximum formation of β-

silicomolybdic acid occurred between pH 1.1 - 2.5, but with no well defined plateau of constant values. The low plateau observed after 10 min. reaction between pH 3.6 and 4.3 probably corresponds to the formation of dominant α-silicomolybdic acid.

Lan gmyhr and Graff (1965) recommended that the pH of solutions for silicomolybdic acid formation to be completed and the results reproducible was between pH 1.5 - 2.3.

(ii) Suppression of phosphate interference

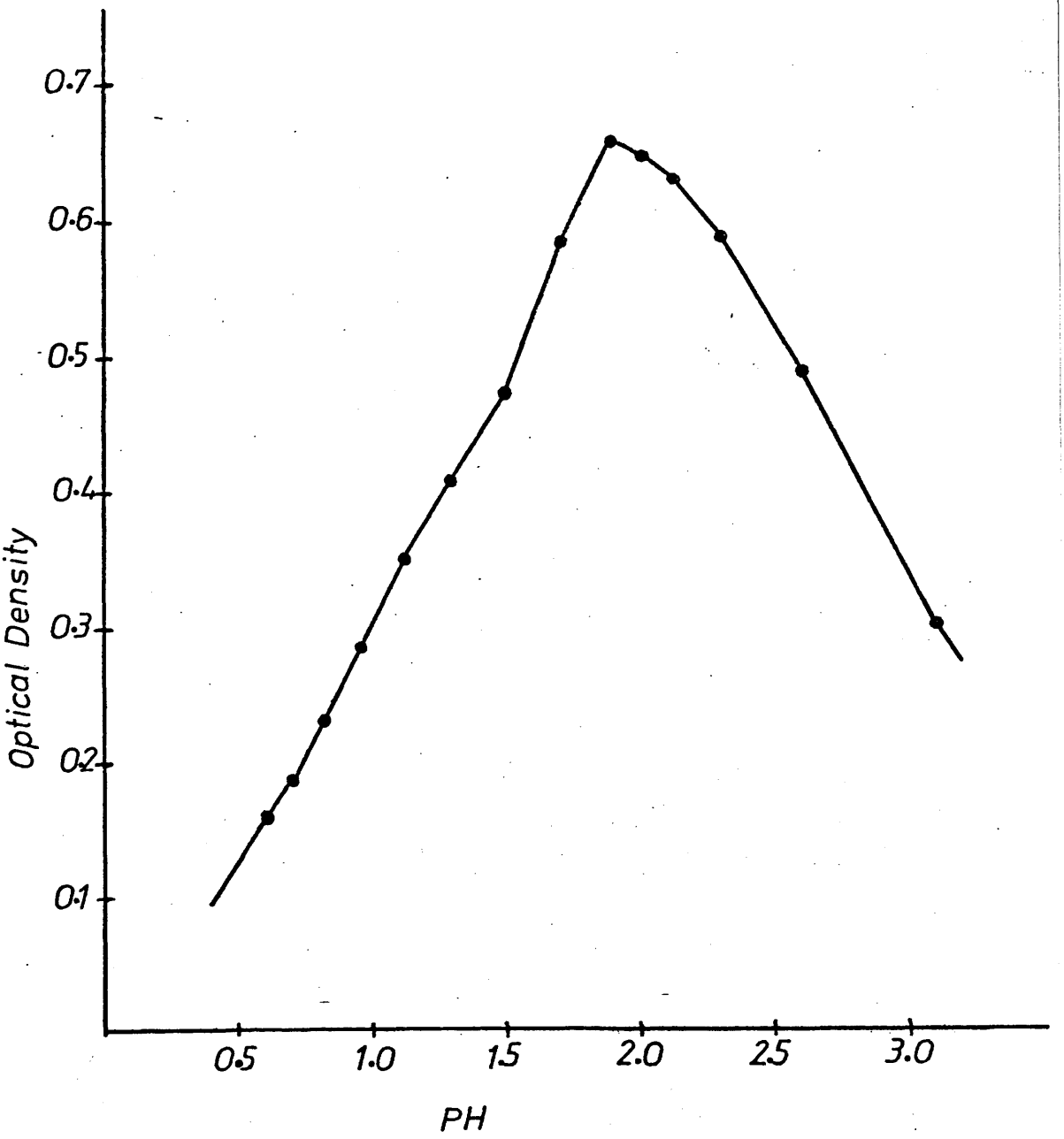
Phosphorus can combine with molybdate to produce molybdo-phosphoric acid. This reaction takes place spontaneously under the conditions used in the procedures recommended and can lead to interference (Table 5.05). This interference can be suppressed (still further) by the addition of oxalic acid at the time of the reduction of the complex. A study was made of the interference of potassium dihydrogen phosphate in amounts ranging from 1 - 25 ppm of phosphorus, on the determination of 0.5, 1.0 and 2.0 ppm of silicon.

The results are shown in Table 5.06. The remarkable suppression by oxalic acid was also illustrated.

It was found that 0.5 ppm of Si can be determined in the presence of 22 ppm phosphorus.

The precision and recovery of silicon in the presence of phosphorus is shown in Table 5.07.

Fig. 5.01 Effect Of Acid Conc. & PH On Formation Of Silicomolybdic Acid



(iii) Interference of Foreign Ions

Of the interfering elements studied by Mullin and Riley (1955), the interferences of copper, ferrous iron, cobalt and nickel are due to the absorption of their ions at 812 nm. Copper at a concentration of less than 10 ppm (Cu:Si = 50 : 1) causes negligible error. Ferric iron interferes with the determination of silicon owing to the precipitation of reddish-brown ferric molybdate during the formation of the silicomolybdic acid. This precipitation may be prevented by making the test solution 0.1 N with sulphuric acid and permits the determination of 30 ppm of ferric iron with a 5% error. The error can be much reduced by reducing the iron to the ferrous state with a solution of hydroxylamine hydrochloride (1 ml of 10% NH_2 OH H Cl) prior to the formation of the silicomolybdic acid.

In this way, 0.2 ppm of silicon can be determined in the presence of up to 100 ppm ferric iron with an error of less than 1%.

5.2 PHOSPHORUS

5.2.1 AN INVESTIGATION OF A SUITABLE ANION-EXCHANGE RESIN METHOD FOR SOIL PHOSPHATE EXTRACTION

The anion-exchange resin method for soil-phosphate extraction was investigated on twelve soil samples under varying experimental conditions. The amounts of resin and soil were the same (1 : 1 g/g), and the shaking time was the same (24 hr.). The same anion-exchange resin was used in the chloride, bicarbonate or hydroxyl form. The amount of phosphorus extracted was dependent on the anionic forms of the resin. It can be concluded from the results given in Table 5.08, that strong-base type anion-exchange resins do affect the pH of soil-water suspensions.

The Cl^- form of AER caused a decrease in the pH of all the soils whereas the OH^- and $H CO_3^-$ forms increased the pH of acid soils. The reason for the preference of OH^- and $H CO_3^-$ form over Cl^- form can be deduc ed from Table 5.08. The OH^- and $H CO_3^-$ forms of AER have a tendency to change the pH of the soils towards neutrality, i.e. a pH at which the availability of phosphorus is maximum and the use of OH^- or $H CO_3^-$ form of AER may, therefore, extract all the available phosphorus easily. Contrary to this, the Cl^- form of AER reduces the pH, especially of acid soils with a pH of less than 6.0 to such an extent that the solubility of phosphorus is reduced and the resin is able to extract low amounts of phosphorus. This is reflected in the result in Table 5.09.

Sibbesen (1978) recommended that resin in the bicarbonate form should be used for both routine as well as more advanced work of the ability of soils to supply phosphate to plants. The bicarbonate form extracted a larger amount of phosphorus from neutral soils (Table 4.05).

The present study correlates with that of Bache and Ireland (1980), who drew similar conclusions in that phosphorus extracted by $H CO_3$-resin was much greater than that by Cl-resin from an acid soil, due to lower total anion and higher desorbing anion concentrations.

A final procedure for the analysis is given in Chapter IV, Section 2.3.2.5.

5.2.2 INTERFERENCES IN THE DETERMINATION OF PHOSPHORUS BY THE MOLYBDENUM BLUE REACTION

(i) The organic matter and the colour of extractant

The introduction of the alkaline extractant produced many

problems, the most important being that quantities of organic matter are dissolved causing the extracts to vary in colour from pale yellow with mineral soils to dark brown. Many of the extracts were highly coloured especially from soils with a high level of organic matter, and difficulties were experienced in obtaining clear filtrates of the soil extracts.

Using activated charcoal to decolourize the soil extracts, introduced new difficulties, not the least being the phosphate content of the carbon. Of the commercially obtainable charcoals produced in the United Kingdom which were examined, many were found unsuitable because of their high soluble phosphate content, even when rewashed twice with bicarbonate solution.

Various studies of the technical aspects of the extracted available phosphate determination have been carried out in ADAS laboratories (1973) under varying experimental conditions, involving many soils of different types having high levels of organic material, extractable phosphate and clay and silt, to compare the levels of available phosphorus extracted with 0.5 M sodium bicarbonate containing charcoal with those obtained after the addition of polyacrylamide to the extractant instead of the charcoal. The procedure incorporating the carbon was considered as the reference method. Each of the laboratories of ADAS centres were recommended to use polyacrylamide instead of charcoal for extracting available phosphorus from any type of soil (ADAS 1973, 1976). In the present study, observations did not correlate with that of ADAS, i.e. neither polyacrylamide nor charcoal proved to be useful, and did not improve the results.

(ii) Hydrogen peroxide

When hydrogen peroxide ($H_2 O_2$) was used to decolourize the soil extracts, it introduced new difficulties. Any residual peroxide results in low phosphorus results (Table 5.10). The addition of a few drops of potassium permanganate ($K Mn O_4$) solution recommended by Thomas and Chamberlin (1980) to the extracts has been found to destroy the excess peroxide without adversely affecting the determination of phosphorus.

(iii) pH and Time

The reaction is performed at a pH below 1, rather than at the optimal pH of about 1.1, to avoid serious interference from dissolved silicate.

Crouch and Molmstadt (1967) suggested that the pH must be below 0.8 to prevent reduction of molybdenum, and for the most rapid results the acid concentration should be between 0.3 N and 0.5 N. While Grasshoff (1966) suggested that serious silicon interference in the determination of phosphorus in sea water by auto-analyzer methods could be avoided by performing the reaction at a pH of less than 1.0.

The use of ascorbic instead of stannous chloride as the reducing agent, meant that the colour could be measured 12hr. after adding the reducing agent (Fig. 5.02). In the case of stannous chloride as a reducing agent, the colour must be measured 10 min. exactly after adding the reducing agent.

(iv) Precision of data for phosphorus by the proposed ascorbic acid and stannous chloride methods

Stannous chloride has not been entirely satisfactory for reducing

the molybdophosphoric acid (Watanable and Olsen, 1965), because organic matter in soil extracts causes an instability of the blue colour. Ascorbic acid as a reducing agent appeared to overcome these objections. The reproducibility of the ascorbic acid method is superior to that of the stannous chloride process; the results are shown in Table 4.08.

The ascorbic acid method, in addition to having the advantages of stable colour for a long period (more than two months), and the excellent colour and sensitivity is widely suited for phosphorus determinations (Watanable and Olsen, 1962, 1965; Alexander and Robertson, 1970; Durge and Paliwal, 1967), as the reductant instead of stannous chloride. A disadvantage of ascorbic acid is that the colour is developed slowly and the solutions should preferably be allowed to stand overnight for at least 12 hr.

(v) Reaction with Silicon

It is well known that under certain conditions of acidity and concentration of molybdate silicon will produce a yellow molybdosilicate complex, which can be reduced to form a molybdenum blue silicon complex. It was, therefore, important to know if there is any interference of silicon under the conditions of the method. A study was made of the possible interference of silicon on the determination of phosphorus.

Mixtures of phosphorus and silicon standard containing 1, 3, 5, 10, 20, 25 µg Si/ml and 5, 10, 20, 30, 50 µg P/ml were run with molybdate reagent in 3.0, 4.0 and 5.0 N H_2SO_4.

The molybdate reagent was therefore 5.0 N with respect to H_2SO_4, 0.72 N after sample and reagent were mixed, compared with

Fig . 5.02 Colour Development Of Molybdenum Blue In The Phosphorus (50 µg P/50 ml, 660 nm)

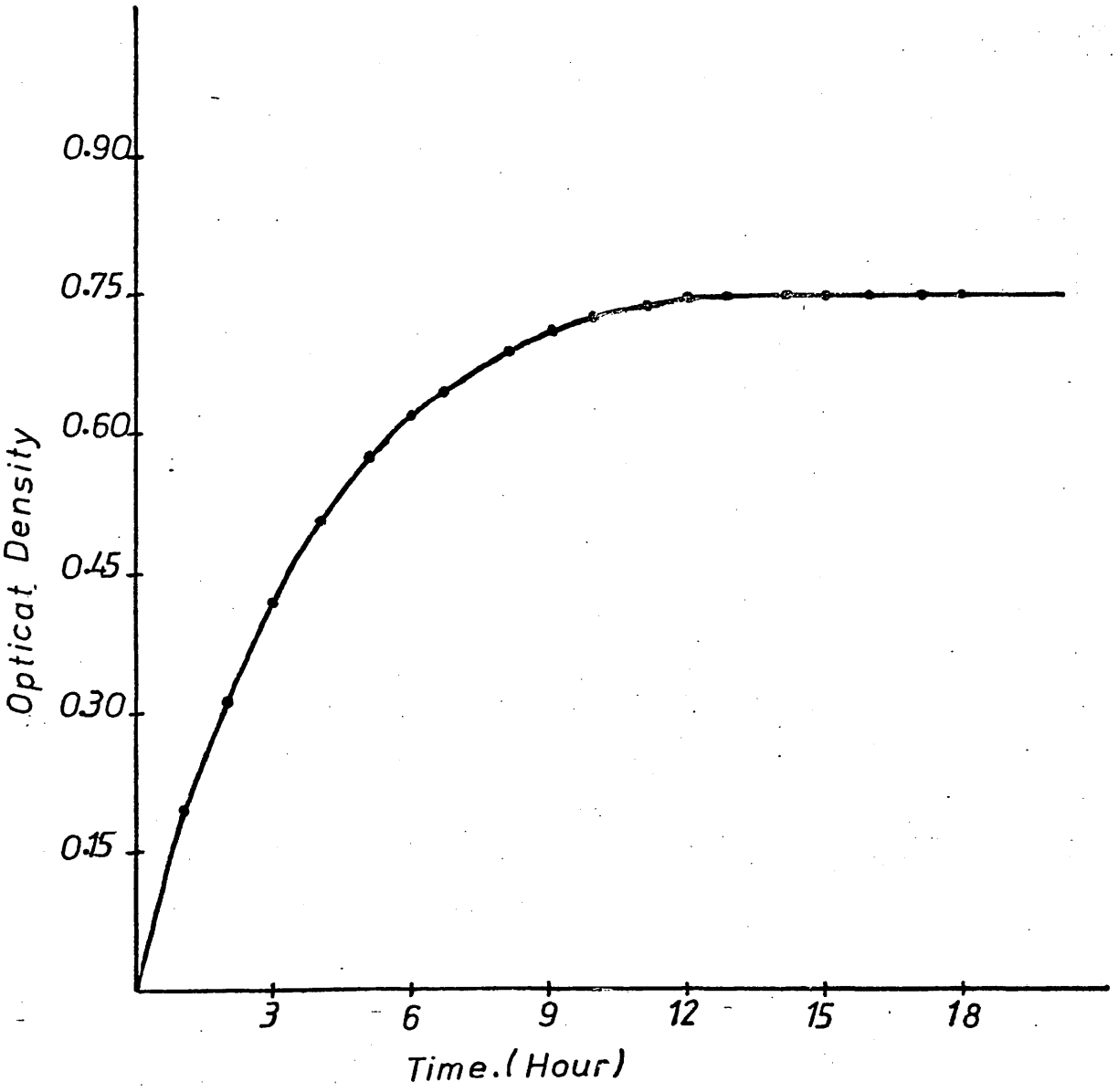


TABLE 5.01

Comparison of Methods for Determination of Silica in Plant Material

(spruce needles) oven-dry

No.	Sample	mg g^{-1} ± S.D.			
		Riley's method Silver crucible	Jeffery Nickel crucible	Official method Platinum crucible	Volk and Weintraub Platinum crucible	Decomposition with HF in teflon vessel
1	Plot 1 BML	6.3 ± 2.1	2.4 ± 1.1	1.8 ± 0.7	5.6 ± 1.7	14.0 ± 1.1
2	Plot 5 BF	5.8 ± 2.2	2.0 ± 1.2	2.3 ± 1.1	6.0 ± 2.0	14.2 ± 0.8
3	Plot 17 BF	6.8 ± 1.8	1.8 ± 0.9	2.0 ± 0.8	5.8 ± 1.6	15.6 ± 1.2
4	Plot 9 BMP	7.3 ± 2.3	2.2 ± 1.0	2.7 ± 1.0	5.6 ± 1.5	12.8 ± 0.9
5	Plot 7 BM	5.6 ± 1.4	1.8 ± 0.6	2.1 ± 0.8	5.1 ± 1.4	12.2 ± 0.8
6	Pitmedden 1	6.2 ± 1.5	1.7 ± 0.8	1.8 ± 1.0	5.5 ± 1.2	12.7 ± 0.6
7	Pitmedden 4	6.6 ± 1.7	1.9 ± 0.7	2.9 ± 1.0	5.9 ± 1.2	13.2 ± 0.8

TABLE 5.02

Effect of Cooling on the Amount of Silicon in Plant Material

(oven-dry) mg g $^{-1}$ ± S.D.

		First instance without cooling in the refrigerator	Second instance with cooling for 2 hr. in the refrigerator	Third instance with cooling for 1 hr. at -18°C	Fourth instance with cooling for 2 hr at -18°C	Fifth instance with cooling for 4 hr. at -18°C	Sixth instance with cooling for 10 hr. at -18°C
1.	Birch (Red slope)	6.4 ± 0.3	8.7 ± 0.4	10.4 ± 0.4	11.1 ± 0.3	11.8 ± 0.5	12.0 ± 0.4
2.	Birch (Black slope)	5.9 ± 0.6	8.3 ± 0.3	9.9 ± 0.3	10.7 ± 0.2	11.2 ± 0.4	11.8 ± 0.5
3.	Cock's foot (Red slope)	6.6 ± 0.5	8.9 ± 0.4	10.1 ± 0.4	11.4 ± 0.5	11.8 ± 0.4	12.2 ± 0.7
4.	Cock's foot (Black slope)	7.1 ± 0.7	9.2 ± 0.5	10.6 ± 0.5	11.2 ± 0.6	11.6 ± 0.5	12.0 ± 0.6

TABLE 5.03

Accuracy and Precision of Data for Silicon by the Proposed Atomic Absorption and Colorimetric Methods

	Sample (spruce needle)	mg g^{-1} ± S.D.	
		Atomic Absorption Method	Colorimetric (Molybdenum blue) Method
1.	Pitmedden 1	12.7 ± 0.6	11.5 ± 1.2
2.	Pitmedden 2	12.2 ± 0.8	11.8 ± 1.4
3.	Pitmedden 3	11.8 ± 0.7	12.1 ± 0.7
4.	Pitmedden 4	13.2 ± 0.8	12.6 ± 1.2
*	Fiunary Forest Compartment 105		
5.	Plot 1 BML	14.0 ± 1.1	13.2 ± 1.4
6.	Plot 3 BML	14.2 ± 0.8	13.5 ± 1.2
7.	Plot 4 BML	14.4 ± 1.2	14.8 ± 1.0
8.	Plot 5 BF	14.2 ± 0.8	16.2 ± 1.6
9.	Plot 14 BF	14.4 ± 0.6	13.6 ± 1.2
10.	Plot 17 BF	15.6 ± 1.2	14.3 ± 1.2
11.	Plot 2 BFP	13.9 ± 0.8	13.1 ± 0.8
12.	Plot 11 BFP	14.4 ± 1.2	15.1 ± 1.1
13.	Plot 9 BMP	12.8 ± 0.9	13.1 ± 0.7
14.	Plot 13 BMP	13.0 ± 1.0	12.3 ± 0.8
15.	Plot 7 BM	12.2 ± 0.8	13.0 ± 0.6
	Overall	13.6 ± 0.9	13.4 ± 1.1

TABLE 5.04

Effect of Acid Concentration on Formation of Silicomolybdic Acid. 50 µg Si + x ml of 1 M H Cl diluted to 40 ml, 3 ml 5% ammonium molybdate and the solution was diluted to 50 ml, and measured at 810 mµ

x ml of 1 M H Cl	pH value	Maximum optical density after 10 min.
2.0 (Blank Solution)	1.90	0.002
0.5	3.50	0.265
0.6	3.10	0.300
0.7	2.60	0.490
1.0	2.30	0.590
1.2	2.10	0.635
1.5	2.00	0.650
2.0	1.90	0.655
2.5	1.70	0.595
3.0	1.50	0.470
4.0	1.30	0.405
5.0	1.10	0.350
6.0	1.00	0.315
8.0	0.90	0.285
11.0	0.80	0.230
15.0	0.70	0.185
20.0	0.65	0.160

TABLE 5.05

Suppression of phosphate interference by means of oxalic acid. In each instance, 3.0 ml of 15% oxalic acid solution (or 3.0 ml deionized water) was added to a mixture of silicate solutions, phosphate, silicate + phosphate. 3 ml of ammonium molybdate was added after 10 min., 12 ml of reducing solution (metol) was added to give the molybdenum blue.

Sample identity		Absorbance	
		660 nm	810 nm
	Without oxalic acid		
	Blank	0.006	0.008
	Silicate solution (5 μg of Si)	0.355	0.677
Increments	Phosphate solution (5 μg of P)	0.540	0.475
	Silicate + Phosphate	0.845	1.150
	With oxalic acid		
	Blank	0.002	0.002
Increments	Silicate solution (5 μg of Si)	0.353	0.679
	Phosphate solution (5 μg of P)	0.004	0.001
	Silicate + Phosphate	0.352	0.678

TABLE 5.06

Suppression of phosphate interference, the overall effect. 2 μg Si + x ml of various concentrations of phosphorus solution, 3 ml ammonium molybdate was added + 15 ml reducing agent, consisting of 3 ml of 15% oxalic acid added and allowed to stand for 3 hr., measured to 810 mμ.

1 ml of various concentrations of phosphorus (ppm)	Maximum Optical Density	
	Blank Without Silicon	Solution (Silicon + Phosphorus)
1	0.000	0.340
2	0.001	0.338
4	0.002	0.340
8	0.002	0.338
10	0.002	0.339
15	0.002	0.340
20	0.003	0.342
22	0.004	0.350
25	0.010	0.362
30	0.015	0.368

TABLE 5.07

The Recovery of Silica in the Presence of Phosphorus

Silica (SiO_2) present (μg)	Phosphorus added (μg)	SiO_2 found (μg)	% Recovery
10	10	9.5	97.5
10	15	9.6	98.0
10	20	10.0	100.0
20	10	18.5	97.8
20	15	19.6	98.0
20	25	23.0	106.2
40	15	38.5	97.8
40	20	47.6	95.2
40	25	42.8	105.5
50	10	47.5	95.0
50	15	50.0	100.0
50	20	50.8	101.2

TABLE 5.08

Effect of chloride, hydroxyl and bicarbonate forms of anion-exchange resin on the pH of soil-watter suspensions.

Sample	1:25 soil-water suspension	1:1:25 soil-AER (Cl^- form)-water suspension	Change in pH caused by AER (Cl^- form)	1:1:25 soil-AER (OH^- form)-water suspension	Change in pH caused by AER (OH^- form)	1:1:25 soil-AER (HCO_3^-) - water suspension	Change in pH caused by AER (HCO_3^- form)
	pH	pH		pH		pH	
1. Pitmedden 2A	6.2	5.1	-1.1	6.5	+0.3	6.6	+0.4
2. Pitmedden 2B	6.5	5.7	0.8	6.7	+0.2	6.8	+0.3
3. Pitmedden 4A	6.3	5.2	-1.1	6.5	+0.2	6.6	+0.3
4. Pitmedden $9A_1$	6.2	5.2	-1.0	6.5	+0.3	6.6	+0.4
5. Fiunary Forest $1A_1$	4.6	3.8	-0.8	5.4	+0.8	5.4	+0.8
6. Fiunary Forest 2A	4.6	3.8	-0.8	5.5	+0.9	5.6	+1.0
7. Savary Glen A_1	4.5	3.6	-0.9	5.2	+0.7	5.3	+0.8
8. Salen Forest $1A_1$ (7 - 9)	4.8	3.9	-1.0	5.9	+1.1	5.9	+1.1
9. Salen Forest $6A_1$ (4 - 6)	4.7	3.7	-1.0	5.7	+1.0	5.8	+1.1
10. Arran	6.8	6.2	-0.6	6.9	+0.1	6.9	+0.1
11. Byre	6.7	6.4	-0.3	6.7	+0.0	6.8	+0.1
12. Craig	6.6	6.2	-0.4	6.8	+0.2	7.0	+0.4

TABLE 5.09

Phosphorus extracted by anion-exchange resin used in the chloride, hydroxyl and bicarbonate form. Shaking time : 24 hr., resin amount: 4 g, soil amount: 4.0 g, water amount: 100 ml.

Sample	mg/100 g ± S.D.		
	HCO_3^- form	OH^- form	Cl^- form
1. Pitmedden Forest 2A	5.10 ± 0.9	4.2 ± 1.1	3.9 ± 0.8
2. Pitmedden Forest 2B	4.5 ± 0.8	3.9 ± 1.0	3.6 ± 0.7
3. Pitmedden Forest 4A	6.0 ± 0.7	4.9 ± 0.8	4.5 ± 0.6
4. Pitmedden Forest $9A_1$	6.0 ± 0.6	4.8 ± 0.7	4.7 ± 0.6
5. Fiunary Forest $1A_1$	2.7 ± 0.4	2.2 ± 0.5	1.9 ± 0.4
6. Fiunary Forest 2A	2.4 ± 0.3	2.0 ± 0.5	1.7 ± 0.5
7. Savary Glen Forest A_1	2.3 ± 0.4	2.0 ± 0.6	1.8 ± 0.4
8. Salen Forest $1A_1$ (7 - 9)	4.2 ± 0.4	3.8 ± 0.6	3.1 ± 0.5
9. Salen Forest $6A_1$ (4 - 6)	4.0 ± 0.5	3.7 ± 0.5	3.0 ± 0.4
10. Arran	9.9 ± 0.6	9.3 ± 0.5	8.9 ± 0.6
11. Byre	9.8 ± 0.5	8.8 ± 0.7	8.2 ± 0.6
12. Craig	14.1 ± 0.9	13.5 ± 1.1	12.8 ± 0.7

TABLE 5.10

Effect of hydrogen peroxide on the intensity of phosphomolybdic acid.

No.	Sample	mg/100 g ± S.D.		
		Without H_2O_2	With H_2O_2	With H_2O_2, addition of $KMnO_4$ solution
1.	Pitmedden 1A	4.2 ± 0.6	3.0 ± 0.5	4.1 ± 0.7
2.	Pitmedden 2A	4.6 ± 0.5	2.8 ± 0.6	4.4 ± 0.7
3.	Pitmedden 4A	5.2 ± 0.8	4.3 ± 0.6	5.2 ± 0.6
4.	Arran	10.0 ± 0.9	8.2 ± 0.8	10.1 ± 0.8
5.	Byre	9.6 ± 0.7	8.1 ± 0.8	9.4 ± 0.6

TABLE 5.11

Effects of addition of varying amounts of Si to phosphorus standard on apparent phosphorus determined by the ascorbic acid method.

Silicon (ppm)	Phosphorus concentration			
	5 µg/ml	10 µg/ml	30 µg/ml	50 µg/ml
	Apparent Phosphorus (ppm)			
1	4	10	30	46
3	5	9	29	47
5	4	10	29	46
10	4	9	30	48
20	5	10	29	49
50	5	11	31	50

TABLE 5.12

Optical density of solutions containing phosphorus of silica. The optical densities were measured in 1 cm cell by 600 spectrophotometer at 660 nm.

Amount of phosphorus present as P µg/50 ml	Amount of silicate added as Si ppm	Optical density	Optical density corrected for blank value (Difference)
0	10	0.002	-
0	20	0.004	-
0	40	0.006	-
0	50	0.008	-
10	20	0.142	0.138
20	40	0.276	0.270
50	50	0.453	0.445
100	50	0.896	0.888
150	50	1.255	1.248

0.48 N when 3 N H_2SO_4 was employed. In general, the silicon effect on the phosphorus system was less with the higher acid concentration (Sowden, 1972), but the differences were not large. The data for the 4.0 N acid concentration are given in Table 5.11. This table indicates that the various amounts of silicon used did not affect the phosphorus values. For instance, 0, 10, 20, 50, 100, 150 p µg/50 ml were used with 10 - 50 µg Si/ml, as shown in Table 5.12, very little effect was found. Murphy and Riley (1962) tested the effect of silicon at 50 µg p/50 ml and found very little effect.

5.3 CONCLUSION

As a result of this investigation, it can be concluded that silicon in soil and plant tissue can be determined by a rapid and routine method using hydrofluoric acid and second mineral acid. Without any detectable loss of silicon through the process, after cooling at -18°C for 2 hr. Phosphorus and iron interferences can be successfully eliminated and silicon completely recovered, but this can only be achieved by careful attention to the details of the method and particularly to concentrations of reagents and pH.

The determination of available phosphorus by anion-exchange resin is recommended. The resin in the bicarbonate form should be used especially for acid soils. The phosphorus concentrations extracted by bicarbonate resin is much greater than by the chloride form. Phosphorus can be determined without any interferences from silica or other foreign ions.

CHAPTER VI

THE ROLE OF ECTOMYCORRHIZA IN THE SURVIVAL AND GROWTH OF SITKA SPRUCE SEEDLINGS ON ACID SOILS

6.1 INTRODUCTION

6.1.1 DEFINITION OF MYCORRHIZA

The name mycorrhiza is used to cover a wide range of structures composed of fungal hyphae and the roots, rhizomes or thalli of other plants (Harley, 1969). Descriptions of associations between fungal hyphae and roots were published in increasing numbers during the latter half of the 19th Century, and in 1885, Frank gave the name mycorrhiza to the composite fungus - not organs of the cupuliferae. Closely similar organs were soon described in other arborescent angiosperms, and mycorrhiza of the same type were found in many conifers (especially in the pinaceae) and also in a few herbaceous angiosperms (Harley, 1969).

While Meyer (1974) stated that young roots are sensitive to soil fungi because of their structure, cutin layers and corresponding barriers are formed only in older roots. On the other hand, the roots spread within a substrate which offers favourable conditions for existence to many fungi. Therefore, numerous fungi may penetrate into the younger parts of roots. Many authors name an infected root as mycorrhizal, provided that the higher plant suffers no damage by the fungus infection and that the infection remains restricted to the root cortex.

There is a broad spectrum of possibilities for the mode of co-existence of plant roots and fungi. The intruder may behave like a harmless parasite which has pierced the cortex cells in order to gain nutrients.

The higher plant may localize the invading fungus to the cortex tissue, but the fungus is able to withdraw organic substances from the host plant without damaging it further (Meyer, 1974).

In other cases, the reaction of the higher plant is more specific. It synthesizes inhibitory compounds during its metabolic response to fungal attack and, as a consequence of this, may digest the penetrated mycelia. Through this digestion, the host plant regains organic compounds previously taken away (Meyer, 1974). There is also the possibility that the higher plant during lysis of mycelia regains mineral or organic nutrients which the fungus has drawn from the soil. In such cases, symbiosis may render advantages to the host plant (Bowen, 1973).

6.1.2 OCCURRENCE OF MYCORRHIZA IN THE PLANT KINGDOM

With respect to the co-existence of higher plants and fungi, there are many transitions from harmless parasitism of fungi to unilateral dependence of higher plants on the mycorrhizal fungus. In comparison with most other parts of higher plants, the tender roots can be infected quite easily, and therefore numerous cases of mycorrhiza in the plant kingdom have been recorded (Meyer, 1974). In general, root hairs cease to form as soon as a mycorrhiza is established. This means that the active surface for nutrient and water uptake is diminished (Meyer, 1974). However, in some cases, fungal hyphae act as additional absorbing organs. The prevalence of mycorrhiza in the plant kingdom and the fact that the root stops root hair formation after fungal infection should be considered in experiments on plant nutrition (Meyer, 1973).

The uptake of nutrients via a root system under natural environmental conditions is greatly influenced by the state of symbiosis. Mycorrhiza of pine and other trees with long and short roots are classed as ectotrophic, on the basis of internal structure (Zak, 1964). The fungus encases the short root with a mantle of variable thickness, colour and texture, and penetrates between epidermal and cortical cells, forming a network of hyphae commonly known as the "Hartig net" (Harley, 1969). The cells increase in radial diameter causing enlargement of the root itself. The stele and apical meristem are not invaded. In contrast, the endotrophic form of mycorrhiza, common to maple, sweetgum and redwood, lack a mantle and exhibit intracellular penetration by hyphae. A third form, the ectendotrophic mycorrhiza, observed on roots of pine and other species, is considered to be transitional between the ectotrophic and endotrophic forms (Zak, 1964). It resembles the ectotrophic form of mycorrhiza, but with intracellular penetration by the fungus. Fungi associated with ectotrophic mycorrhiza of forest trees are largely basidiomycetes, principally in the Amanitaceae, Boletaceae, Cortinariaceae, Tricholomataceas, Rhizopogonaceae, Sclerodermataceae (Zak, 1964).

6.1.3 ANATOMICAL FEATURES

In most of the mycorrhiza the mycelia pierce into the interior of the cortex cells. As the mycorrhizal fungus attacks the host primarily in the same way as a parasite, the intracellular hyphae might be considered as haustoria (Meyer, 1974), which are often noticed in the pathogenic fungi. It appears that the host plant attempts to resist the invading hyphae by forming a cap of membraneous substance at the place of

penetration (Meyer, 1974). The localized secretion of membrane substance certainly represents a defence reaction and may be successful in encasing the penetrating fungus (Harley, 1969).

In some mycorrhiza a high content of tannins-whose secretion is also considered to be a defence mechanism is obvious. The nucleus of infected cortex cells often swells and exhibits hyperchromicity (Hadley and Williamson, 1971). This is an indication that the metabolic activity of the nucleus increases (Meyer, 1974). In general, the fungus settles in the outer layers of the root cortex, but when it tries to penetrate further into the inner layers of the root cortex, it can be overcome by the resistance of the host (Harley, 1969). Hadley and Williamson (1971) proposed the hypothesis that the transfer of nutrients from fungus to host occurs before digestion sets in, and that lysis is only a defence reaction and not a prerequisite for growth stimulation of the host plant.

Meyer (1974) recognized two main groups of mycorrhiza: ectomycorrhiza and endomycorrhiza. In the endomycorrhiza, the fungal associate lives with one part of its mycelium within the root cells, that means intracellular, while in the ectomycorrhiza it develops among the cortex cells of the root (intercellular). In the endomycorrhiza as well as in the ectomycorrhiza the fungal mycelia invade not only the roots, but a more or less larger part thrives outside the roots in the soil. In the ectomycorrhiza the mycelium between the root cells forms a network known as the Hartig net (Harley, 1969; Meyer, 1974). This net creates a large common surface of contact between fungus and higher plant and thus facilitates the exchange of substances. Furthermore, in ectomycorrhiza

the root is often surrounded by a fungal network, the fungus mantle. This sheath encloses the root apices and tender parts of roots without leaving any gap, so that there is no direct contact between the younger roots and the soil and all nutrients absorbed into the host must pass through the fungus mantle (Meyer, 1974). Between ecto- and endomycorrhiza there are anatomical transitions that can be named ectendomycorrhiza. In some ectendomycorrhiza distinct fungal partners have been described (Mikola, 1965; Wilcox, 1971). Endomycorrhiza vary more than ectomycorrhiza and are by far the more prevalent type (Meyer, 1974). Ectomycorrhiza are more unique and exhibit a rather definite pattern. Ectomycorrhiza appear to be a more advanced form of symbiosis than endomycorrhiza. The majority of forest trees have ectomycorrhiza (ECM) (Trappe, 1962), and most non-woody species, including a large number of agricultural plants, form endomycorrhiza (EDM) usually of the vesicular-arbuscular type (Gerdemann, 1968; Mosse, 1973).

The terms ectomycorrhiza, endomycorrhiza and ectendomycorrhiza used in this review have been changed or proposed by Peyronel et al. (1969) to replace the formerly used terms ectotrophic, and endotrophic mycorrhiza.

Another term called Pseudomycorrhiza, was first used by Melin (1917) to describe intracellular roots in which the roots did not produce the dichotomous branching characteristic of true mycorrhiza. Usually the root was invested with a fungal sheath which rarely became pseudoparenchymatous, and the intercellular hyphae were coarse and thick

walled (Marks and Foster, 1973). Intracellular penetration occurred and the lumens of the cells were filled with hyphae. Ectomycorrhiza in particular is so affected by local conditions as to become dominant in the root surface zone (Harley, 1969).

6.1.4 MYCORRHIZA AND FORESTRY PRACTICE

(i) Ecological Distribution of Fungi

The functioning of mycorrhiza has an important bearing on practical problems of forestry (Harley, 1969). They are important especially in the reafforestation of treeless areas, in the introduction of exotic trees, and in the raising of seedlings and transplants in nurseries (Zak, 1964). It is usually true that mycorrhizal fungi are potentially present as spores or actually present as mycelia in old forest areas, and that any planted tree will encounter them (Harley, 1969).

Asceptic culture methods have also shown that a single host species may form mycorrhiza with several species of fungi belonging to more than one genus. Zak and Bryan (1963) and Zak and Marx (1964) found that a single host-tree could at one and the same time associate with many different symbionts and a single root with two or three.

Work on the ecological distribution of Basidiomycetes shows quite clearly that, in any area of forest, a large number of potential mycorrhiza formers are usually present (Harley, 1969). In contrast to sites within naturally forested zones, the treeless areas are devoid of naturally occurring mycorrhizal fungi (Slankis, 1961). Many cases have been reported from such places of trees failing to become established if they were not mycorrhizal before planting, or if they were not inoculated with suitable fungi (Harley, 1969).

In native forests, there are many fungi which form ectomycorrhiza and are best adapted to the conditions prevailing on that particular site (Meyer, 1973).

(ii) Primary or Secondary Treeless Sites

Man often tries to extend forests or tree plantations to sites which either have never borne trees or were treeless for a long period as in the Prairies, peat soils, or industrial wastelands. Little is known about the survival of ectomycorrhizal fungi in soils that were free of woody plants for very long periods (Meyer, 1973). Some faculative mycorrhizal fungi such as Cenococcum graniforme, Xerocomus subtomentosus or Laccaria laccata might survive for several years as free-living saprophytic mycelia after the trees were removed (Harley, 1969; Meyer, 1973). It must be assumed, however, that spores and possibly mycelia of obligate ectomycorrhizal fungi may reach such soils. Wilde (1954) observed ectomycorrhiza on seedlings which were raised in fields that had been denuded sixty years previously and stated "once a forest soil, always a forest soil". But the origin of the mycorrhizal fungi was not studied in his experiments.

(iii) Artificial Inoculation

The failure of schemes of afforestation and the establishment of exotic tree species has been ascribed sometimes correctly to the absence of suitable mycorrhizal fungi or of favourable conditions for mycorrhizal development. Success has often accompanied the inoculation of the stock with mycorrhiza-formers (Harley, 1969). It is important, however, to get the matter into proper perspective. It is possible to grow mycotrophs

in uninfected conditions, for it is not obligatory that they be associated with their fungi except in an ecological sense (Harley, 1969).

Application of nutrients to tree nurseries will bring about this, but it is not an economic proposition. It is impracticable to maintain high levels of soil nutrients during the whole period of growth of forests and plantations.

The aim of nurseries should, therefore, be to raise transplants of maximum vigour and size which are adequately equipped with mycorrhizal organs.

The actual process of inoculating sites or plants may be performed in various ways, and these need consideration in the light of field and laboratory researches (Harley, 1969).

The use of soil or humus from forest or other selected sites where mycorrhizal development readily occurs, is open to criticisms (Harley, 1969).

(iv) Techniques of Inoculation

There are three types of inocula which have been used for mycorrhizal inoculation in nurseries:-

(a) Soil from natural forests, plantations or old nurseries.

(b) Mycorrhizal seedlings.

(c) Pure cultures of mycorrhizal fungi of these inocula.

Soil has been most widely used in forestry practice for the first introduction of mycorrhizal fungi. A thin layer of soil is taken from an old nursery or an established plantation, usually spread on the top of a

nursery bed and mixed thoroughly with the soil beneath (Harley, 1940). The same method is still commonly used in various parts of the world if plants are raised in open beds on natural soil (Meyer, 1973). The demonstration by Robertson (1954) that spores have been used in attempts to inoculate seeds. Although mycorrhizal infection is known to spread easily through the air (Robertson, 1954), efforts using spores for artificial inoculation have not always been successful. Some positive results have been reported (Theodorou, 1967), but the method has not reached the stage of practical application (Mikola, 1973). Moser (1956 - 1963) has outlined methods for the culture preservation, and use of mycorrhizal fungi, and has examined practical means of applying the inoculum in various forms to plants in the nursery. The complexity of problems which have yet to be adequately studied may be comprehended if one considers the variations, genetic and phenetic, of the fungi and of their hosts against the background of environmental variation. As Moser has shown, the fungi vary in their dependence on temperature, humidity, pH and nutrient supply, and there is a genetic strain- variation with species with respect to their physiological demands and mycorrhizal potential (Harley, 1969).

Application of mycorrhizal soil is the easiest and simplest method of nursery inoculation, it is also quite a reliable method (Mikola, 1973). Soils from natural pine forests and healthy plantations most probably contain a large variety of mycorrhizal fungi, among them species which are effective and well suited for nursery conditions (Mikola, 1973).

6.1.5 THE ECTOMYCORRHIZA OF FOREST TREES

(i) Structure and Development

The structure, development and distribution of the mycorrhizas of many of the forest trees of temperate regions are so similar that they can be grouped together as a natural kind (Marks and Foster, 1973) and it is reasonable to assume that their modes of functioning as absorbing organs and their ecological roles are also similar. The species of trees known to form ectomycorrhiza belonged mainly to the Pinaceae among the gymnosperms, and to the Betulaceae, Fagaceae and a few other angiosperm families (Harley, 1969). The root system of the beech colonizes the soil within the immediate area of the tree canopy and produces a large number of fine roots in the surface layer of the soil (Harley, 1969; Clowes, 1954). The accumulation of rootlets near the soil surface is especially evident under woodland conditions (Marks and Foster, 1973). There appears to be a differentiation of the ultimate laterals into "long" and "short" roots, that is, into these of potentially indefinite growth in length, which are the main roots of the system, and their branches which are of restricted growth in length and are relatively short-lived. The short roots are often termed the "Feeding Roots", and to them is ascribed the main function of absorption (Clowes, 1954; Harley, 1969). In natural soils it is mainly the shortest roots which become modified, after fungal infection (Clowes, 1954), into mycorrhizal organs. When this has happened, the whole of the rootlet is enclosed by a fungal sheath and the apex is surrounded and covered with fungus (Harley, 1969).

Mycorrhizal short roots usually develop many branches, each

of which is also of restricted growth in length (Clowes, 1954), so that short lateral systems are formed which are completely enclosed in fungus. These roots are found most abundantly in the humus layers of the soil where their size (length, diameter and branchiness) reaches its maximum. Even in rich mineral soils, mycorrhizal infection of short roots occurs but here they are smaller (Harley, 1969; Marks and Foster, 1973).

(ii) Depth in Soil

In general, mycorrhiza are most equally distributed throughout the soil profile. In the upper humus layers, more root tips are converted into mycorrhiza than in deeper layers (Meyer, 1973). Apparently the conditions for mycorrhizal formation are better in humus than in the lower mineral B horizon (Harley, 1969). In the B horizon, the proportion of mycorrhiza declines still further with increasing soil depth. Mycorrhiza were found extending to considerable depths (Meyer, 1973).

Lyr (1963) discussed the reasons for the decrease of mycorrhizal frequency (percentage of root tips converted into mycorrhiza) with increased depth of soil. Several factors might be involved:-

(a) Decrease in oxygen content. This factor, according to Lyr, may play a subordinate role.

(b) Increase in CO_2 concentration. According to Penningsfeld (1950), below one meter the CO_2 concentration can increase to 3-4%.

(c) Changes in microflora, in the composition of organic soil components, or in nutritional status of soil and roots (Harley, 1969).

(iii) The effect of soil pH and Temperature

Ectomycorrhiza are generally assumed to be acidophilic. Most species tested in pure culture have shown maximum mycelial growth at pH 4-6 (Slankis, 1974). The fact that some mycorrhizal fungi thrive over a wide pH range 2.9 - 6.0) (Mikola, 1948).

Melin (1953) suggested that fungi forming ectomycorrhiza in slightly acidic and neutral soils differ from those in acid, support of this view is provided by the fact that white-coloured ectomycorrhiza and brown-coloured ectendomycorrhiza were formed with pinus radiata seedlings in podsolic soils at pH 4.5 or 6.2 (Slankis, 1973), but the pH requirements of the ectomycorrhiza can be influenced by nutrients. Richards and Wilson (1963) have questioned the view that sparse development of ectomycorrhiza in neutral or alkaline soil is due to the acidophilic nature of mycorrhiza fungi. This suggests that indirect effects of soil pH on the availability of soil nitrogen may be more important to mycorrhiza formation than direct effects on the fungi per seedlings (Slankis, 1974). Seedlings potted in top soil taken from a young pine plantation, produced more mycorrhiza at pH 7.5 with less soil nitrogen than at pH 5.8 with more nitrogen. The latter treatment increased the nitrogen content of the roots. The inhibitory effect of alkaline soils on mycorrhiza formation is ascribed to increased availability of nitrogen (Hatch, 1937). The optimum pH for mycelial growth of mycorrhizal fungi is always on the acid side of neutrality (Harley, 1969).

Optimal temperature for colonization and infection of roots by mycorrhizal fungi may differ considerably from those for mycelial

growth in culture (Slankis, 1974). Optimum temperatures for mycelial growth in culture vary with the medium used (Hacskaylo and Palmer, 1965) and have limited value in predicting the behaviour of the fungus in the rhizosphere (Bowen, 1973). A decrease in temperature from 25°C to 16°C reduced the mycelial growth of a 'Rhizopogon luteolus' strain in pure culture by 50% (Slankis, 1974). While almost no hyphal growth was observed in the rhizophere of Pinus radiata seedlings (Theodorou and Bowen, 1970).

In natural habitats, mycorrhiza formation often occurs at temperatures well below those required for maximum growth of mycelium in vitro (Slankis, 1974). At 10°C to 15°C, mycelial growth of "Cenococcum graniforme" in culture is poor, yet this fungus is common in spruce forests of Northern Finland where the ground remains frozen until mid-summer and soil temperatures rarely reach 20°C (Mikola, 1948). Formation of ectomycorrhiza may begin in the Spring when the temperature in the upper soil layer reaches (10°C to 12°C) (Lobanow, 1960). Mikola (1948) suggested that mycorrhiza fungi adapt to temperatures. "Cenococcum graniforme" occurs over a wide range of climatic zones. For most species the optimum temperature lies between about 16°C and 27°C (Harley, 1969).

(iv) Effect of Soil Moisture and Aeration

Soil moisture is very important for mycorrhiza formation (Slankis, 1974). Ectomycorrhiza generally are more abundant in moist locations and lowland areas than in drier sites (Vlasov, 1955; Sobotka, 1965). With daily watering of potted "Pinus virginiana" seedlings,

about 83% of the short roots became mycorrhizal compared to 2.4% with watering every fourth day (Worley and Hacskaylo, 1959). In soils with excess water, oxygen deficiency limits development of both the symbiotic fungi and tree roots (Melin, 1953). Mycorrhizal fungi are strongly aerobic (Melin, 1953; Harley, 1969). Respiration rates in mycorrhiza are higher than in non-infected roots (Melin, 1953).

The tolerance of mycorrhiza for excess moisture depends on the physiological state of the roots and their ability to supply oxygen to the fungus (Slankis, 1974).

6.1.6 ECOLOGY OF EXTOMYCORRHIZA

(i) Mycorrhiza formation

The intensity of infection depends upon conditions of the habitat and the trees concerned are often forest dominants, in temperate or subartic climates and an acid soil. It is usual to find that mycorrhiza can flourish on a range of soils between the extreme podsols with a raw-humus horizon, and the brown forest soils that are characteristic of many temperate regions (Harley, 1969; Meyer, 1973). Variations in the intensity of mycorrhizal development may be observed. Two sets of factors - (1) those affecting availability of soil nutrients and (2) those affecting photosynthesis, seem to be most important in affecting growth have been shown to depend particularly upon the supplies of nitrogen, phosphorus and potassium in available forms (Harley, 1969). Experimental work and the investigation of some species under woodland conditions, show that trees growing on soils which are well furnished with available nutrients are less intensely infected than their counterparts

growing elsewhere (Zak, 1964; Meyer, 1974). Light intensity, which affects carbohydrate synthesis in the leaves has it seems, a dual effect on mycorrhizal infection (Harley, 1969).

(ii) Mycorrhiza and Absorption

There is general agreement that a relative increase of root surface area is exhibited by seedlings which become mycorrhizal as compared with their uninfected counterparts. This is due to the increase in size and complexity of the short axes, and is further magnified by the hyphae which may radiate from the mycorrhiza into the substrate (Harley, 1969). It is equally certain that a simple increase of area does not alone explain the success of mycotrophs in difficult sites, nor the stimulation of seedlings which become infected (Harley and McCready, 1950).

The fungal sheath, which is interposed between the host-root and the soil, calls the tune in the activities of absorption from the soil (Harley, 1969). It is well known from the work of Harley and McCready, (1950), Melin and Nilsson (1950) and Harley (1969) that absorption of soil nutrients into, and translocation of them away from mycorrhiza occurs. The absorption of nutrients by mycorrhizal roots proceeds by a process depending in rate upon factors affecting the rate of metabolism, such as temperature and oxygen supply. It is also affected by inhibitors and poisons, especially by those affecting energy-releasing processes in the tissues (Harley, 1969). The absorption of phosphate, nitrogen and alkali metals, is rapid at the oxygen level available (Harley, 1969; Meyer, 1974), but the primary site of absorption is into the fungus. Phosphate in

particular, is mainly accumulated in the fungus (Harley and Brierley, 1954).

Forest trees which bear ectomycorrhizas are typically shallow-rooting (Harley, 1969), and exploit intensively the upper horizons of the soil. In particular, the absorbing roots are especially developed in the upper humus layers. Harley (1940), Redmond (1957), Lobanow (1960), Lyr (1963 and Mikola and Laiho (1962) have all made this point. There is an almost horizontal exploitation by the spreading mother-roots, the mycorrhizal branches of which grow generally upwards into the newly-forming humus layers. The extent of localization of exploitation varies both with the species and with the type of soil (Harley, 1969).

Werlich and Lyr (1957) estimated the distribution of absorbing roots and mycorrhizas with depth in the soil of beech woods and pine roots. Mycorrhiza were especially concentrated in the upper humic layers but were present in the deeper horizons also.

Pine mycorrhiza went deeper than beech. Lobanow (1960) has also shown that pine mycorrhiza can be found at a considerable depth (1 - 1.5 m). Ectomycorrhiza are typically organs of absorption of nutrients from the humus layers (Harley, 1969). It is reasonable to suspect and indeed there is some supporting evidence, that the release of soluble material from decaying leaf-litter is not a steady process (Harley, 1969; Bowen, 1973). Newly-fallen forest litter quickly loses its soluble minerals which are carried in solution downwards through the soil horizons. Much of this soluble mineral matter is removed as the solution passes through the biologically active surface layers. It is

to be expected that the significance of the high accumulation rate by mycorrhizal organs lies in the exploitation of these flushes of released nutrients, and the mycorrhiza compete effectively with the other denizens of the surface layers (Harley, 1969). In other seasons, when the absorption rate is slow, phosphate and presumably other ions may pass by the active route of translocation to the host (Meyer, 1974).

(iii) Mycorrhiza and Disease

The efficiency of mycorrhiza as absorbing organs and of the avidity of their fungal sheaths in accumulation, may be thought to provide evidence of the selective advantage of the ectomycorrhizal habit (Meyer, 1974). It is also of selective advantage that root systems, the short-roots of which tend to prevent ageing should have the capacity to form an association which results in the greater functional longevity of their absorbing organs (Harley, 1969). The mycorrhizal root system has, in addition, other properties that may be ecologically significant. For instance, Harley (1940) pointed out that infected roots are more frost and draught-resistant than their uninfected counterparts. Similar conclusions were reached by Lobanow (1960). Adverse conditions which led to the collapse of the cortex and death of uninfected roots may not permanently affect mycorrhizal roots, so that they may recover physiological activity (Harley, 1969; Meyer, 1974). Any differential effect of this sort may be viewed as an additional mechanism which increases the effective absorbing area of the root system (Harley, 1969).

Zak (1964) has expressed the view that improved nutrition alone is insufficient explanation for the demonstrated benefit of mycorrhiza in

many areas. In support of this, he pointed to results of White (1941) and Briscoe (1959) in which the application of fertilizers alone failed to encourage the healthy growth of young trees and the added factor of inoculation with mycorrhizal fungi was necessary for successful growth. This might be because mycorrhiza formation protected the rootlets against parasitic invasion (Harley, 1969). Boullard (1960) has supported this view in his discussion of biological factors relevant to the problems of reafforestation, and it is the contention of those who have studied the so-called pseudomycorrhizal infection that mycorrhizal fungi successfully compete with pseudomycorrhizal mycelia. Mikola (1965) gave examples of how ectomycorrhizal fungi supersede ectendomycorrhiza fungi on the new rootlets when seedlings are transplanted from nursery soil to woodland soil.

6.2 MATERIALS AND METHODS OF ANALYSIS

Samples were collected from four different sites in compartment 7, Pitmedden Forest in August 1978. Samples were collected from six blocks in Forest site, compartment 105, Fiunary Forest in June 1979. Samples were collected from five blocks in Pasture Site, compartment 302, Fiunary Forest in June 1979.

The Fermentation layer (F) is the major site for mycorrhiza production. Nursery seedlings have no mycorrhiza when planted out, whereas self-regenerated seedlings have fully developed mycorrhiza. All samples were dried at 40^{o}C.

Chemical Analysis

All laboratory analyses were performed in triplicate. The

basic method employed to bring the total metals present in mycorrhiza into solution is explained in Chapter III, Section 3.3.6.

6.3 RESULTS AND DISCUSSION

Growth responses to ectomycorrhizal fungi have now been reported on many occasions, and the response has usually been interpreted as being due to increased nutrient uptake from soils low in one or several nutrients. Nutrient relations of any plant in soil consists of at least two distinct phases - (i) uptake from the soil itself, and (ii) use of the absorbed nutrient for plant growth.

In plant nutrition these two phases have frequently not been separated, relatively little detail is known of the efficiency of nutrient use in plants and its integration with the dynamics of plant growth (Bowen, 1973). Ectomycorrhiza benefit forest trees by aiding in absorption of organic and inorganic nutrients. Some indications are given that the efficiency of the use of nutrients in mycorrhizal and non-mycorrhizal trees may be worthwhile.

6.3.1 TREE RESPONSES

The following evidence has been used to deduce a mycorrhizal response in trees:

(i) A correlation between vigorous seedlings and mycorrhizal infection, the seedlings may have been mycorrhizal because they were more vigorous or because of some associated genetic characters (Bowen, 1973). Such observations however, have been confirmed by controlled inoculation studies (Björkman, 1942; Hatch, 1937). The results of

Hatch's study (1937) with plants grown in soil in pots revealed the following:-

(i) large increases in dry weight, percentages of nitrogen, phosphorus and potassium, and the total amount of these per seedling due to inoculation.

(ii) For nitrogen, phosphorus and potassium respectively, the uptake per g. of root in mycorrhizal plants was 1.8, 3.0, 2.0 times that of non-mycorrhizal plants, thus strongly suggesting a more efficient nutrient uptake by mycorrhizal plants.

Most analyses of ectomycorrhizal responses deal with the major nutrients, nitrogen, phosphorus and potassium. The increases in uptake will arise because of greater root growth following relief of a deficiency of another ion by the mycorrhiza, or from greater uptake rates by the mycorrhizal association itself. Absorption of $H_2PO_4^-$, K^+, Ca^{++}, SO_4^-, Na^+, NO_3^-, NH_4^+ and Mg^{++} have been demonstrated either with mycorrhiza or mycorrhizal fungi (Hatch, 1937; Zak, 1964; Bowen, 1973). Bowen and Theodorou (1967) show two more points about mycorrhizal response:

(i) significant differences between different mycorrhizal fungi can be obtained in terms of plant response and phosphate uptake, and

(ii) although a deficiency can be partly overcome by mycorrhizal inoculation, the extent of the response will depend also on the nutrient level of the soil. The responses obtained by the mycorrhizal infected trees as shown in Tables 6.03 and 6.04 were accounted for in terms of phosphorus in the Forest and Pasture Sites. Finding a response in such a situation was ascribed to the distribution of mycorrhizal fungi.

6.3.2 NUTRIENT UPTAKE FROM SOLUTIONS

Here the physiological aspects of nutrient uptake by mycorrhiza and uninfected roots are related to soil situations. Harley (1969) gave a detailed account of some aspects of ion uptake from solutions by mycorrhiza as follows:-

(a) Mycorrhizal Structural Characters

The fungal compartment, the fungus sheath around mycorrhiza and the Hartig net forms a compartment external to the root. A well developed mantle of beech mycorrhiza can be 40 μm thick (Harley, 1969). Considerable variation in mantle thickness occurs between fungi and in ectendomycorrhiza the mantle may be quite inconspicuous. Sometimes absent or only one hypha wide (Bowen, 1973). Mantle thickness is also affected by temperature changes (Wilcox, 1971), and depending on the ionic composition of uptake solutions,on the uptake characteristics of the fungus forming the mantle (Bowen, 1973), and on its thickness and compactness, entry of ions to the higher plant may be entirely via the fungus, partly via the fungus and partly directly to the root (Harley, 1969; Meyer, 1974).

The position of the mantle determines that an ion will encounter the fungus first and, where the ion is in very low concentration and the mantle is compact, most of the ion in solution will be absorbed by the fungus, very little having direct access to the higher plant cells (Bowen, 1973).

Volume: Another general feature of uptake of nutrients from solution is that uptake is more closely related to volume, than to root

length or surface area (Russell, and Newbould, 1969). As well as the mantle, radial extension of cortical cells which sometimes accompanies mycorrhizal transformation will increase volume uptake from solutions over short periods considerably.

(b) Mechanisms of Uptake

A detailed treatment of mechanisms of ion uptake by plants is given by Briggs et al. (1961), Dainty (1969). As an ion moves to a plant cell it first encounters the cell wall with a net negative charge which correlates with the carboxyl groups of polyuronic acids of the cell wall. This can lead to adsorption and/or exchange of cations which leads to some modification of the ionic composition of the solution.

6.3.3 UPTAKE FROM SOILS

(a) Tree Root Characteristics

Morphological features of the mycorrhizal root system are particularly relevant to the physical bases for the mycorrhizal response proposed by Hatch (1937). He proposed the nutritional response was due to increase in absorbing surface of the roots caused by increased diameter and branching of mycorrhiza to the growth of hyphae into soil and to the greater longevity of mycorrhiza. These parameters have rarely been measured with different mycorrhizal fungi with a view to assessing their importance in differences between mycorrhizal types and uninfected roots in uptake of nutrients from soil (Bowen, 1973). The characteristics of the root or mycorrhiza involved in uptake are:-
(i) their absorbing power for ions and water, including maintenance of these properties (Harley, 1969), (ii) abundance and distribution of roots,

and (iii) the effective radius of the root or mycorrhiza (Bowen, 1973), that means the root plus root hairs or mycorrhiza plus hyphal extensions. Organized aggregates of fungi (as mycelial strands and rhizomorphs) growing from mycorrhiza are treated as analogous to root growth.

(b) Water Uptake

The movement of ions to mycorrhiza by convection in water assumes that mycorrhiza have a sustained water uptake function (Bowen, 1973). The physiology of water absorption by mycorrhiza has been little studied (Bowen, 1973; Meyer, 1974), but it would be most surprising if they did not have this function. Lobanow (1960) observed very low root absorption surface/leaf transpring surface ratios for some woody plants compared with herbaceious plants and non-mycorrhizal tree species and suggested that the deficit of surfaces required to absorb water were made good by external hyphae of ectomycorrhiza. A parallel situation probably occurs to that with the vesicular-arbuscular endomycorrhizal association (Harley, 1969; Mosse, 1973). Theodorou and Bowen (1970) indicated a greater drought resistance of mycorrhizal seedlings.

(c) Phosphate Uptake

(i) Readily soluble (available) phosphate

Soil solution concentrations of phosphate are insufficient to account for convection supplying the phosphate needs of most plants (Bowen, 1973). It seems, therefore, that differences in abosrbing power of different mycorrhiza will play a role in differences between mycorrhizal fungi in stimulation of tree growth in phosphate-deficient soils

Fig. 6.01 Relation ship Of [Al] Conc. In Sitka Spruce Mycorrhiza & Needles. Roots Forest Site.

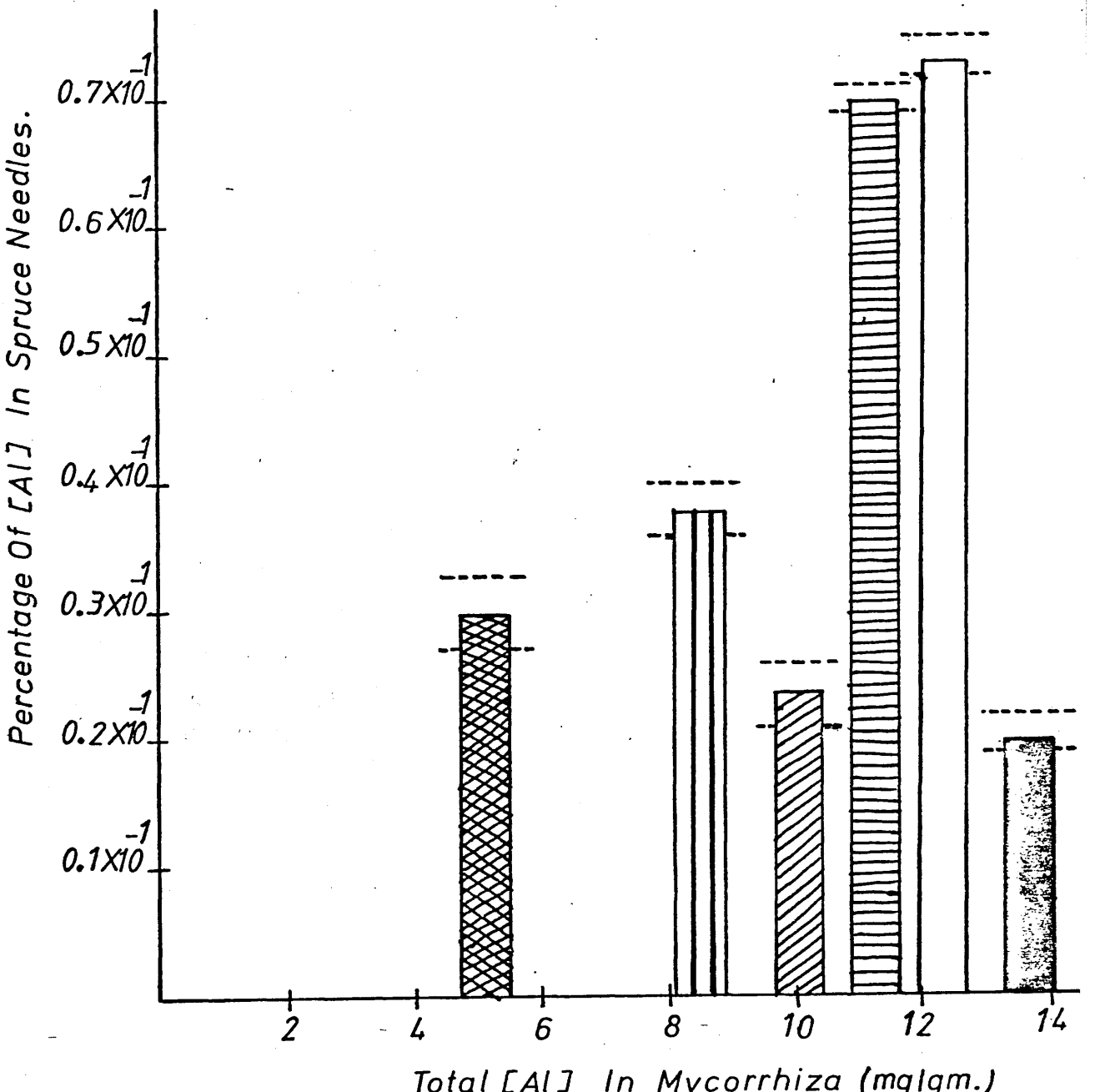


Fig. 6.02 Relationship Of [Al] In Sitka Spruce - Mycorrhiza/V Needles.

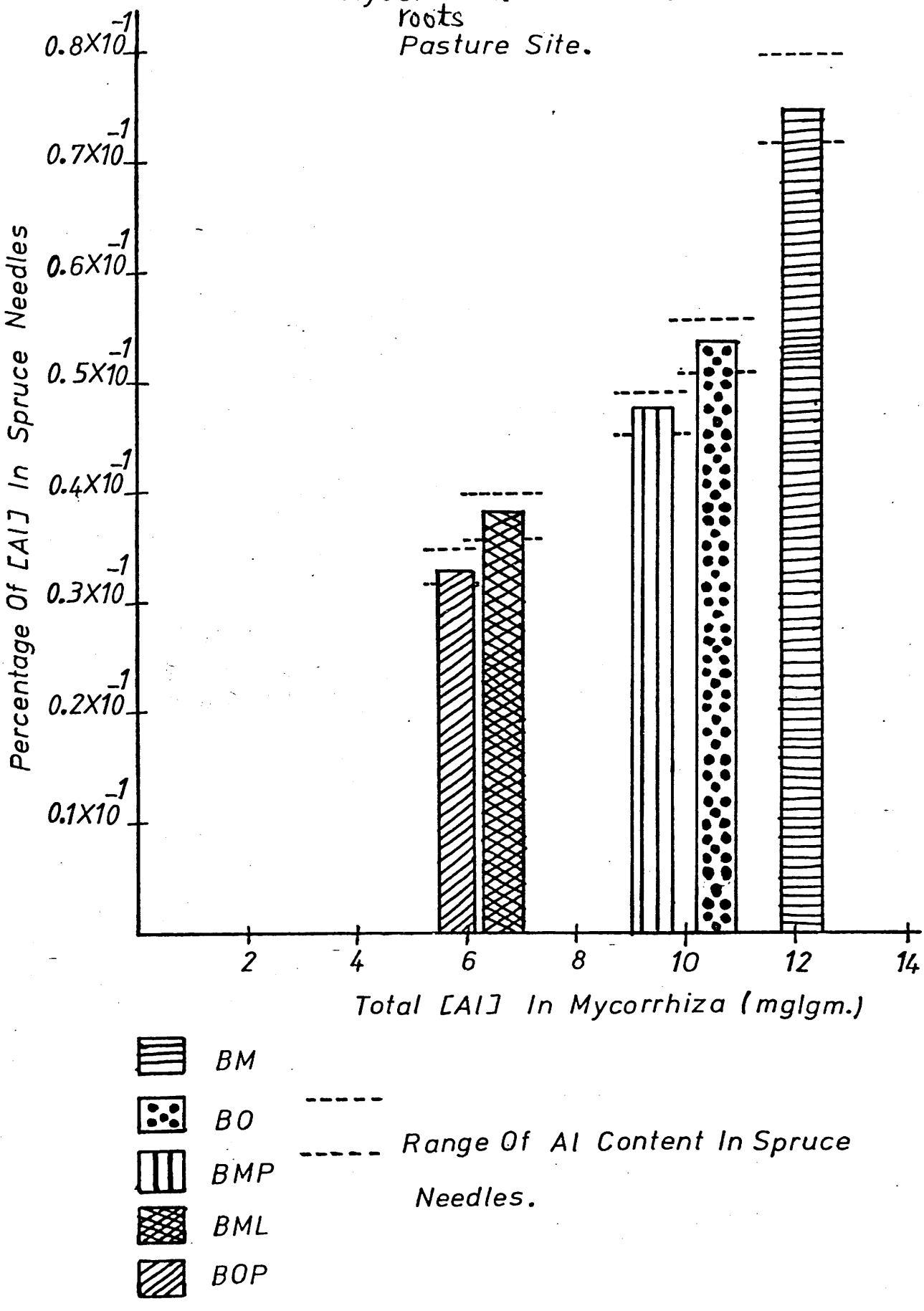


Fig. 6.03 Relationship Of [P] Conc. In Sitka Spruce-Mycorrhizal V Needles.
roots
Forest Site.

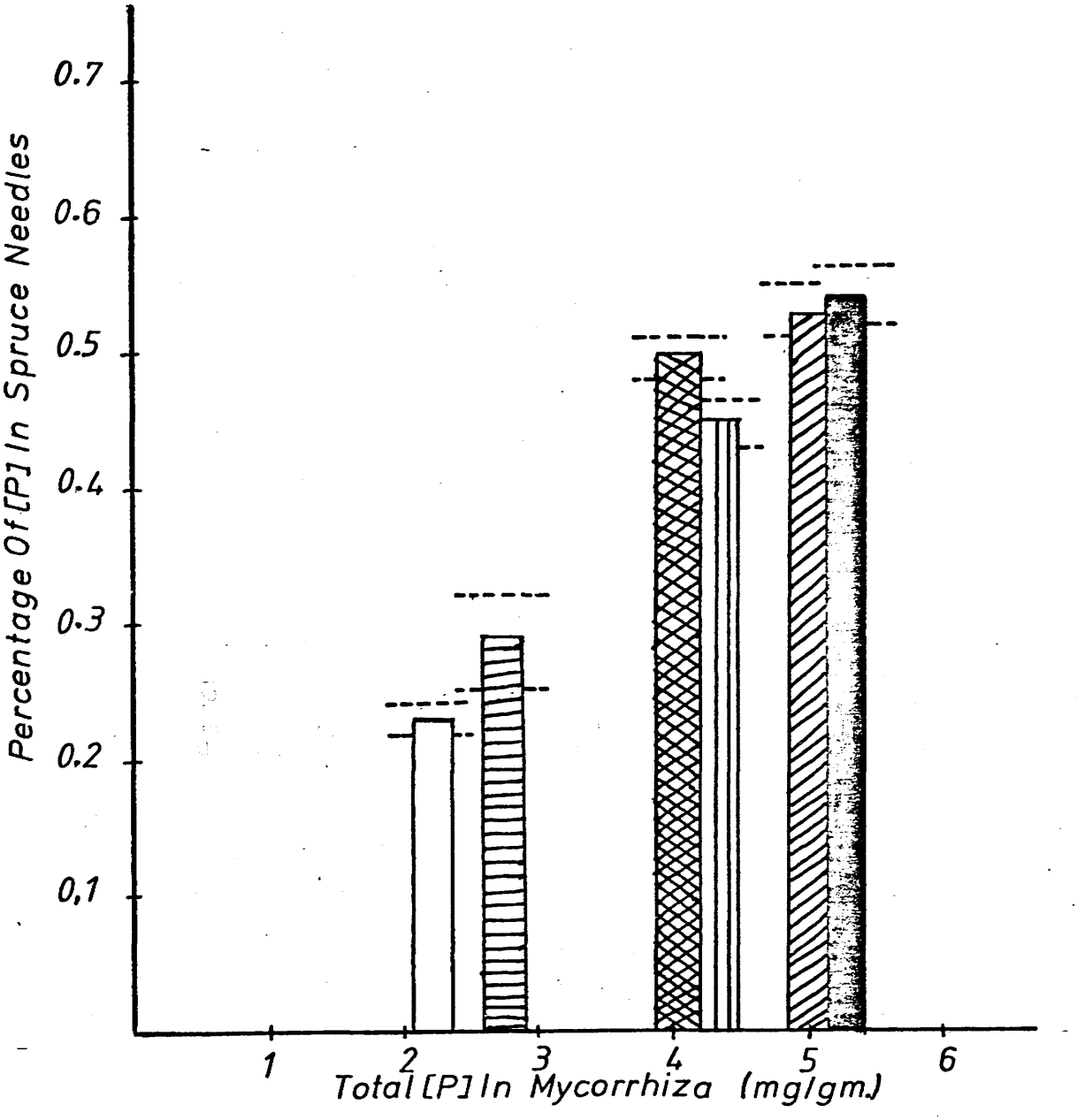
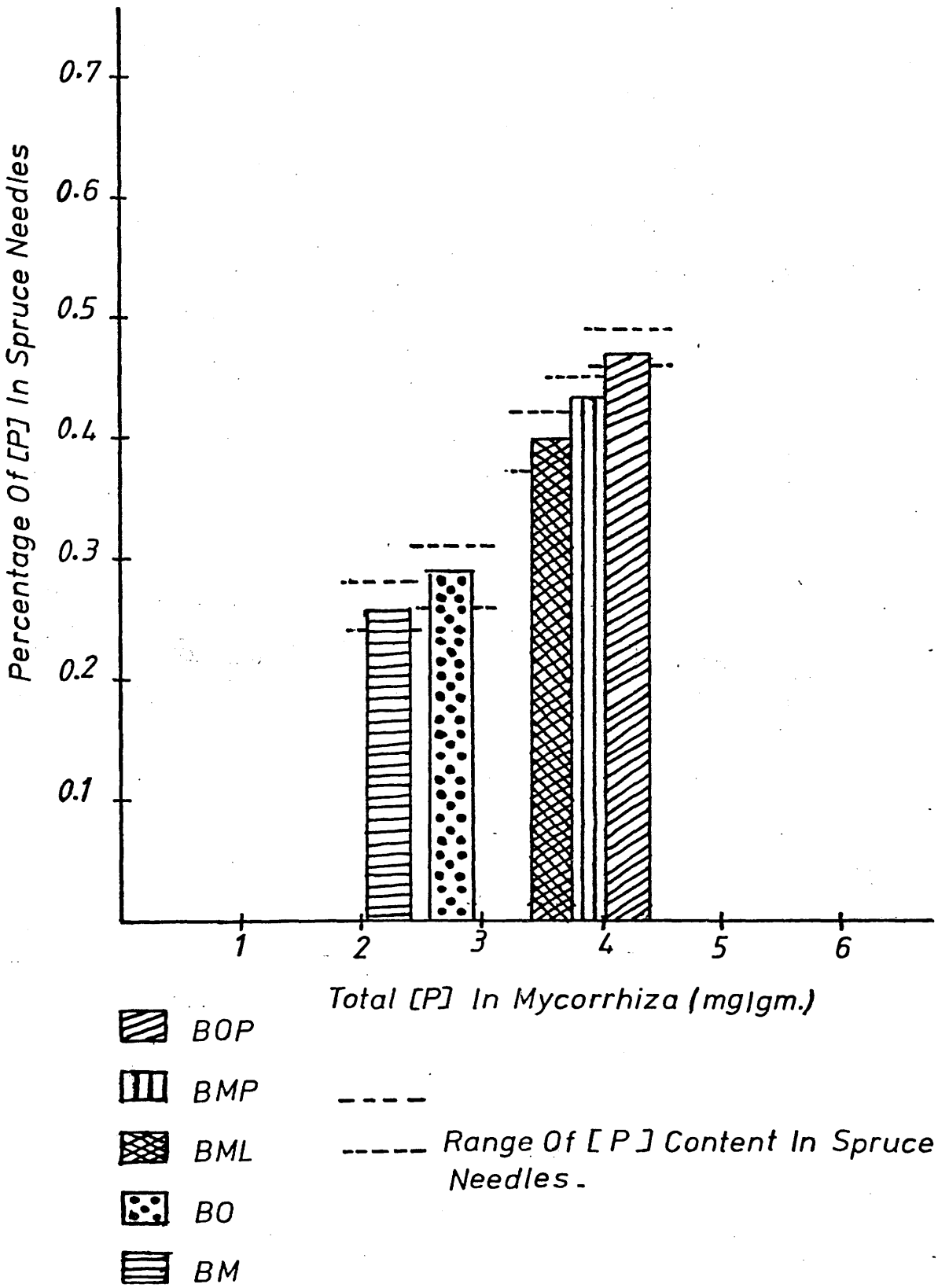


Fig. 6.04 Relationship Of [P] Conc. In Sitka Spruce - Mycorrhizal V Needles. roots Pasture Site.



(Bieleski, 1973). However, differences in the absorbing power may well be important in rapid uptake of large amounts of phosphate when flushes of these arise by flushes of decomposition, or from leaf leachates, (see Table 6.07). Increased diameter of mycorrhiza over that of the uninfected root should contribute to increased phosphate uptake/cm of root (Harley, 1969).

The results shown in Figure 6.03 indicate the range of total phosphorus in mycorrhiza and the range and average of percentage of phosphorus in sitka spruce needles. There is a high correlation between mycorrhizal and spruce needles levels of phosphorus.

(ii) Poorly soluble phosphates

Mineral forms, mycorrhiza could have a solubilizing effect on poorly soluble phosphates. These ideas have not been critically tested experimentally (Bowen, 1973). Solubilization of mineral phosphate by mycorrhizal fungi can readily be shown in laboratory media by Bowen and Theodorou (1967), who reported a response of mycorrhizal and non-mycorrhizal P-radiata to rock phosphate.

(iii) Organic phosphates

In most soils, the organic phosphate is the dominant fraction of the total phosphate (see Table 4.07). Since most ectomycorrhiza are formed in the humus layer (Melin, 1953; Harley, 1969), questions have been raised about the ability of mycorrhizal fungi to utilize complex organic matter.

Bowen and Theodorou (1967) reported that 80 - 93% of phosphorus in decomposing P-radiata litter was in various organic forms, much of

this may have been bound up in microbial cells and is not available to other micro-organisms until death of the cell.

Organic phosphates will be used readily by a wide range of soil micro-organisms as carbohydrate and energy sources (Harley, 1969; Bowen, 1973), and because of their positional advantage in being spread throughout the soil, micro-organisms will absorb most of the readily available organic phosphates rather than the higher plant (Bowen, 1973). While Went and Stark (1968) and Harley (1969) suggested that, it may be necessary for plant to take up little more than is lost by leaching and litter fall, and trapping these nutrients in competition with other micro-organisms. Most efficient trapping will, of course, arise with mycorrhizal fungi with extensive mycelial growth from the mycorrhiza.

The advantage of the mycorrhizal association, in contrast to uninfected plants, in use of organic phosphates is the ability of mycelia to penetrate soil pores and soil organic matter at distances from the root (see Tables 6.03 and 6.07), thus competing positionally with other soil micro-organisms and then translocating absorbed phosphate to the plant. The ability of certain mycorrhizal fungi to produce antibiotics against soil micro-organisms (Marx, 1969).

(d) Nitrogen Uptake

In a case such as from Forest and Pasture sites, it could be expected that differences between mycorrhiza in rate of nitrate absorption would lead to some differences in nitrate uptake (see Table 3.23), however, the growth of hyphae and mycelial strands into soil will shorten movement paths considerably and increase the rate of transfer

from soil (Bowen, 1973), however, where nitrate is low in soils, it appears that diffusion to roots will be the dominant factor (Nye, 1969). Nitrate is not absorbed by soil and will, therefore, diffuse more freely than most other major plant nutrients.

The uptake of ammonium ions from soil by mycorrhiza will be aided considerably by longevity and fungal growth into soil (Harley, 1969). On the other hand, the ability of both mycorrhizal fungi and higher plants to absorb organic forms of nitrogen was indicated by Miller (1967), who found mycorrhizal root systems of Pseudotsuga menziesii and of P-radiota had greater abilities to absorb organic nitrogen compounds from soil than did non-mycorrhizal roots and that differences occurred between mycorrhizal fungi in the use of amino acids.

(e) Uptake of other ions

Mycorrhiza could assist uptake by increase in size of this effective root diameter and fungal growth into soil, the results given in Tables 6.05, 6.06 and 6.07 reveal that larger quantities are absorbed by mycorrhizal plants (Forest site) compared with non-mycorrhizal (Pasture site), from soils with low levels of base saturation. It was found that they have increased potassium, calcium and silicon uptake in the Forest site than Pasture site (see Table 3.22).

Voigt (1971) suggested this was due to greater hydrogen ion production by mycorrhiza and exchange for cations from clay surfaces. Respiration of mycorrhiza was 2.4 times that of non-mycorrhizal short roots. None of the studies have distinguished between the mycorrhiza

and their associated micro-organisms (Nye, 1969; Bowen, 1973).

6.3.4 THE USE OF ABSORBED NUTRIENTS

(a) Movement from Fungus to Host

Details of nutrient movement from fungus to the higher plant have been concentrated mainly on phosphate (Harley, 1969). In P-radiata where the Hartig net abuts the endodermis. Microradiography studies (Bowen, 1968) have shown little movement occurs to adjoining cortical cells, and release of phosphate for the higher plant is at the endodermis.

However, the restricted Hartig net in other systems suggests movement first to cortical cells and then to the stele (Bowen, 1973).

Metabolic inhibitors prevent the movement of phosphate from fungus to the host plant (Harley, 1969). Phosphate passes to the root tissue as inorganic orthophosphate (Harley and Loughman, 1963).

(b) Storage of Nutrients

Most of the existing information on nutrients in the sheath of mycorrhiza is on phosphate (see Tables 6.03 and 6.07).

A detailed study of this was performed by Harley and his workers at Oxford. Their studies with excised roots (Harley, 1969) showed that some 90% of phosphate remained in the sheath, in a pool, not mixing with incoming phosphate, and that this stored phosphate was released to the plant over a period when external phosphate supplies were removed. Their studies and those of Jennings (1964) showed there are two main 'phosphorus pools', a small pool integrated with metabolism

of the cell and a larger non-metabolic storage pool. Storage of phosphate could theoretically be as organic phosphates, inorganic polyphosphates etc. No evidence for high accumulation of inorganic or organic polyphosphates has been forthcoming from mycorrhizal fungi despite efforts to detect them (Bowen, 1973), while Jennings (1964) suggested storage as orthophosphate. Harley (1969) pointed out that maintenance of a high phosphate uptake and storage of phosphate was likely to be ecologically important in situations where large phosphate accessions (e. g. with flushes of decomposition and in leaf leachates). Non-mycorrhizal plants absorbed less phosphate (see Table 6. 04) and translocated it more readily to the tops but for a limited period. With mycorrhizal plants translocation to the tops was initially slower but was sustained and eventually more phosphate moved to the tops than with non-mycorrhizal plants (see Table 6. 03). The storage of other nutrients has been observed at the same time as with phosphate (see Table 6. 05), Harley (1969) suggested little storage capacity for potassium.

(c) Efficiency of Nutrient Use

Applied nutrients can eliminate the mycorrhizal response in deficient soils (see Tables 6. 03 and 6. 05). It has been concluded that the nutritional mycorrhizal response is simply one of increased nutrient uptake. Earlier claims for growth-promoting substances being involved in the response (Rayner and Jones, 1944) have, correctly been criticized and accounted for on the basis of manurial treatments. The efficiency of plant use of a limiting nutrient after absorption is a little explored field. The necessary experiments to examine efficiency of nutrient use, or other

physiological parameters of mycorrhizal and non-mycorrhizal plants is to compare and examine the growth and total nutrients contents. Circumstantial evidence indicates:-

(i) Note in Tables 2.03, 2.04, that BF treatment (i.e. the seedlings planted in the mycorrhiza layer) is well ahead followed by the two treatments BFP and BMP. Moreover, the contents of phosphorus, nitrogen, potassium and silicon are highly significantly different in dry weight than the others (see Table 3.22) in the case of spruce needles.

(ii) Auxin and Cytokinin production by mycorrhizal fungi is known to occur and these may profoundly affect host metabolism. Cytokinin production may well explain prolongation of life of the cortex of mycorrhiza (Bowen, 1973). Hormones may affect hydrolysis of starch in infected cells (Meyer, 1974). Evidence is now accumulating that patterns of translocation of assimilates and nutrients in higher plants are affected largely by auxin and cytokinins (Letham, 1967). Björkman (1942) indicated relationships between carbohydrate physiology of tree species, mineral nutrient status, and mycorrhizal development. This and subsequent studies have been discussed by Harley (1969). There may be a competition between the mycorrhizal fungi and the growing buds and young shoots of a tree in respect to the effect of the auxin produced. The mycorrhizal fungi with their auxin secretion may be able to compete successfully with the auxin production of the top of the tree and a consequence of it form their bodies (Meyer, 1974). Another important factor in the carbohydrate physiology of mycorrhiza is the ability of fungal partners to convert the absorbed sugars into compounds which

the higher plant cannot influence (Harley and Lewis, 1965 a). The fungal partner intervenes in the carbohydrate metabolism of its host plant also by acting as a sink. This enhances the translocation of sugars to the root tips (Meyer, 1974).

Obviously nutrient uptake and use cannot be divorced from other aspects of the physiology of the plant (Bowen, 1973).

6.3.5 ECTOMYCORRHIZA AND SOIL ALUMINIUM TOXICITY

Ectomycorrhiza benefits are not limited in the case of forest trees to:-

(a) Aiding in absorption of inorganic and organic nutrients (Hatch, 1937; Melin, 1963).

(b) Supplying trees with growth-regulating substances (Slankis, 1973).

(c) Deterring root pathogens (Zak, 1964).

(d) Increasing host plant resistance to draught (Theodorou and Bowen, 1970; Lobanov, 1960; Bowen, 1973).

(e) It can be concluded that, there is evidence that ectomycorrhiza decreases soil aluminium toxicity and deter uptake by roots (see Figure 6.01). It was indicated by Zak (1971) that ECM decrease soil toxicity He suggested that in nature the mycorrhizal fungus may aid tree growth by protecting absorbing roots from soil phytotoxins.

While Allen et al. (1980) suggest that growth hormones such as IAA and cytokinins may be present at higher concentrations in plants that are mycorrhizal than in those that are not.

There is also some evidence that plants with mycorrhiza are better equipped to withstand stress conditions such as occur during transplanting or periods of drought, in soils containing toxic levels of manganese or salt (Hayman, 1980).

(i) Aluminium concentration in the Soil

Chemical analyses of soil samples collected from compartment 105, Fiunary Forest revealed the different treatments have a significant effect on the concentrations of soluble aluminium in soil (see Table 3.07). The most significant effect is in the Fermentation treatment (where the seedlings were planted in the mycorrhiza) (see Figures 6.01 and 2.01).

The level of extractable (soluble) aluminium is significantly decreased.

(ii) Aluminium Concentration in Sitka Spruce Needles

The different treatments have indicated a significant effect on the concentration of aluminium in tree foliage (needles) in both sites (Forest and Pasture) (see Tables 6.01 and 6.02).

Aluminium concentrations in needles are significantly decreased in the Fermentation plots. The range and average for aluminium content (%) and the range of total aluminium in mycorrhiza (mg g^{-1}) are shown in Figures 6.01 and 6.02. The percentage of aluminium content in BF treatments is 0.2×10^{-1}, while the percentage of aluminium in self-regenerated seedlings planted in mineral soil treatment is 0.73×10^{-1}.

The influence of the fertilizer and organic matter in decreasing the aluminium content is remarkable (Figures 6.01 and 6.02) on the growth

of sitka spruce, regardless of the ectomycorrhizal condition. But heavy applications of fertilizer (nutrients) to trees are not an economic proposition. Not only is it impracticable to maintain high levels of soil nutrients during the whole period of growth of forest trees and plantations (especially phosphate and lime), but also the land available and utilized for forest establishment is most frequently marginal land that is unsuited to intensive preparation, cultivation and fertilization.

The possible role of ectomycorrhiza in eliminating aluminium toxicity could be hormonally controlled and accounted for in terms of auxin production, e.g. cytokinin regulates the endogenous auxin content. It is known that in addition to auxins, mycelia of symbiotic fungi may produce cytokinins (Miller, 1971) and gibberellins (Gogala, 1971). Auxins and cytokinins have been shown to mobilize nutrients and control their translocation in higher plants (Thimann, 1972). It is possible that under certain conditions these hormones may enhance auxin production in the hyphae to a degree that is auto inhibitory to hyphal development and consequently to auxin synthesis (Slankis, 1973).

6.4 CONCLUSION

There is no doubt that ectomycorrhiza improved the survival and growth of sitka spruce seedlings on acid soils. Seedlings with this ectomycorrhizal fungus have a root system that was physiologically capable of tolerating adverse soil conditions and increasing absorption of essential nutrients from low concentrations, due to the better physiological status of the trees. Mycorrhizal benefits are not limited to improved phosphorus uptake and other nutrients, but there is also some evidence that eliminating soil aluminium toxicity is also taking place.

TABLE 6.01

Relationship of aluminium content in sitka spruce - mycorrhiza and needles. Forest Site, compartment 105.

No.	Sample Experimental Plots		Mycorrhiza mg g^{-1} ± S.D.			Spruce Needles Percentage	
1.	Plot 1	BML	4.62 ± 0.75			0.027	
2.	Plot 3	BML	5.40 ± 1.25	5.15 ± 1.05		0.033	0.030
3.	Plot 4	BML	5.50 ± 1.15			0.031	
4.	Plot 5	BF	13.80 ± 0.60			0.019	
5.	Plot 14	BF	14.10 ± 1.20	13.60 ± 0.84		0.021	0.020
6.	Plot 17	BF	12.88 ± 0.72			0.022	
7.	Plot 2	BFP	10.10 ± 0.50			0.022	
8.	Plot 11	BFP	9.85 ± 0.55	10.05 ± 0.55		0.026	0.024
9.	Plot 19	BFP	10.20 ± 0.60			0.023	
10.	Plot 9	BMP	8.50 ± 1.10			0.038	
11.	Plot 13	BMP	8.40 ± 0.70	8.30 ± 0.90		0.040	0.038
12.	Plot 20	BMP	8.10 ± 0.90			0.036	
13.	Plot 7	BM	10.80 ± 0.70			0.070	
14.	Plot 10	BM	11.30 ± 0.50	11.30 ± 0.66		0.069	0.070
15.	Plot 21	BM	11.70 ± 0.80			0.071	
16.	Plot 12	SR BM	12.25 ± 0.85	12.30 ± 0.88		0.072	0.073
17.	Plot 15	SR BM	12.40 ± 0.90			0.075	

TABLE 6.02

Relationship of Aluminium content in sitka spruce - mycorrhiza and needles. Pasture Site, compartment 302.

No.	Sample Experimental Plots	Mycorrhiza mg g^{-1} ± S.D.		Spruce Needles Percentage	
1.	Plot BM	11.80 ± 0.40 12.30 ± 0.55 12.50 ± 0.25	12.20 ± 0.40	0.080 0.075 0.072	0.075
2.	Plot BO	10.30 ± 0.30 10.50 ± 0.60 10.80 ± 0.70	10.53 ± 0.53	0.056 0.054 0.051	0.054
3.	Plot BML	6.20 ± 0.80 6.80 ± 0.60 7.00 ± 0.90	6.67 ± 0.77	0.036 0.040 0.038	0.038
4.	Plot BOP	5.70 ± 0.40 6.10 ± 0.60 5.90 ± 0.30	5.90 ± 0.43	0.031 0.035 0.033	0.033
5.	Plot BMP	9.00 ± 0.50 9.40 ± 0.42 9.60 ± 0.60	9.33 ± 0.50	0.046 0.049 0.045	0.047

TABLE 6.03

Relationship of phosphorus content in sitka spruce - mycorrhiza and needles. Forest Site, compartment 105.

No.	Sample Experimental Plots		Mycorrhiza mg g^{-1} ± S.D.			Spruce Needles Percentage	
1.	Plot 1	BML	3.8 ± 0.2			0.48	
2.	Plot 3	BML	4.0 ± 0.4	4.0 ± 0.4		0.49	0.50
3.	Plot 4	BML	4.2 ± 0.6			0.51	
4.	Plot 5	BF	5.1 ± 0.5			0.56	
5.	Plot 14	BF	5.4 ± 0.8	5.2 ± 0.6		0.55	0.54
6.	Plot 17	BF	5.2 ± 0.5			0.53	
7.	Plot 2	BFP	5.0 ± 0.5			0.52	
8.	Plot 11	BFP	5.3 ± 0.8	5.0 ± 0.5		0.55	0.53
9.	Plot 19	BFP	4.8 ± 0.3			0.53	
10.	Plot 9	BMP	4.4 ± 0.6			0.46	
11.	Plot 13	BMP	4.2 ± 0.3	4.2 ± 0.4		0.45	0.45
12.	Plot 20	BMP	3.9 ± 0.3			0.43	
13.	Plot 7	BM	2.5 ± 0.5			0.25	
14.	Plot 10	BM	2.9 ± 0.7	2.7 ± 0.5		0.32	0.29
15.	Plot 21	BM	2.8 ± 0.3			0.30	
16.	Plot 12	SR BM	2.3 ± 0.2	2.2 ± 0.2		0.24	0.23
17.	Plot 15	SR BM	2.1 ± 0.3			0.22	

TABLE 6.04

Relationship of Phosphorus content in sitka spruce - mycorrhiza and needles. Pasture Site, compartment 302.

No.	Sample Experimental Plots	Mycorrhiza mg g^{-1} ± S.D.		Spruce Needles Percentage	
1.	Plot BM	2.4 ± 0.3)		0.26)	
		2.5 ± 0.4)	2.5 ± 0.3	0.28)	0.26
		2.0 ± 0.2)		0.24)	
2.	Plot BO	2.7 ± 0.4)		0.29)	
		2.9 ± 0.3)	2.8 ± 0.3	0.31)	0.29
		2.5 ± 0.2)		0.27)	
3.	Plot BML	3.5 ± 0.3)		0.39)	
		3.9 ± 0.5)	3.6 ± 0.3	0.42)	0.39
		3.4 ± 0.2)		0.37)	
4.	Plot BMP	3.7 ± 0.3)		0.43)	
		3.6 ± 0.3)	3.8 ± 0.3	0.41)	0.43
		4.0 ± 0.4)		0.45)	
5.	Plot BOP	4.0 ± 0.2)		0.46)	
		4.2 ± 0.3)	4.2 ± 0.2	0.47)	0.47
		4.3 ± 0.2)		0.49)	

TABLE 6.05

Mycorrhiza analysis: Mineral contents, in Forest Site (compartment 105)

No.	Sample		mg g^{-1} ± S.D. (air-dry 40°C)						
			Fe	Ca	K	Na	Mg	Mn	Ni
1.	Plot 1	BML	3.38 ± 0.25	3.28 ± 0.20	1.95 ± 0.21	1.66 ± 0.12	3.00 ± 0.30	0.18 ± 0.02	Nil
2.	Plot 3	BML	3.95 ± 0.35	3.60 ± 0.15	1.80 ± 0.20	1.60 ± 0.10	2.92 ± 0.20	0.20 ± 0.03	Nil
3.	Plot 4	BML	3.55 ± 0.25	3.85 ± 0.15	2.08 ± 0.32	1.75 ± 0.15	2.90 ± 0.15	0.22 ± 0.02	Nil
4.	Plot 5	BF	11.10 ± 0.40	3.20 ± 0.15	2.55 ± 0.25	1.75 ± 0.15	3.55 ± 0.20	0.25 ± 0.05	0.03
5.	Plot 14	BF	11.55 ± 0.60	3.10 ± 0.12	2.65 ± 0.15	1.65 ± 0.10	3.60 ± 0.12	0.26 ± 0.03	0.02
6.	Plot 17	BF	10.90 ± 0.30	3.25 ± 0.15	2.60 ± 0.20	1.63 ± 0.10	3.25 ± 0.14	0.24 ± 0.03	Nil
7.	Plot 2	BFP	8.38 ± 0.35	3.22 ± 0.18	2.28 ± 0.12	1.60 ± 0.10	3.20 ± 0.15	0.30 ± 0.04	0.02
8.	Plot 11	BFP	8.20 ± 0.30	3.10 ± 0.10	2.25 ± 0.15	1.42 ± 0.10	3.32 ± 0.12	0.27 ± 0.04	Nil
9.	Plot 19	BFP	8.15 ± 0.25	3.00 ± 0.15	2.46 ± 0.14	1.45 ± 0.15	3.00 ± 0.10	0.25 ± 0.03	Nil
10.	Plot 9	BMP	4.95 ± 0.30	2.80 ± 0.10	1.86 ± 0.12	1.42 ± 0.10	2.70 ± 0.15	0.21 ± 0.03	Nil
11.	Plot 13	BMP	4.53 ± 0	2.75 ± 0.12	1.67 ± 0.11	1.35 ± 0.10	2.68 ± 0.20	0.23 ± 0.03	Nil
12.	Plot 20	BMP	5.20 ± 0.30	2.55 ± 0.15	1.65 ± 0.10	1.36 ± 0.12	2.60 ± 0.12	0.20 ± 0.02	Nil
13.	Plot 7	BM	6.50 ± 0.40	2.25 ± 0.15	1.50 ± 0.10	1.40 ± 0.10	2.50 ± 0.10	0.21 ± 0.02	Nil
14.	Plot 10	BM	7.10 ± 0.50	2.30 ± 0.10	1.46 ± 0.14	1.36 ± 0.12	2.62 ± 0.12	0.22 ± 0.02	Nil
15.	Plot 21	BM	6.75 ± 0.35	2.35 ± 0.12	1.48 ± 0.12	1.37 ± 0.10	2.57 ± 0.12	0.20 ± 0.03	Nil
16.	Plot 12	SR BM	6.60 ± 0.40	2.20 ± 0.15	1.42 ± 0.10	1.32 ± 0.10	2.48 ± 0.12	0.21 ± 0.03	Nil
17.	Plot 15	SR BM	6.00 ± 0.20	2.60 ± 0.15	1.40 ± 0.10	1.33 ± 0.11	2.50 ± 0.15	0.23 ± 0.03	Nil

TABLE 6.06

Mycorrhiza analysis: Mineral contents, in Pasture Site (Compartment 302)

No.	Sample	Mg g^{-1} ± S.D. (air-dry at 40°C)						
		Fe	Ca	K	Na	Mg	Mn	Ni
1.	Plot BOP	4.95 ± 0.30	2.36 ± 0.15	1.90 ± 0.12	1.52 ± 0.12	2.80 ± 0.14	0.21 ± 0.02	Nil
2.	Plot BML	4.20 ± 0.35	3.80 ± 0.20	1.95 ± 0.15	1.60 ± 0.10	2.92 ± 0.12	0.19 ± 0.02	Nil
3.	Plot BMP	4.90 ± 0.30	2.32 ± 0.15	1.80 ± 0.10	1.48 ± 0.12	2.66 ± 0.14	0.22 ± 0.03	Nil
4.	Plot BO	6.20 ± 0.40	2.25 ± 0.12	1.66 ± 0.14	1.40 ± 0.10	2.60 ± 0.10	0.22 ± 0.03	Nil
5.	Plot BM	6.60 ± 0.45	2.20 ± 0.10	1.46 ± 0.14	1.32 ± 0.12	2.57 ± 0.13	0.20 ± 0.02	Nil
6.	Fiunary, Savary Glen	6.25 ± 0.40	2.10 ± 0.10	1.70 ± 0.12	1.25 ± 0.15	1.50 ± 0.10	0.32 ± 0.04	0.04

TABLE 6.07

Litter and mycorrhiza analysis: Mineral content in Pitmedden Forest, (compartment 7)

No.	Sample	mg g^{-1} ± S.D. (air-dry 40°C)								
		P	K	Al	Ca	Mg	Fe	Na	Mn	Ni
1.	Pit. $1A_o$ L+F	4.08±0.10	0.94± 0.12	0.72± 0.10	1.96 ± 0.14	0.58± 0.14	7.30± 0.80	0.89± 0.10	0.15± 0.02	Nil
2.	Pit. $2A_o$ L+F	4.36±0.14	0.90± 0.10	0.54± 0.08	2.38 ± 0.14	0.78± 0.12	8.60± 0.55	1.06± 0.14	0.11 ± 0.02	Nil
3.	Pit. $3A_o$ L+F	4.45±0.17	1.52± 0.18	0.43± 0.06	2.68± 0.16	1.26± 0.14	6.70± 0.70	1.12 ± 0.10	0.13± 0.02	Nil
4.	Pit. $4A_o$ L+F	4.55±0.15	1.20± 0.10	0.52± 0.08	2.60± 0.10	0.98± 0.14	8.10± 0.60	0.90 ± 0.10	0.14± 0.02	Nil

CHAPTER VII

SILICON IN RELATION TO PLANT GROWTH

7.1 THE SILICON AND PHOSPHORUS CONTENTS OF PLANT POLYSACCHARIDES

7.1.1 INTRODUCTION

Silicon (Si) was one of the first elements to which attention was directed in this work. Considerable advances have been made recently in the estimation of trace amounts of silicon in biological samples and elucidating its mode of action and its location (Birchall, 1978; Schwarz, 1973). Although some doubt still exists regarding the type of bonding involved it is now generally accepted that silicon exists in close association with a range of polysaccharides and is thought to have a structural role possibly as a cross linking agent. It would appear to date that with regard to plant polysaccharides silicon is mainly present in the pectic fraction (Birchall, 1978; Schwarz, 1973). However, from studies in this laboratory with starch and related polysaccharides, some parallels in behaviour were noted between pectin and potato starch which could not readily be explained in the latter case in terms of bound phosphate.

It was therefore decided to look more closely at the silicon and phosphorus contents of a range of polysaccharide components paying particular attention to starch samples.

7.1.2 EXPERIMENTAL

7.1.2.1 Materials

Commercial samples of the following polysaccharides were analysed and sources are listed below:-

Citrus pectin (Sigma Chemical Company Limited); Apple pectin 240 and 250 (British Drug Houses Limited); Glycogen and sodium alginate (British Drug House Limited); Maize, Rice, Wheat starch (Hopkin and Williams Limited); Potato starch, Soluble starch (Hopkin and Williams Limited); Dextran 80, 150 and 500 (Pharmacia Limited); Fresh potato starch samples were prepared in the laboratory by published methods (Rees and Duncan, 1972). Amylopectin and amylose samples were prepared from the starch using n-butanol. Potato pectin was prepared in the Agricultural Chemistry Department by Dr. M. Jarvis.

7.1.2.2 Methods of Analysis

7.1.2.2.1 Equipment and Reagents

Polyethylene ware, rather than glassware, should be employed whenever possible, in order to minimize silicon contamination. The glassware must be steeped in a nitric sulphuric acid mixture (1 : 1) to dehydrate the silicon, rinsed by deionized water and steeped in deionized water before use.

Reagents for silicon determination are described previously in Section 3.4.3.2.

Reagents for phosphorus determination are described previously in Section 4.2.3.2.3.1

Aristar perochloric acid 72% (w/v).

7.1.2.2.2 Preparation of Standard Polysaccharide Solutions

A 1.0 gm sample of polysaccharide was wetted with a few drops of ethanol, shaken and left for about 2 min., then boiled for 5 min. with

60 ml. deionized water. If after this time, the solution was not complete, a few drops of 1.0 M H_2SO_4 were added and the contents heated once more, then removed and cooled slightly and the volume adjusted to 100 ml with water.

7.1.2.2.3 Acid Digestion

To a 1.0 gm sample of polysaccharide was added 6 ml 72% (w/v) H Cl O_4 in a 500 ml conical flask. The neck of the flask was constricted by the insertion of a filter funnel plus thermometer. The flask was placed on a sand bath and the contents maintained at 125°C. The digestion of the sample was carried out until clear. As the digestion was completed, dense white fumes of H Cl O_4 ceased. After cooling sufficiently, the contents were made up to 100 ml with water.

7.1.3 ANALYSIS FOR SILICON

7.1.3.1 Colorimetric Method

A 5 ml aliquot of sample and 5 ml deionized water were pipetted into 50 ml volumetric flask (the pH of this solution was about 1.9), 3 ml of molybdate reagent was added. The contents of the flask were mixed by swirling and a yellow colour developed. After exactly 10 min., 15 ml of reducing agent (Metol solution) was added. The volume was made up to 50 ml, the contents mixed well and allowed to stand for 3 hr. to complete the reduction.

All analyses were carried out at least in triplicate.

7.1.3.2 Atomic Absorption

Silicon was determined mainly in the clarified ashed samples and

occasionally in the polysaccharide solutions direct. A dual beam instrument was employed (Perkin Eluner 306) and matrix effects were minimised by making up the silicon standards in the same acid mix as was employed for the ashing step. The analysis was also checked by the method of standard additions.

7.1.3.3 Bound Versus Free Silicon

This was determined essentially by the method of Schwarz (1973) employing the above colorimetric procedure. Free silicon (Si) was determined in non-ashed samples. Total Silicon (Si) was determined in pre-ashed samples. All analyses were carried out at least in triplicate.

7.1.4 ANALYSIS FOR PHOSPHORUS

7.1.4.1 Colorimetric method

The ascorbic acid procedure was employed, as described previously in Chapter IV, Section 2.3.2.3.1.

Phosphorus was determined mainly in the clarified ashed samples.

7.1.5 RESULTS AND DISCUSSION

The presence of substantial quantities of silicon (1.4 - 2.3 mg g^{-1} dry-weight) was confirmed in all pectin samples employed, irrespective of the source (Table 7.01). In the samples analysed, the silicon content of citrus pectin was found to be consistently higher than for potato and apple. The quality of the product in the case of apple pectin (240 as against 250) did not appear to influence the silicon content. Potato pectin was found to have a silicon content between that of citrus and apple pectin. In the case of all other polysaccharide samples, with the exception of

potato starch, negligible quantities of silica (< 0.2 mg g^{-1} dry-weight) were detected (Table 7.01). These findings are broadly in line with published data (Schwarz, 1973; Birchall, 1978). Silica was, however, identified in potato starch in significant amounts (0.4 - 0.8 mg g^{-1} dry-weight) which contrasted with starches from other sources. Early literature (Samec, 1927) did make reference to silica being present in potato starch but this has since tended to be ignored with more emphasis being on the phosphate moiety present (Posternak, 1935). The composition and constitution of potato starch have been the subject of a comparatively large number of early investigations, the analytical work has usually been confined to the determination of ash, nitrogen, moisture and phosphorus. (Samec, 1927; Posternak, 1935; Lampitt and Goldenberg, 1940; Smith, 1968). All samples of potato starch analysed, whether commercial or laboratory prepared, contained substantial amounts of silica although some variation in amount depending on the source was noted as for phosphate (Tables 7.01 and 7.03).

Winton and Winton (1935) and Smith (1968) state that the composition of the potato is influenced by locality, seasonal variations, temperature, the degree of maturity of the potato, the methods of culture and the fertilizers used.

Fractionation of the starch revealed again as for phosphate (Lampitt and Goldenberg, 1940) that the silica content present was associated with the amylopectin component, little if any being detected in the amylose fraction (Table 7.01). When the same polysaccharide source was employed throughout, consistent values were recorded for

silica irrespective of the analytical procedure applied (Table 7.02). Phosphate was not found to interfere in any of the analyses. Attempts to confirm the binding of silica to amylopectin by direct colorimetric analysis as adopted by Schwarz (1973), or after dialysis or mild acid treatments, at most reduced the final silica content of the sample by some 15% which would tend to suggest that the silica is tightly bound to the amylopectin fraction (Table 7.01). Potato starch does differ in a number of respects from most other starches viz. density, berefringence and swelling power as well as resistance to attack by α-amylose in vitro (Badenhuizen, 1965) and electrophoretic mobility (Samec et al., 1920). Most of these properties have been attributed to the presence of phosphate in the amylopectin fraction (Posternak, 1935). The results obtained here suggest that silica is present in the same order of concentration as phosphate (Table 7.03) and could, therefore, contribute to these properties. This realisation could lead to a fuller understanding of the behaviour and industrial roles of this particular starch source.

From the limited information available on the silica content of potato tubers (Burton, 1966), it is likely that most of the silica present is associated with the starch grain fraction which can comprise some 75% of the dry weight of the tuber, with a small but significant in the cell wall pectin fraction which accounts for some 0.5% of the tuber dry weight.

All samples of potato starch analysed, whether commercial or laboratory prepared, contained substantial amounts of phosphorus, although some variation in amount depending on the source (Table 7.03)

was noted. Posternak (1935) has concluded that the phosphorus in potato starch is bound to the polysaccharide as a phosphoric ester to the C_6 atom of the glucose residues in the starch macromolecule. Earlier Samec (1927) had found that potato starches contained 0.13% phosphorus as monophosphoryl esters as terminal groups on the glucose chains, while French (1975) indicated that potato starch contained 0.05% - 0.12% phosphorus as ester-linked phosphate. The phosphate was linked mainly or exclusively to the amylopectin (French, 1975). Phosphorus is present in wheat and rice starch (Table 7.03). In the case of maize starch, dextran and sodium alginate, phosphorus levels were negligible. Phosphorus was however identified in pectins in amounts (0.3 - 0.42 mg g^{-1} dry weight). Potato pectin was found to have a phosphorus content less than citrus and apple pectin.

7.2 ALUMINIUM, PHOSPHORUS AND SILICON INTERACTIONS

7.2.1 INTRODUCTION

Although it is doubtful if any plant physiologist today would place silicon in the list of essential nutrients, there is nevertheless increasing evidence that silicon can produce beneficial effects on plant growth. For the most part, these effects have been observed amongst gramineous species and the best examples are seen where silicon decreased manganese toxicity (Jones and Handreck, 1967; Kluthcouski and Nelson, 1980), and alleviated iron toxicity and increased yields (Okuda and Takahashi, 1962 , 1964). The latter were interested in the interaction between silicon and iron from the problem of iron toxicity in

barley and rice.

McKeague and Cline (1963) found that monosilicic acid was adsorbed by iron and aluminium oxides, adsorption of monosilicic acid depended on pH in a manner resmebling the adsorption of monosilicic acid by soils. Another effect noted was the improved resistance to fungal and insect attack. Most workers are of the opinion that phosphate renders aluminium non-toxic because of its precipitation in the acid soil or in the culture solution (Pierre and Stuart, 1933; Wright, 1937; Foy et al., 1978).

This study was conducted to determine the effect of silicon (Si) and phosphorus alone and in combination with plant polysaccharide (Khalil and Duncan, 1981) on the appearance of aluminium and its precipitation in soil solution or standard aluminium solutions.

7.2.2 EXPERIMENTAL

7.2.2.1 Materials

The materials used in this study were the same as described previously (7.1.2.1). The composition of plant polysaccharides and the contents of phosphorus and silicon are given in Tables 7.01 and 7.03.

7.2.2.2 Methods of Analysis

7.2.2.2.1 Equipment and Reagents

Polyethylene ware, rather than glassware, was employed whenever possible, in order to minimise silicon contamination. 0.5 M ammonium acetate buffer solution: 77 g of anhydrous ammonium acetate was dissolved in water, pH of solution adjusted to 6.2 by 2 M CH_3 COOH solution, the volume made up to two litres.

7.2.2.2.2 Preparation of Standard Polysaccharide Solutions

Standard polysaccharide solutions are the same as described previously in article 7.1.2.2.2

7.2.2.2.3 Preparation of Standard Aluminium Solution

0.8792 g. of $Al_2(SO_4)_3 K_2 SO_4 {}^2{}_4H_2O$ was dissolved in water and diluted to one litre in a volumetric flask and filtered if necessary. This solution contained 50 µg Al per ml.

7.2.2.2.4 Preparation of Standard Phosphate Solution

0.1976 g of $KH_2 PO_4$ was dissolved in water and diluted to one litre in a volumetric flask. This solution contained 45 µg P per ml.

7.2.2.2.5 Preparation of Standard Silica Solution (100 µg Si O_2 /ml)

Pure silica was ignited in a vitreosil crucible over a meker burner for 20 min., cooled in a desiccator and 0.10 g. was weighed into a silver crucible together with 2.0 gm Na OH pellets. The covered crucible was heated for 10 min. at 750 - 800°C, cooled and ~20 ml H_2O added. It was heated on a steam bath and then poured into a litre beaker containing 20 ml 2.5 N H_2SO_4 and 600 ml H_2O. It was mixed on a magnetic stirrer and made to one litre, the resulting solution containing 100 µg Si O_2 per ml. Solution was stored in plastic bottles in a refrigerator.

7.2.2.2.6 Procedure

(a) In case of aluminium solution

10 ml standard phosphate solution, silica standard solution or polysaccharide solutions were added to 10 ml standard aluminium solution

in 4 oz extraction bottles. The pH adjusted at 6.2. Shaken on a rotatory shaker for 20 hr. The solution was filtered through a Whatman filter paper No. 42.

(b) In case of soil solution

To 2.0 g of soil sample, 100 ml of 0.5 M ammonium acetate buffer solution (pH 6.2) was added in 4 oz extraction bottles, 10 ml of phosphate standard solution, silica standard solution and polysaccharide solutions were added to bottles. 10 ml deionized water was added in case of blank. The contents were shaken on a rotatory shaker for 20 hr. The solutions were filtered through a Whatman filter paper No. 42.

7.2.3 ANALYSIS FOR ALUMINIUM

7.2.3.1 Colorimetric Method

Aluminium was determined by the oxine-chloroform method of Riley (1958) as described previously in Chapter III, section 3.4.3.1. All analyses were carried out at least in triplicate.

7.2.3.2 Atomic Absorption

Aluminium in soil solution was determined also by this method. A dual beam instrument was employed (Perkin and Elmer, 306).

7.2.4 RESULTS AND DISCUSSION

The results obtained in this investigation revealed that the influence of phosphorus, silica and polysaccharide solutions when added to standard aluminium solution, or soil aluminium solution was considerable (Tables 7.04 - 7.06). Phosphorus and silica were sharply reduced and precipitated aluminium in solution (Figures 7.02 and 7.03). The

percentage of precipitated aluminium was 63. 6 and 57. 7 respectively, after addition of 14. 5 m mole phosphorus and 16. 4 m mole silicon to 18. 5 m mole aluminium (Table 7. 04). Therefore, the ratio of phosphorus to aluminium was 1 : 1. 27, and the ratio of silicon to aluminium was 1 : 1. 12.

The precipitation of aluminium occurred at pH 6. 2 in the case of soil solution. Some earlier workers (Pierre and Stuart, 1933; Wright, 1937) have advanced the opinion that the chief remedial action of phosphate in overcoming aluminium toxicity takes place within the plant where it renders aluminium inactive by precipitation. Regarding the adsorption of silica, McKeague and Cline (1963), Hingston and Raupack (1967), Jones and Handreck (1963) have shown that oxides of aluminium and/or iron adsorb large amounts of silicon from monosilicic acid solutions and all conclude that the concentration of monosilicic acid in soil solutions is largely controlled by an adsorption reaction involving aluminium and iron oxides. The above facts suggest possible competition between phosphorus and silicon for adsorption or precipitating aluminium concentration in solutions. In soil solutions, the effectiveness of phosphorus and silicon for precipitating aluminium and reducing the concentration level is high. Phosphorus is slightly better than silicon (Figures 7. 01 and 7. 02) in these experiments. The influence of polysaccharide solutions for reducing or precipitating aluminium concentration in standard solution, or soil solutions is also significant (Tables 7. 04 - 7. 06).

The percentage of aluminium precipitated varies from 5. 4% - 57. 6%. The effect of amylopectin samples (A and C) for precipitating aluminium in solution is very high (Figures 7. 01 - 7. 03). The effect of

amylopectin sample after phosphatase treatment and subsequent dialysis, for precipitating aluminium is reduced by 27.3% due to phosphorus loss and at most, the final silica content of the sample is reduced by some 15% which confirms that the silica is tightly bound to the amylopectin, and the precipitation process depends upon the contents of both phosphorus and silica in the polysaccharide samples (Tables 7.01 and 7.03).

In the case of pectin samples, their influence in precipitating aluminium is almost the same, but citrus pectin did slightly better than apple pectin (Figures 7.01 - 7.03).

The effect of all potato starch samples in precipitating aluminium in solution varied from 36.9% - 42.7%, except for one potato sample (Majestic) (Figures 7.01 - 7.03) which contained less silicon.

In the case of wheat and rice starches, the influence in precipitating aluminium was less than other polysaccharide samples which could be due to the presence only of phosphorus (Table 7.03), and with only negligible quantities of silicon (Table 7.01).

In the case of maize, starch, dextran, sodium alginate, glycogen samples which had negligible amounts of phosphorus or silica (Tables 7.01, 7.03), their effects in precipitating aluminium very small (Figures 7.01 - 7.03).

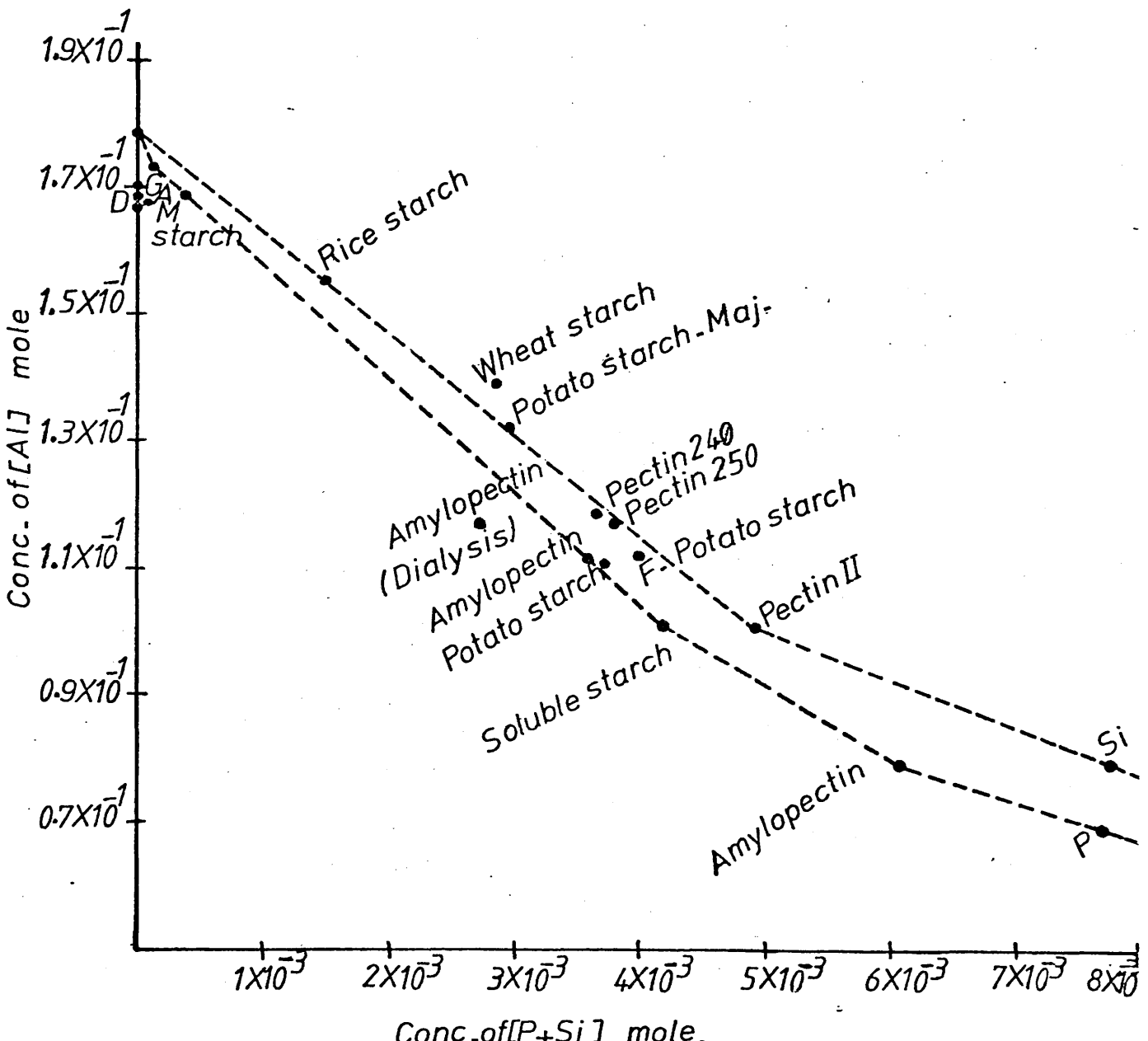
7.3 PHOSPHORUS AND SILICON INTERACTIONS

(Relation of silicon to soil available phosphate)

7.3.1 INTRODUCTION

From time to time, suggestions or claims have been made that silicon (Si) is involved in the nutrition of higher plants, regarding the

Fig. 7.01 Effect of Polysaccharide on Aluminum Precipitation.



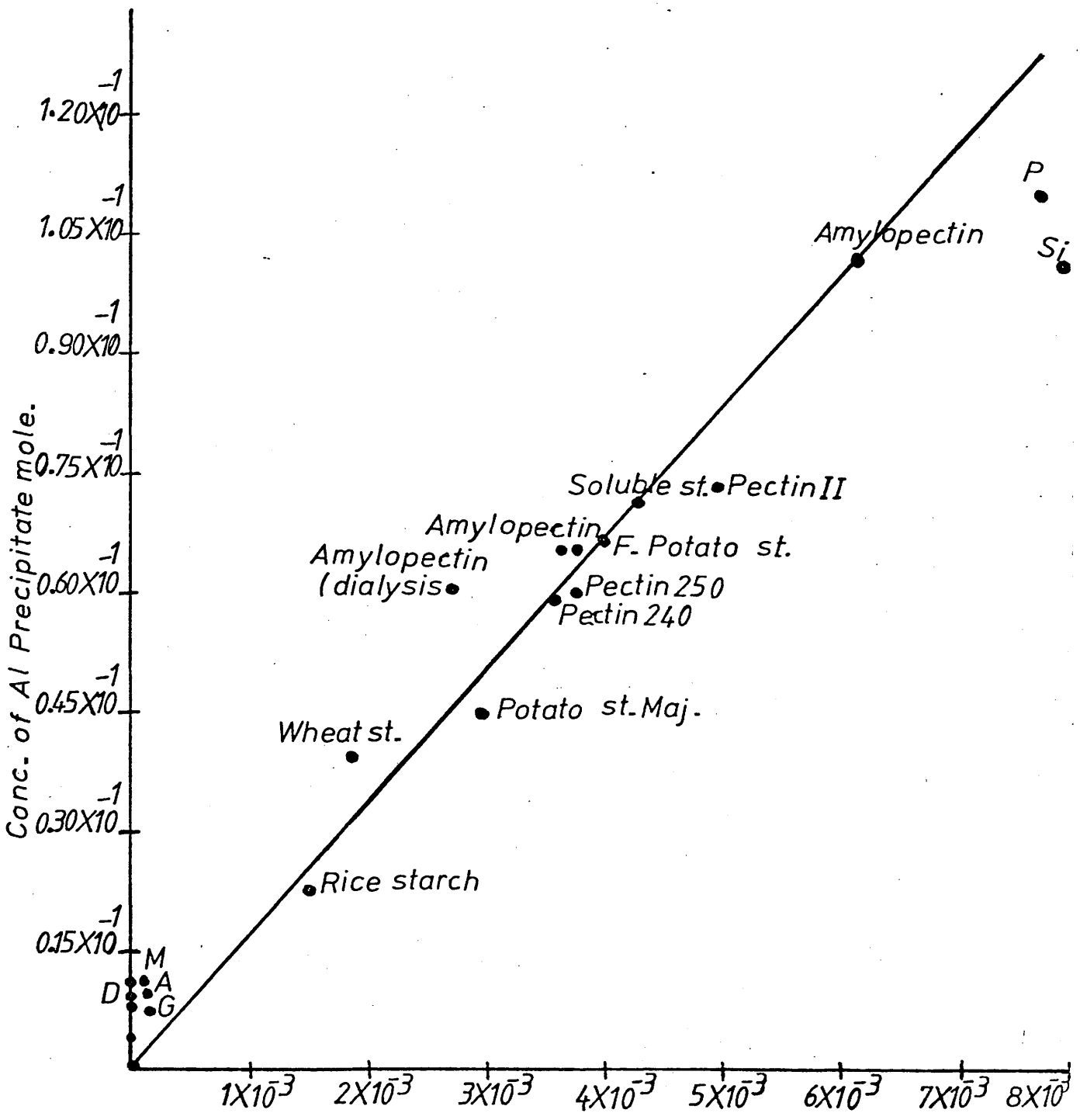
A = Alginate

D = Dextran

G = Glycogen

M = Maize

Fig. 7.02 The Influence of [P+Si] Contents of Polysaccharide Aluminum Precipitation.



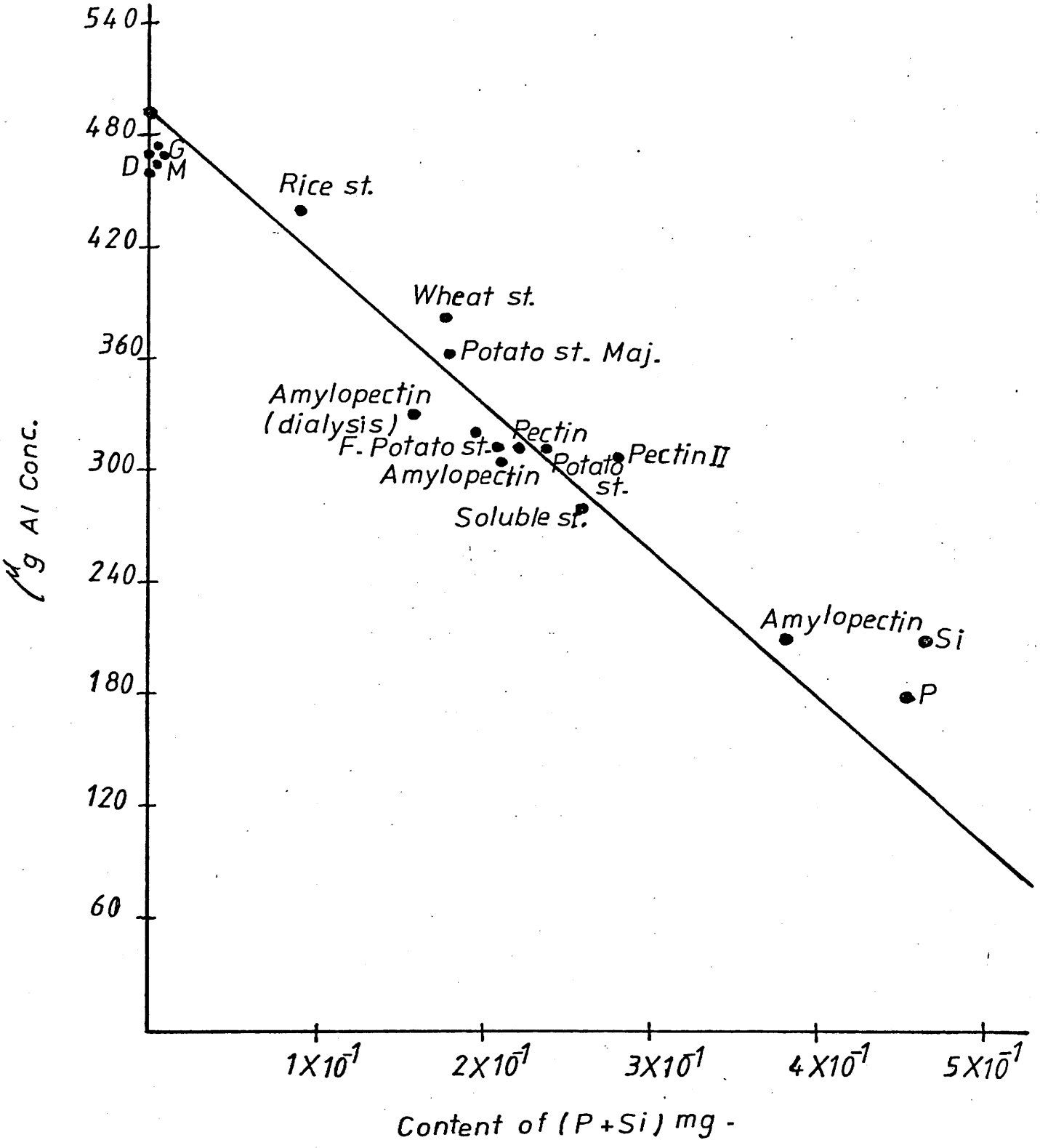
A = Alginate. Conc. of [P+Si] mole.

D = Dextran

G = Glycogen

M = Maize st.

Fig. 7.03 Effect of Polysaccharide on Aluminum Pption



essential nature of silicon (Si) and its possible relation to phosphorus (Lipman, 1938; Raleigh, 1939; Iler, 1979). It is usually difficult to judge or prove that silicon is essential for plant growth (Okula and Takahashi, 1964), but at least in the case of beet, silicon (Si) appears to be an indispensable element for growth, according to Raleigh (1939).

The importance of silicon in the nutrition of rice and barley has been emphasized by Okuda and Takahashi (1964). It was demonstrated that silicon is useful to the young plants as a nutrient. Silicon is also necessary in order that the rice plants may open and, in general, appears to be necessary for normal growth (Iler, 1979). Among the best known experiments are those at Rothamsted Experimental Station (Russell, 1973), where the addition of soluble silicates increased the growth of cereals, particularly at low levels of phosphate supply.

Hence, it was decided that compounds of silicon (Si) may have played an important role, perhaps necessary in the availability of phosphate in soil.

7.3.2 EXPERIMENTAL

7.3.2.1 Materials

Citrus pectin (Sigma Chemical Company Limited).

7.3.2.2 Methods of Analysis

7.3.2.2.1 Equipment and Reagents

Polyethylene ware, rather than glassware, should be employed whenever possible, in order to minimize silicon contamination. The glassware must be steeped in a nitric sulphuric acid (1 : 1) mixture to dehydrate the silica. Rinsed by deionized water and steeped in deionized water

before used.

0. 5 M Acetic acid solution: 28. 3 ml of glacial acetic acid (Analar) was diluted to one litre.

0. 5 M ammonium acetate buffer solution: 38. 5 g. of unhydrous ammonium acetate was dissolved in water, the pH adjusted at 6. 2 by 2 M CH_3 COOH. The volume made up to one litre.

Standard phosphate solution: 50 µg per ml. Reagents for phosphorus determination are described previously in Chapter IV, Section 2. 3. 2. 1. 1.

7. 3. 2. 2. 2 Preparation of standard polysaccharide solution (10 , 20, 40 mg per ml)

It is prepared as the same as described previously in Section 7. 1. 2. 2. 2.

7. 3. 2. 2. 3 Procedure

(a) Acetic acid solution (acidic media pH 2. 9)

To 2. 0 g of soil sample, 100 ml of 0. 5 M CH_3 COOH solution was added into polyethylene extraction bottles, 10 ml of citrus pectin solution (0 - 400 mg) was added. 10 ml deionized water was added in the case of the blank. The contents were shaken on a rotatory shaker for 20 hr. and the solutions filtered through a Whatman filter paper No. 42.

(b) Ammonium acetate buffer solution (pH 6. 2)

To 2. 0 g of soil sample, 100 ml of 0. 5 M ammonium acetate solution was added into polyethylene extraction bottles, 10 ml of citrus pectin solution was added (0 - 400 mg). 10 ml deionized water was added in the case of blank (without treatment). Shaken on a rotatory shaker for

20 hr. The solution was filtered through a Whatman filter paper No. 42.

7.3.3 ANALYSIS FOR PHOSPHATE

Colorimetric Method

Phosphorus was determined by the ascorbic acid method, which was described previously in Chapter IV, Section 2.3.2.3.1.

7.3.4 RESULTS AND DISCUSSION

There has long been interest in possible interactions between silica (or silicon) and phosphate in soils. Although silicon is apparently not essential to the growth of most plants (Iler, 1979), it has been shown that the addition of soluble silicon (Si) to soil or culture solutions has a beneficial effect, which has increased the availability of soil phosphate (Tables 7.07 and 7.08).

Table 7.07 contains data for the quantities of silicon actually added, and the effect of these various quantities in releasing phosphorus at pH 2.9.

Table 7.08 contains data for the quantities of silicon actually added, and the effect of those various quantities in releasing phosphorus at pH 6.2. It now seems clear that this effect because the plant utilizes silicon or (silicate) instead of phosphate ion, as first believed (Jones and Handreck, 1967) but rather because the silicate ion is able to displace the phosphate ion from the surface of soil or colloidal material (Iler, 1979), thus increasing the availability and the amount of phosphorus to the plant. Previously Iler (1955) in an earlier publication claimed on the role of silicon in plant nutrition concluded that silicate in the soil facilitates

the uptake of phosphorus, and it was shown also that soluble silicon (or silicate ion) is adsorbed by certain components of the soil, particularly clays.

The results in Tables 7.07 and 7.08 have indicated that phosphate ion was released slightly more at pH 6.2 than acidic media pH 2.9. For the effect of silicon in higher concentration than normal, it could lower the activity of aluminium ion in solution and so prevent it from precipitating phosphate. While little is known of the mechanism, or speed of this reaction, it remains a possibility.

Secondly, a theory that has been suggested by Jones and Handreck (1967) is that silicic acid competes against phosphate for a place on the surface of hydrated sesquioxides, while one can imagine a long-term effect in which gibbsite is silicified into kaolinite, thereby lowering its affinity for phosphate. One cannot imagine a short-term competition between silicic acid and phosphate ion for adsorption on a sesquioxide surface, for the simple reason that they are attracted to different kinds of sites. Silicic acid being an acid, is attracted via a hydrogen bond to an oxygen atom bridging two metal atoms, while phosphate, being a base, is attracted to the metal atoms (Jones and Handreck, 1967).

It therefore seems clear that the addition of silicon may have a nutritional effect because it displaces phosphate ion from the adsorbed condition on the soil, thus making phosphate more available to the plant.

It has earlier been shown by Bastisse (1946) that phosphate ion can be liberated from the adsorbed state on certain soils by the addition

of soluble silica, it is especially true of lateritic soils which adsorb phosphate ion rapidly, so that it becomes unavailable to the plants because of the formation of insoluble iron and aluminium phosphates. In soils of this type, the addition of silica displaced the adsorbed phosphate ion. Another possibility for the displacement of phosphate ions from soil by soluble silica would appear to be that silica masks the active adsorption centres of the colloid and is held more strongly than the phosphate ion, thus tending to prevent the adsorption of phosphate (Iler, 1979).

7.4 CONCLUSION

Analysis of several plant polysaccharides confirmed the presence of silica (Si) and phosphorus in all pectin samples analysed and revealed its presence in potato starch. In the latter case, the silica (Si) was concentrated in the amylopectin fraction. Other samples analysed contained less than 0.10 mg g^{-1}. It would appear that most of the silica present in potato tubers is located in the starch grain and that some of the properties of potato starch traditionally attributed to phosphate could be influenced by the silica present.

The influence of silica and phosphorus in polysaccharides for precipitating aluminium in solution is significant. The percentage of precipitated aluminium is 63.6 and 57.7 respectively, after re-addition of 14.5 m mole phosphorus and 16.4 m mole silica to 18.5 m mole aluminium. The results have indicated that the addition of soluble silica to soil or culture solutions has a beneficial effect, by increasing the availability of soil phosphate. It therefore seems clear that the addition of silica may have a nutritional effect because it displaces phosphate ions

from the adsorbed sites on the soil, making phosphate more available to the plant.

TABLE 7.01

Silica content of polysaccharides (mg g^{-1} DM) determined by atomic absorption spectrophotometry.

No.	Polysaccharide and Source	Concentration mg g^{-1} ± S.D.
1.	Citrus pectin, grade II	2.30 ± 0.12
2.	Apple pectin, grade 240	1.40 ± 0.05
3.	Apple pectin, grade 250	1.45 ± 0.05
4.	Potato pectin	1.79 ± 0.08
5.	Commercial potato starch	0.63 ± 0.04
6.	Soluble starch	0.57 ± 0.03
7.	Laboratory prepared potato starch (cv King Edwards)	0.80 ± 0.06
8.	Laboratory prepared potato starch (cv Majestic)	0.47 ± 0.05
9.	Fresh potato starch	0.75 ± 0.07
10.	Laboratory prepared potato amylopectin (A)	1.90 ± 0.10
11.	Laboratory prepared potato amylopectin (C)	0.70 ± 0.03
12.	Laboratory prepared potato amylopectin (A) dialysis	1.50 ± 0.09
13.	Laboratory prepared potato amylose	0.05 ± 0.02
14.	Wheat starch	0.08 ± 0.02
15.	Rice starch	0.05 ± 0.00
16.	Maize starch	0.02 ± 0.00
17.	Glycogen	0.03 ± 0.00
18.	Dextran 80	0.00
19.	Dextran 150	0.00
20.	Dextran 500	0.00
21.	Sodium alginate	0.00

TABLE 7.02

Comparison of colorimetric and atomic absorption methods for estimating silica in polysaccharide samples (mg g^{-1} DM ± S.D.).

No.	Polysaccharide and Source	Colorimetry		Atomic absorption	
		Ashed	Non-Ashed	Ashed	Non-ashed
1.	Citrus pectin	2.40 ± 0.12	0.00	2.30 ± 0.12	2.42 ± 0.14
2.	Apple pectin 240	1.42 ± 0.08	0.00	1.40 ± 0.05	1.45 ± 0.07
3.	Apple pectin 250	1.43 ± 0.04	0.00	1.45 ± 0.05	1.47 ± 0.06
4.	Commercial potato starch	0.63 ± 0.05	0.00	0.63 ± 0.04	0.64 ± 0.03
5.	Laboratory prepared amylopectin (A)	1.92 ± 0.12	0.00	1.90 ± 0.10	1.93 ± 0.09
6.	Laboratory prepared amylopectin (C)	0.71 ± 0.04	0.00	0.70 ± 0.03	0.71 ± 0.04
7.	Soluble starch	0.56 ± 0.05	0.00	0.57 ± 0.03	0.54 ± 0.05
8.	Wheat starch	0.69 ± 0.02	0.00	0.68 ± 0.01	0.09 ± 0.05

TABLE 7.03

Phosphorus content of polysaccharides (mg g^{-1} DM) determined by colorimetric (Ascorbic acid) method.

No.	Polysaccharide and Source	Concentration mg g^{-1} ± S.D.
1.	Citrus pectin, grade II	0.40 ± 0.06
2.	Apple pectin, grade 240	0.34 ± 0.05
3.	Apple pectin, grade 250	0.42 ± 0.06
4.	Potato pectin	0.30 ± 0.05
5.	Commercial potato starch	1.56 ± 0.07
6.	Soluble starch	1.95 ± 0.09
7.	Laboratory prepared potato starch (cv King Edwards)	1.48 ± 0.08
8.	Laboratory prepared potato starch (cv Majestic)	1.30 ± 0.07
9.	Fresh potato starch	1.60 ± 0.10
10.	Laboratory prepared potato amylopectin (A)	1.93 ± 0.08
11.	Laboratory prepared potato amylopectin (C)	1.45 ± 0.08
12.	Laboratory prepared potato amylose	0.012 ± 0.00
13.	Wheat starch	1.62 ± 0.08
14.	Rice starch	0.80 ± 0.07
15.	Maize starch	0.02 ± 0.01
16.	Glycogen	0.00
17.	Dextran 80	0.00
18.	Dextran 150	0.00
19.	Dextran 500	0.00
20.	Sodium alginate	0.015 ± 0.01

TABLE 7.04

Effect of phosphorus, silicon, polysaccharide solutions, addition of varying amounts of (P + Si) to aluminium standard solution on apparent aluminium. 10 ml polysaccharide solutions (100 mg of sample) added to 500 µg Al.

No.	Polysaccharide solutions (100 mg) various amounts of (P + Si)	Al µg found			% Recovery	% Precipitated or Eliminated
1.	Blank (Standard Al solution)	495	±	7	99.2	
2.	Phosphorus (0.45 mg P)	182	±	9	36.4	63.6
3.	Silicon (0.46 mg Si)	211	±	12	42.3	57.7
4.	Amylopectin A	212	±	9	42.4	57.6
5.	Amylopectin C	305	±	8	61.2	38.8
6.	Amylopectin A (dialysis)	349	±	12	69.7	30.3
7.	Citrus pectin, grade II	309	±	6	61.8	38.2
8.	Apple pectin 240	322	±	12	64.4	35.6
9.	Apple pectin 250	316	±	11	63.3	36.7
10.	Potato starch H and W	303	±	15	60.6	39.4
11.	Soluble starch	286	±	8	57.3	42.7
12.	Fresh, potato starch	315	±	15	63.1	36.9
13.	Potato starch (cv Majestic)	364	±	9	72.8	27.2
14.	Wheat starch	385	±	14	77.0	23.0
15.	Rice starch	431	±	11	86.1	13.9
16.	Maize starch	461	±	8	92.1	7.0
17.	Dextran 150	465	±	6	93.1	6.9
18.	Dextran 500	472	±	5	94.2	5.8
19.	Sodium alginate	460	±	6	92.0	8.0
20.	Glycogen	473	±	11	94.6	5.4

TABLE 7.05

Effect of Phosphorus, Silicon and Polysaccharides on Aluminium precipation in soil

No.	Treatment	Concentration of Aluminium mole	Concentration of (P + Si) mole
1.	Blank (Soil + 100 ml CH_3 COOH)	1.788×10^{-1}	0.000
2.	Phosphorus	0.692×10^{-1}	7.711×10^{-3}
3.	Silicon	0.802×10^{-1}	7.898×10^{-3}
4.	Amylopectin (A)	0.796×10^{-1}	6.102×10^{-3}
5.	Amylopectin (C)	1.129×10^{-1}	3.644×10^{-3}
6.	Amylopectin (A), dailysis	1.176×10^{-1}	2.711×10^{-3}
7.	Citrus pectin	1.041×10^{-1}	4.915×10^{-3}
8.	Apple pectin 240	1.190×10^{-1}	3.661×10^{-3}
9.	Apple pectin 250	1.185×10^{-1}	3.779×10^{-3}
10.	Commercial potato starch	1.125×10^{-1}	3.728×10^{-3}
11.	Soluble starch	1.074×10^{-1}	4.271×10^{-3}
12.	Fresh, potato starch	1.128×10^{-1}	4.033×10^{-3}
13.	Potato starch (cv Majestic)	1.333×10^{-1}	2.966×10^{-3}
14.	Wheat starch	1.396×10^{-1}	2.847×10^{-3}
15.	Rice starch	1.562×10^{-1}	1.525×10^{-3}
16.	Maize starch	1.696×10^{-1}	4.067×10^{-3}
17.	Glycogen	1.711×10^{-1}	8.065×10^{-5}
18.	Sodium alginate	1.660×10^{-1}	2.542×10^{-5}
19.	Dextran 80	1.700×10^{-1}	0.000
20.	Dextran 150	1.686×10^{-1}	0.000
21.	Dextran 500	1.666×10^{-1}	0.000

TABLE 7.06

The influence of (P + Si) contents of polysaccharide on Aluminium precipiation

No.	Treatment	Concentration of Aluminium (mole) precipitated	Concentration of (P + Si) mole
1.	Blank	0.000	0.000
2.	Phosphorus	1.096×10^{-1}	7.711×10^{-3}
3.	Silicon	0.985×10^{-1}	7.898×10^{-3}
4.	Amylopectin (A)	0.992×10^{-1}	6.102×10^{-3}
5.	Amylopectin (C)	0.659×10^{-1}	3.644×10^{-3}
6.	Amylopectin (A), dialysis	0.612×10^{-1}	2.711×10^{-3}
7.	Citrus pectin	0.747×10^{-1}	4.915×10^{-3}
8.	Apple pectin 240	0.598×10^{-1}	3.661×10^{-3}
9.	Apple pectin 250	0.603×10^{-1}	3.779×10^{-3}
10.	Commercial potato starch	0.663×10^{-1}	3.728×10^{-3}
11.	Soluble starch	0.714×10^{-1}	4.271×10^{-3}
12.	Fresh, potato starch	0.660×10^{-1}	4.033×10^{-3}
13.	Potato starch (CV Majestic)	0.455×10^{-1}	2.966×10^{-3}
14.	Wheat starch	0.392×10^{-1}	2.847×10^{-3}
15.	Rice starch	0.226×10^{-1}	1.525×10^{-3}
16.	Maize starch	0.092×10^{-1}	4.067×10^{-5}
17.	Glycogen	0.077×10^{-1}	8.065×10^{-5}
18.	Sodium alginate	0.129×10^{-1}	2.542×10^{-5}
19.	Dextran 80	0.088×10^{-1}	0.000
20.	Dextran 150	0.103×10^{-1}	0.000
21.	Dextran 500	0.122×10^{-1}	0.000

TABLE 7.07

Effect of soluble silicon on phosphate availability. 2 g of soil + 100 ml of 0.5 M CH_3 COOH and various concentrations of silica in citrus pectin solution, at pH 2.9.

No.	Soil + pectin solution	Concentration of Silicon µg Added	Concentration of available phosphorus mg/100 g ± S.D.	Increasement mg/100 g
1.	2 gm soil + 100 ml CH_3 COOH + 10 ml H_2O	0.00	10.26 ± 0.46	0.00
2.	2 gm soil + 100 ml CH_3 COOH + 10 ml (100 mg pectin)	230	12.32 ± 0.86	2.06
3.	2 gm soil + 100 ml CH_3 COOH + 10 ml (200 mg pectin)	460	15.14 ± 1.18	4.88
4.	2 gm soil + 100 ml CH_3 COOH + 10 ml (400 mg pectin)	920	18.66 ± 2.28	8.40

TABLE 7.08

Effect of soluble silicon on phosphate availability. 2 g of soil + 100 ml 0.5 M CH_3COONH_4 + various concentrations of silicon in citrus pectin solution, at pH 6.2

No.	Soil + pectin solution	Concentration of Silicon µg added	Concentration of available phosphorus mg/100 g + S.D.	Increasement mg/100 g
1.	2 gm soil + 100 ml 0.5 M $CH_3COO NH_4$ + 10 ml water	0.00	12.32 ± 0.80	0.00
2.	2 gm soil + 100 ml 0.5 M $CH_3COO NH_4$ + 10 ml pectin (100 mg)	230	15.67 ± 1.13	3.35
3.	2 gm soil + 100 ml 0.5 M $CH_3COO NH_4$ + 10 ml pectin (200 mg)	460	17.75 ± 1.25	5.43
4.	2 gm soil + 100 ml 0.5 M $CH_3COO NH_4$ + 10 ml pectin (400 mg)	920	21.22 ± 2.45	8.90

GENERAL DISCUSSION

The most salient conclusion drawn from the experimental results obtained in this investigation definitely shows that the problem of aluminium toxicity, and phosphate availability are very closely inter-related. Phosphate deficiency is the cause of failure of spruce on brown forest soils. The prediction made in Chapter III on the basis of field evidence and chemical considerations, reinforce the conviction that the spruce suffer from aluminium toxicity, and seek protection in the organic rich A horizon, where organic matter masks the aluminium sites (Figure 2.04), and/or lowers the pH of injury.

Aluminium in the soil solution has been identified (Wright, 1943; Clarkson, 1966; Foy, 1974; Foy et al. 1978) as a main factor responsible for poor growth in these acid soils.

In many plants, aluminium tolerance appears to be closely associated with the efficiency of phosphorus use. Aluminium tolerance coincides with the ability to tolerate low phosphorus levels.

It must be admitted that Fiunary, and Savary Glen soils have high allophane contents (Fullerton, 1972). Moreover, these soils have abnormally high loss on ignition values for the brown earths A horizons - over 35%.

As far as the crop itself was concerned, the survey by Fullerton (1972) found that leading shoot increments were very low in the first ten to twenty years.

Aluminium and Plant Growth

Aluminium appears to affect root growth in particular, and excess aluminium accumulating in roots reduces their capacity for translocating phosphorus. Thus even in soils containing ample phosphorus excess aluminium will cause a phosphorus deficiency. Amelioration of such soils involves suppression of aluminium activity, for example, by liming, and addition of organic matter. The toxic amount of aluminium in a soil will depend upon other soil properties such as pH and phosphorus content and upon the type of plant to be grown. In culture solutions very small quantities of aluminium can be toxic (Jackson, 1967; Hesse, 1971).

General Effects

Aluminium toxicity is an important growth limiting factor for plants in many acid soils below pH 5.0, but can occur at pH levels as high as 5.5 (Foy, 1974). This problem is particularly serious in strongly acid subsoils that are difficult to lime, and it is intensified by heavy applications of fertilizers.

Strong subsoil acidity (aluminium toxicity) reduces plant rooting depth, increases susceptibility to drought (Foy et al., 1978), and decreases the use of subsoil nutrients.

The symptoms of aluminium injury are not always easily identifiable. In some plants, the foliar symptoms resemble those of phosphorus deficiency (overall stunting, small, dark green leaves, purpling of stems and leaves, yellowing and death of leaf tips). In other plants, aluminium toxicity appears as an induced calcium deficiency or reduced calcium

transport problem (Curling or rolling of young leaves and collapse of growing points or petioles) (Foy et al., 1978).

Aluminium-injured roots are characteristically stubby and brittle. Root tips and lateral roots become thickened and turn brown (Foy et al., 1978). The root system as a whole is curtailed with many stubby lateral roots but lacking in fine branching. Such roots are inefficient in absorbing nutrients and water (Foy, 1974).

Physiological Effects

Much of the physiological research on the mechanism of aluminium toxicity has involved a single plant species or variety (Foy et al., 1978). In general, aluminium has been shown to interfere with cell division in plant roots, fix phosphorus in less available forms in the soil and in or on plant roots, decrease root respiration, interfere with certain enzymes governing the deposition of polysaccharides in cell walls, increase cell wall rigidity and interfere with the uptake, transport and use of several elements (phosphorus, potassium, calcium, magnesium) and water by plants (Foy, 1974; Rorison, 1965).

Other effects on root metabolism appear to require the presence of aluminium within the cytoplasm. Among these are the dislocation of cell division in young root tips, aluminium interference in DNA replication, reduction in the rate of sugar phosphorylation and of phosphorus incorporation in RNA (Jackson, 1967). Clarkson (1968) observed that aluminium treatment inhibited root elongation and cell division, and that it interfered with the distribution of phosphorylated intermediates in

such a way as to depress respiratory metabolism.

Both Wright (1943) and Clarkson (1968) suggested that the aluminium toxicity mechanism was an internal precipitation of aluminium in the roots inducing phosphate deficiency.

The suspected sites of aluminium-phosphate interaction are within the root tissue and along the root surface.

McCormick and Borden (1972) identified by photomicrographic techniques the sites of phosphate fixation by aluminium within plant roots. The growth response was attributed to the elimination of aluminium toxicity.

Possible Methods for Overcoming Aluminium Toxicity

Either the aluminium must be immobilised or the tree must be protected. Immobilisation of aluminium requires adsorption on the aluminous sites by humate, hydroxyl, silicate or phosphate. The problems of economics and practicality must be borne in mind.

1. Influence of liming for reducing aluminium toxicity

The application of lime to acid soils is commonly aimed at raising the soil pH to near neutrality, conditions favourable for plant growth, in the belief that effects such as low base status (Reeve and Sumner, 1970; Kamprath, 1970), and rendering aluminium inactive, aluminium toxicity, and phosphate fixation will be eliminated, or at least favourably affected. Phosphorus fixation and aluminium toxicity behaved as independent growth-limiting factors. The apparent interaction between

aluminium and phosphorus lasted only until aluminium was eliminated as a toxic factor and resulted in improved ability of the plants to take up phosphorus, rather than to an improved rate of supply of phosphorus by the soil.

The effect of lime on yield on the experimental plots in Fiunary Forest is shown in Figures 2.02 and 2.03.

The lime requirement taken as the amount necessary to give the highest yield was in good agreement with the amount of lime required to reduce the aluminium toxicity.

Table 2.03 on the mean heights, shows that the influence of lime was necessary to obtain maximum growth (or to eliminate aluminium toxicity). This affect only lasted for the first three years. The addition of small amounts of lime, gives a benefit for a short time. Hence this highlights the difficulty of adding high quantities of lime to spruce trees which have already been established. Therefore, although liming would immobilise the aluminium, this may not be a suitable treatment for spruce.

2. Effect of organic matter on aluminium toxicity

It is well known that organic compounds are capable of forming complexes with metals such as aluminium by surface absorption, chelation and other reactions (Mortensen, 1963).

Hence, one could postulate that the forest 'humate' is bound more tightly to the aluminium than the grassland 'humate', or one could propose that it increases the acidoid : basoid ratio more effectively (Fullerton, 1972). A high base saturation from the litter may also play

a part.

The same result would not be expected from a long established coniferous forest, because there the soil processes are dominated by podzolisation and lead to accumulation of allophane in the C horizon (Fullerton, 1972).

The beneficial effects from additions of organic matter, or by planting spruce seedlings in the organic matter layer, in very acid soils, for reducing soluble aluminium and increasing crop yield is demonstrated in Figures 2.03 and 2.04. The effects can be attributed to complexing or masking of aluminium by components of the organic material. Many investigators have shown that organic matter can influence the relationship between pH and the quantity of aluminium in the soil (Clark and Nichol, 1966; Evans and Kamprath, 1970; Thomas 1975). Recently, Iler (1979) claimed that organic acids which form chelates with Al^{3+} or Fe^{3+} apparently release silicic acid from combination with these elements in soil or conversely remove these elements from the surface of the silica, permitting it to dissolve. The addition of organic matter to an acid soil decreases the concentration of aluminium in soil solution and decreases the effects of aluminium toxicity. Field observations also indicated the beneficial effects of organic matter in highly acid soils (Tables 2.03 and 2.04).

3. Effect of phosphorus on aluminium toxicity

The beneficial effects of applying phosphorus to acid soils can be due largely to fixation of aluminium, and for reducing aluminium toxicity (Table 3.22), results in increased crop yields (Figures 2.01 - 2.03).

The aluminium concentration was reduced in solution by 63.6%, after addition of 14.5 m mole phosphorus to 18.5 m mole aluminium.

The results indicated the ability of plants to grow successfully by the addition of phosphorus when comparing the growth and utilization of phosphorus by plant species on these soils (Figures 2.01 and 2.03). The phosphorus rendered aluminium inactive because of precipitation in the soil and eliminated the toxic action of aluminium by supplying phosphorus in sufficient amounts both to precipitate aluminium and in addition, provide sufficient quantities of phosphorus for normal plant metabolism. Phosphate from a phosphate fertilizer tends to be positionally fixed and moves very slowly from where the fertilizer has been placed, unless the soil is cultivated or disturbed, because of the very low solubility of the soil phosphates. This has the consequence that little phosphate will be transferred from the surface to the subsoil by leaching (Russell, 1973). However, the soil solution on this occasion contained more organic phosphorus compounds in solution than inorganic (Table 4.07).

In general, if a phosphate fertilizer is added to a soil, an annual crop usually takes up only about 5 to 10% of the phosphate added (Russell, 1973), even if it responds well to the phosphate, though phosphate-demanding crops on phosphate-poor soils may give higher recoveries.

Pierre and Stuart (1933) have advanced the opinion that the chief remedial action of phosphate takes place within the plant where it renders aluminium inactive by precipitation.

4. Influence of mycorrhiza on aluminium toxicity

Ectomycorrhiza benefit forest trees by:-

(i) Aiding the absorption of inorganic and organic nutrients (Tables 3.22, 6.03 and 6.05).

(ii) Supplying trees with growth-regulating substances Stankis, 1974).

(iii) Deterring root pathogens (Zak, 1964).

(iv) Increasing host plant resistance to drought (Theodorou and Bowen, 1970; Bowen, 1973).

(v) Decreasing aluminium soil toxicity (Figure 6.01), (Table 3.22).

Under these conditions the attributes of mycorrhiza assume particular importance.

The uptake of nutrients from soil and litter from the relatively large inter-root distances of trees is achieved by longevity of mycorrhizal roots and particularly by growth of mycelial strands into soil (Bowen, 1973).

The implications of longevity for transfer in the soil are the same for both diffusive and convective flow (Bowen, 1973).

Mycelial strand production is a greatly variable property between mycorrhizal fungi. The advantages of mycorrhizal fungi are considered to be:-

(i) Confers high penetration of large inter-root distances (Bowen, 1973).

(ii) Confers positional advantage for competition with other micro-organisms for both inorganic and organic nutrients (Went and Stark, 1968; Harley, 1969).

The role of ectomycorrhiza in overcoming aluminium toxicity and improving the growth of spruce is now recognized (Figures 2.01 and 2.02). Ectomycorrhiza should be now recommended for commercial practice in forestry to obtain healthy plants and good yield. It is abundantly clear that the presence of mycorrhiza is an ecologically significant factor which can no longer be ignored or passed over in a superficial manner (Harley, 1969).

5. Effect of silicon on aluminium toxicity

The results obtained in Chapter VII have shown that silicon (Si) has an influence in reducing aluminium concentration in soil solution. It reduces aluminium concentration by 57.7% (Figure 7.02). Silicon (Si) is known to reduce the internal toxicity of manganese in barley leaves (Foy et al., 1978), and soybeans (Kluthcouski and Nelson, 1980) and may play a similar role in detoxifying aluminium.

Silicon (Si) also precipitates aluminium in soil solution and reduces its toxicity to plants (Figures 7.01 and 7.02).

Results in Tables 7.07 and 7.08 shows that the addition of soluble silicon to soil solution has a beneficial effect, which has increased the availability of soil phosphate. This could be because the silicate ion is able to displace phosphate ion from the surface of soil, or it could lower the activity of aluminium ion in solution and so prevent it from precipitating phosphate.

It is not surprising therefore bearing in mind the early hopes of Jones and Handreck (1967) that silicon might be a partial substitute for phosphate as a fertilizer.

6. The influence of polysaccharide on aluminium toxicity

The influence of some polysaccharide solutions for reducing or precipitating aluminium concentration was quite effective.

The percentage of aluminium precipitated varied from 54. - 57. 6. The precipitation process depends upon the contents of phosphorus and silicon (Si) in the polysaccharide samples (Figures 7. 01 and 7. 03). The polysaccharide fraction could thus be viewed as a natural product of the soil environment just as is the humic acid fraction.

Complex or salt formation with metal cations (for example, aluminium) could influence both persistence and solubility of the polysaccharides (Martin et al., 1966) and could influence a plant's ability to survive under aluminium toxic conditions.

Possible Methods of improving these problem soils:-

Some recommendations on this point were put forward at the end of this study. Where aluminium toxicity exists, the soil may be amended by additions of organic matter and by liming. Liming would immobilize the aluminium but this may not be a suitable treatment for spruce, as it might be difficult to apply lime to spruce trees already established.

Ectomycorrhiza could by now be safely recommended and employed in forest sites to obtain healthy plants and a good yield. It is abundantly clear that the presence of mycorrhiza is an ecologically significant factor which may suggest an ecological solution at low cost.

Mycorrhiza enables the tree to mineralise the humus and supply it with nutrients, particularly nitrogen and phosphate. Other

recommendations are:-

(1) The second rotation will be more successful in the same profile (i.e. replanted). Tables 2.01 and 2.05 because the seedlings will be planted in the fermentation layer, or organic layer, the soil been inoculated by appropriate mycorrhiza fungi.

(2) When planting in the pasture site on basalt brown earth it is better to plant in the turf layer.

If the site has only a thin organic layer, it is advisable to carry out an allophane test. If it gives a strong positive reaction, it is advisable not to plant in that site.

Aspects to be further investigated

Growth improvements caused by ectomycorrhiza have been recognized. There are many outstanding problems:-

Can the addition of phosphorus fertilizers on a given soil be lessened by appropriate manipulation of mycorrhizal infection and if so, can such a benefit be encouraged in any way?

Of particular importance is a requirement for further information about the physiological and metabolic factors that control fungal colonization of root surfaces and their invasion into roots.

More information is needed about host-plant metabolites that stimulate or inhibit hormone production by the fungus and determine whether or not these hormones induce and maintain the specific physiological state in infected roots.

Satisfactory solutions to the above problems will contribute greatly to the advancement of research in this area.

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